Ben-Gurion University of the Negev
Department of Chemical Engineering

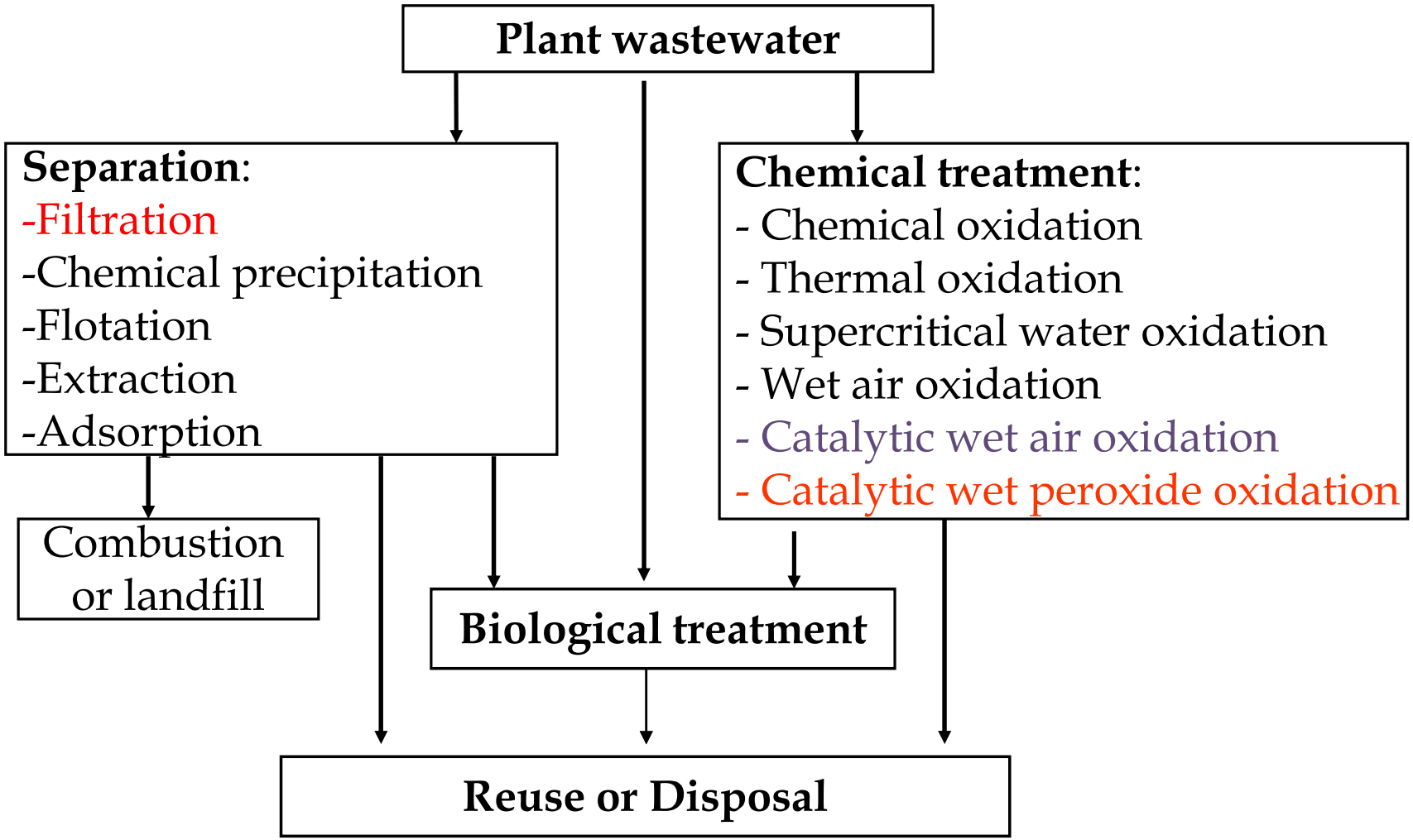
Blechner Center for Industrial Catalysis & Process Development

Fixed-bed catalytic wet peroxide oxidation of phenol with titania and Au/titania catalysts in dark

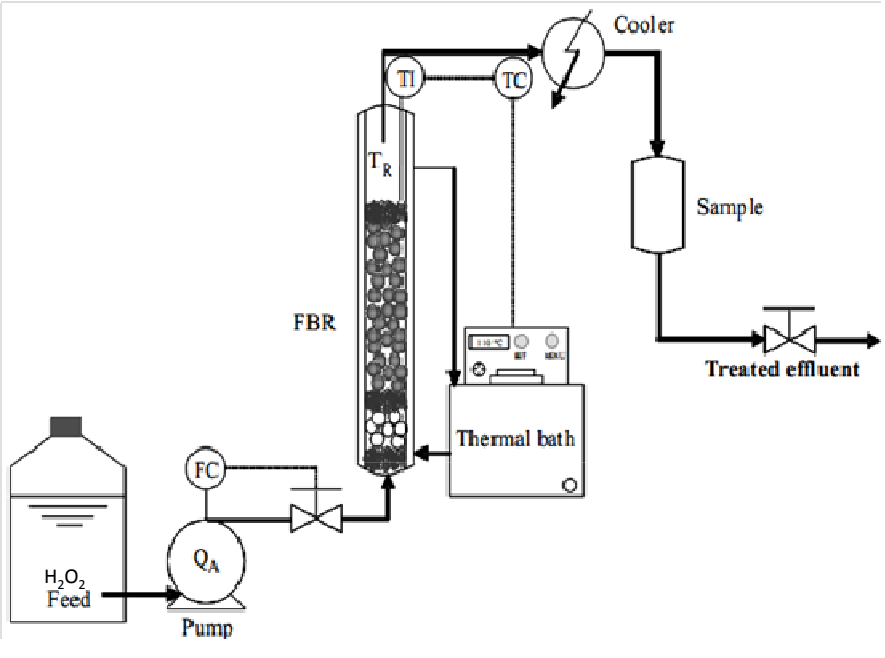
M.V. Landau, M.Ferentz, M.Herskowitz

2-nd World Congress on Petrochemistry and Chemical Engineering. October 29, 2014, Las Vegas, USA

Technologies used for treatment of industrial wastewater



Catalytic filtration concept

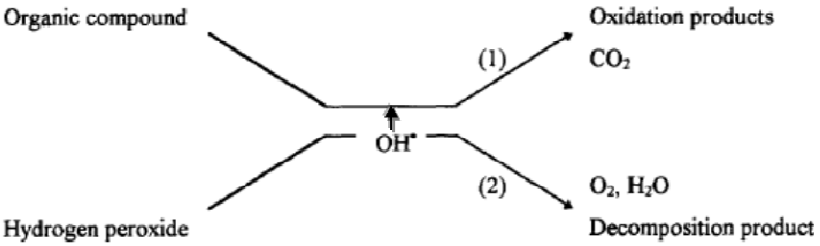


<u>Regular Filtration</u>:

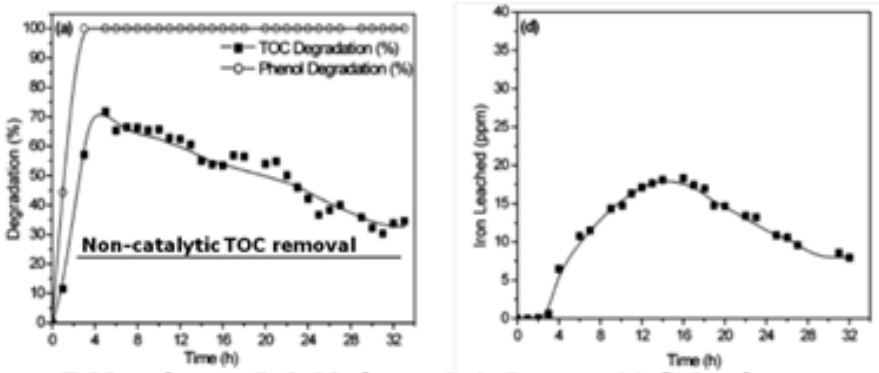
- **adsorption, rejection, accumulation → limited capacity**

<u>Catalytic filtration</u>:

- **chemical transformation of recalcitrant organic compounds to highly biodegradable by oxidation → unlimited capacity**



CWPO



F.Martinez, J.A.Melero, J.A.Botas, M.S.Pariente, R.Molina. Ind.Eng.Chem. Res., 45,4396,2007

Wastewater purification
Plant of Makhteshim - Agan Co. , Ramat Hovav, Israel

> 60 Units producing fine chemicals

2000 m^3/day :

TOC: 2500 mg/L

AOX: 500-700 mg/L

TDS: 2-2.5 g/L

CWO homogeneous, Oxidant – O_2

LOPROX (Bayer Co.)

P(O_2) = 35 bar
T = 250 ˚C



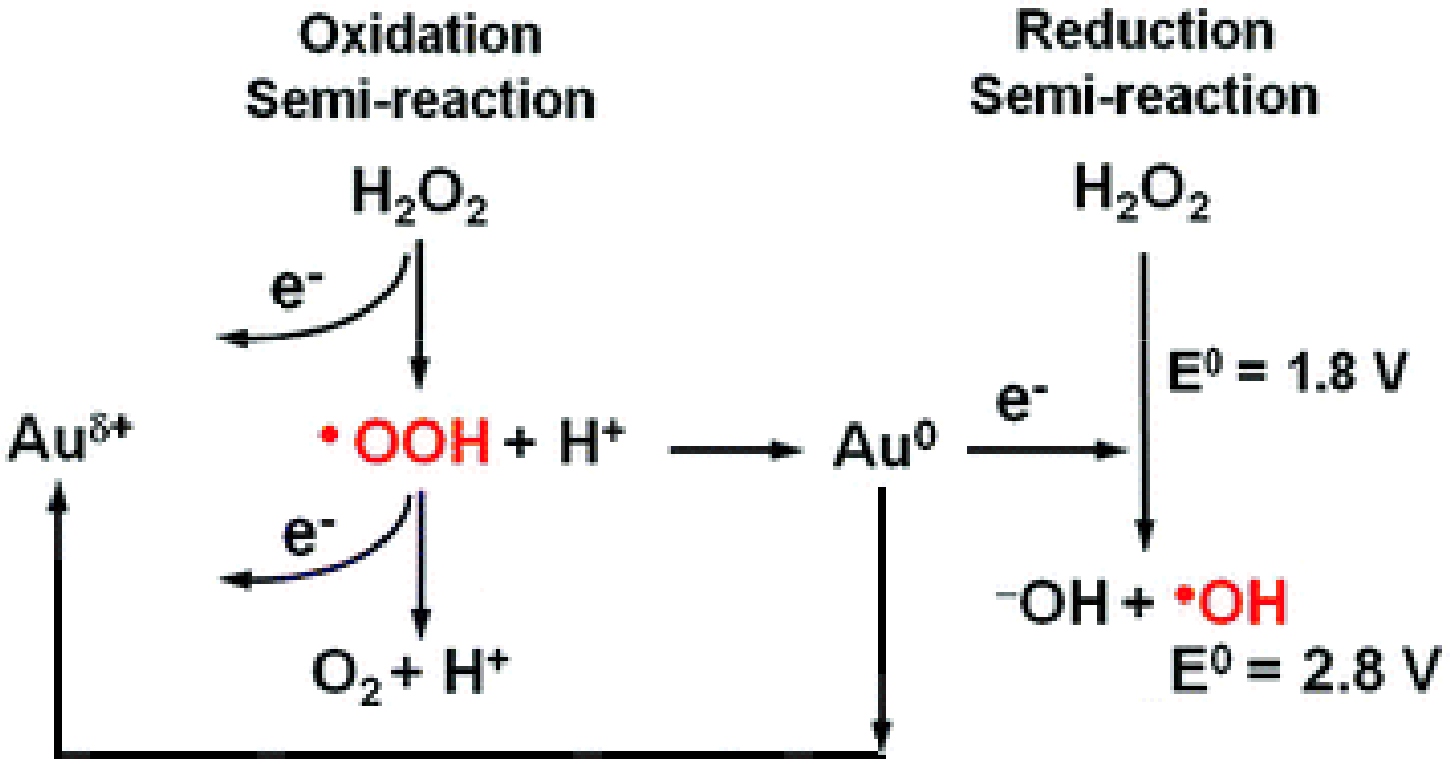
> 80% AOX reduction

Biological treatment **MBR** (membrane bio-reactors)

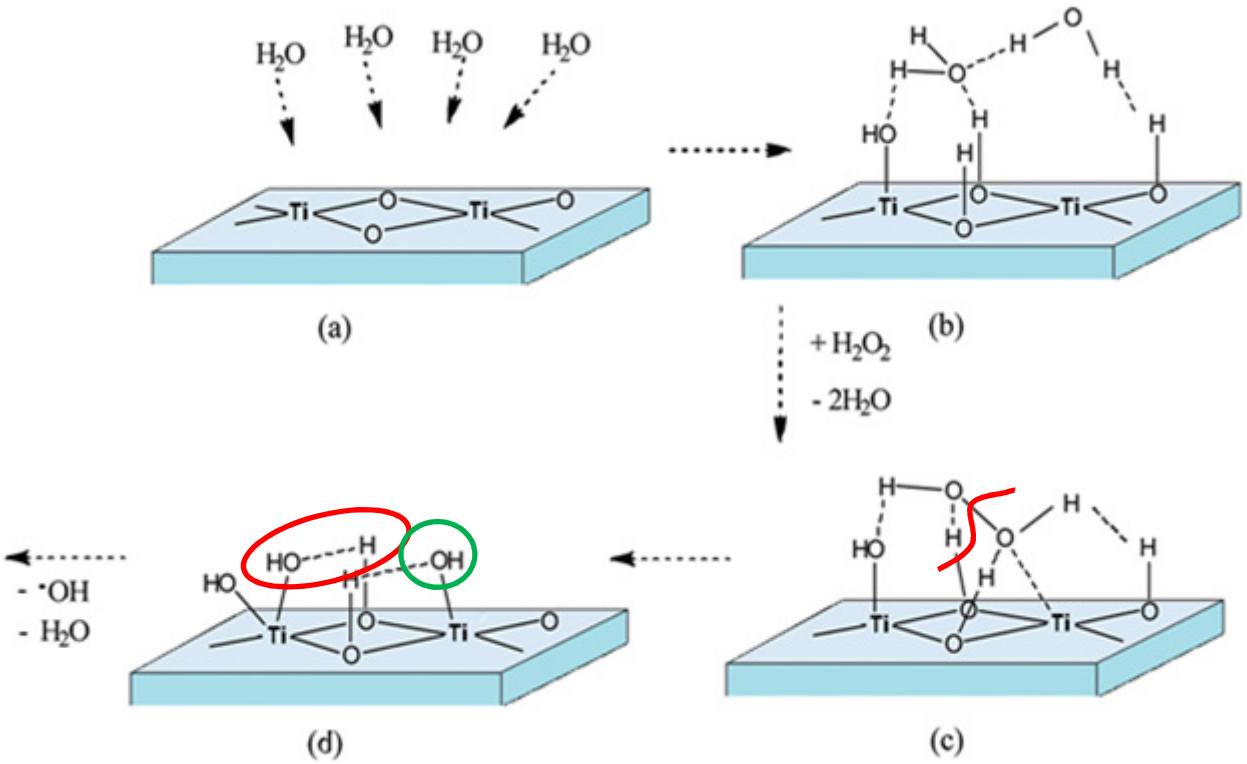
Desalination (reverse osmosis unit)

Clean sweet Water

Au nanoparticles are efficient catalysts for production of OH radicals from H_2O_2



Adsorption and further decomposition of H_2O_2 in reaction at TiO_2 surface according to DFT calculations



(a) Bare surface cluster

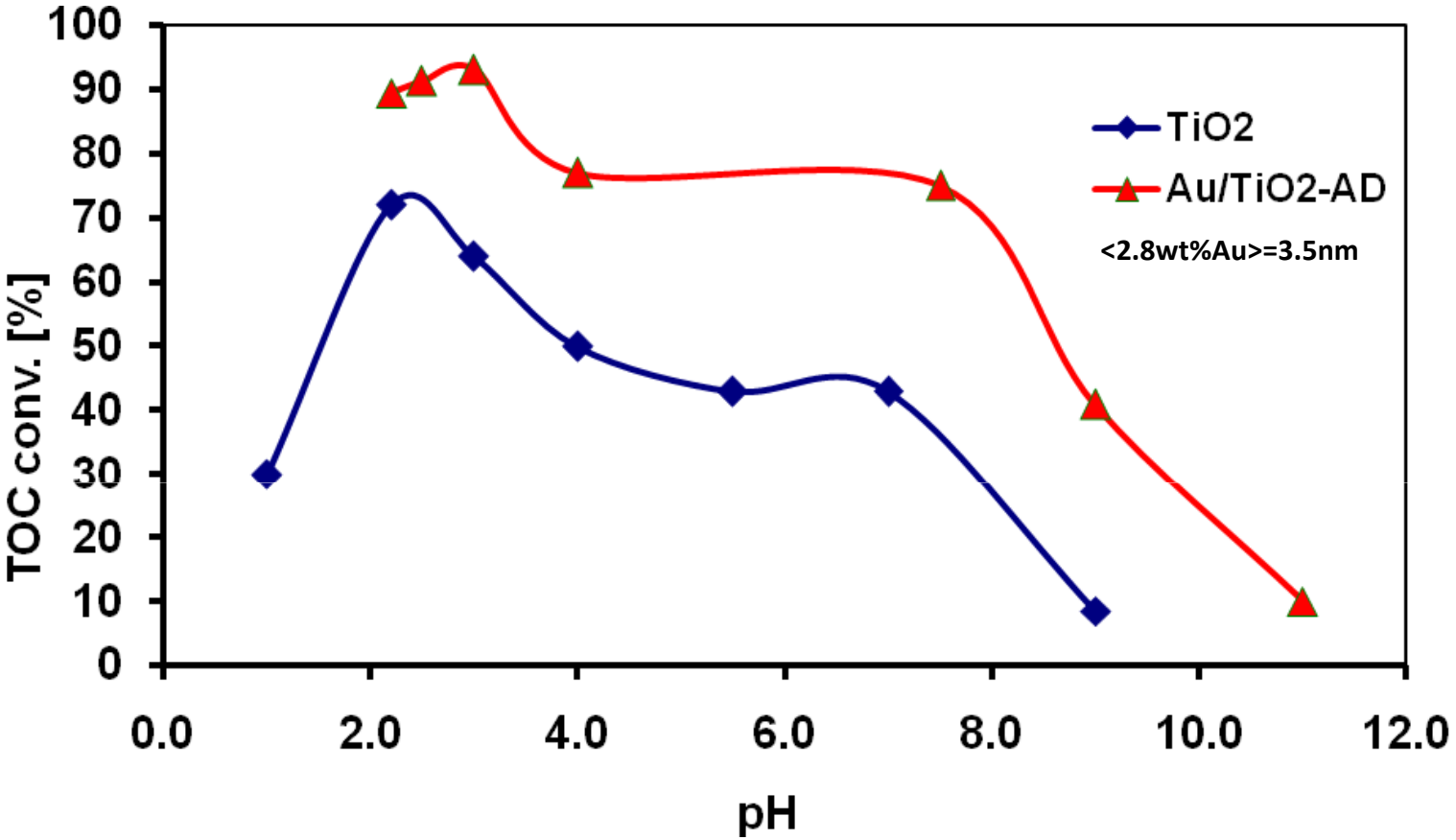
(b) Chemisorption of a H_2O_2 molecule

(c) Transition-state for the cleavage of the O–O bond in H_2O_2

(d) Adsorbed water and ·OH radical

C. M. Lousada, A. J. Johansson, T. Brinck and M. Jonsson, J. Phys. Chem. C 2012, 116, 9533–9543

Both Au and TiO_2 are active in phenol CWPO working without leaching



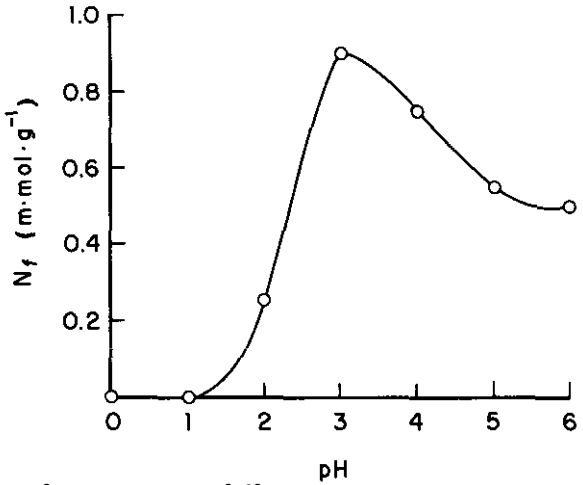
Treatment conditions:

T = 80°C; LHSV = 3.5 h^{-1};P = 1 atm, H_2O_2/PhOH = 1.5stoich.

M.Ferentz, M.Landau, M.Herskowitz, Catal.Today, 2014, Accepted for publication.

Several known phenomena are consistent with the extreme dependence of TiO_2 activity on solution pH

Adsorption isotherm of H_2O_2 by ≡TiOH at different pH at a T=298K



L. T. Kubota, Y. Gushikem, A.M. Mansanares and H. Vargas.
J. of Colloid and Interface Science 173, 372-375, 1995

The sorption of the H_2O_2 by ≡TiOH can be explained by the dissociation reaction of the hydroxyl groups in the acid solution

$$\equiv TiOH + H^+ \rightarrow \equiv Ti^+ + H_2O.$$

H_2O_2 **Adsorption** is a result of the coordination of H_2O_2 with the Lewis acid site $\equiv Ti^+$, forming a complex species, $\equiv Ti^+(H_2O_2)$.

At higher pH the concentration of these acid sites decreases

- At higher pH became significant the scavenging of ·OH radicals with carbonate ions in solution increasing in sequence of carbonate moieties:

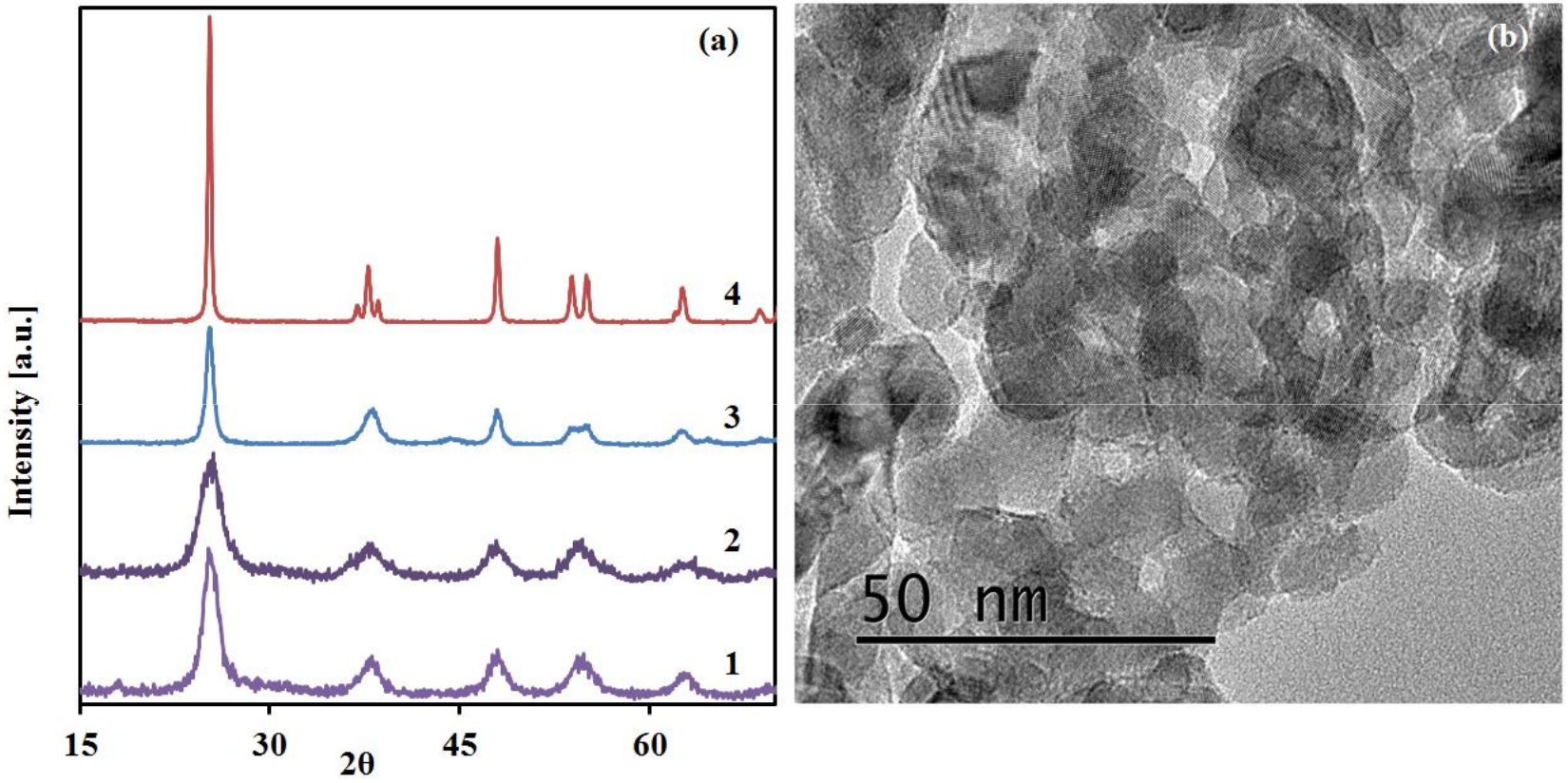
$$H_2CO_3 < HCO_3(-) < CO_3(2-)$$

which stability in this sequence is favored by increasing of solutions pH.

- Lessening of the H_2O_2 (pKa = 11.56) stability: $H_2O_2 \leftrightarrow H^+ + OOH^-$ followed by disproportionation upon basification: $H_2O_2 \rightarrow H_2O + O_2$

So, **the optimal pH** for catalytic decomposition of H_2O_2 forming ·OH radicals is **2,5-3.0**

Four titania materials used in present study represented aggregates of anatase nanocrystals with different size



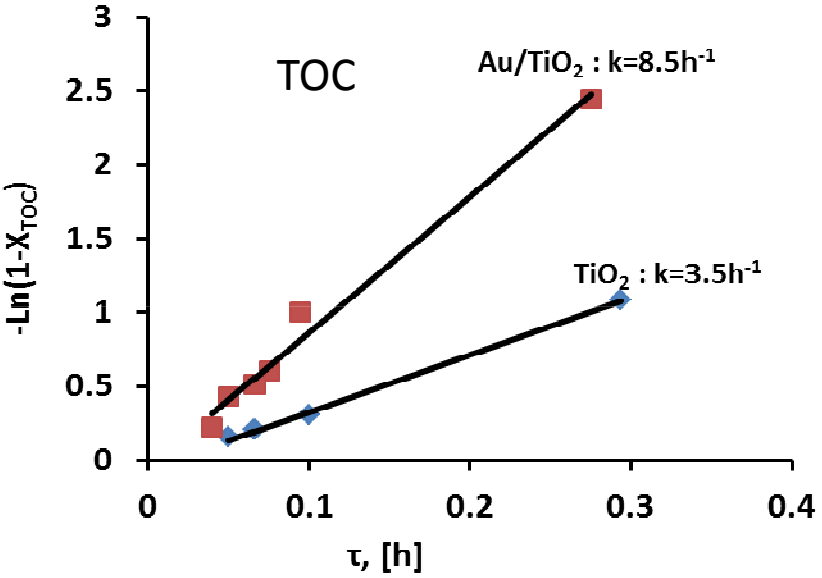
1 – TiO_2-II; 2 – TiO_2-III; 3 – TiO2-IV; 4 – TiO_2-I;

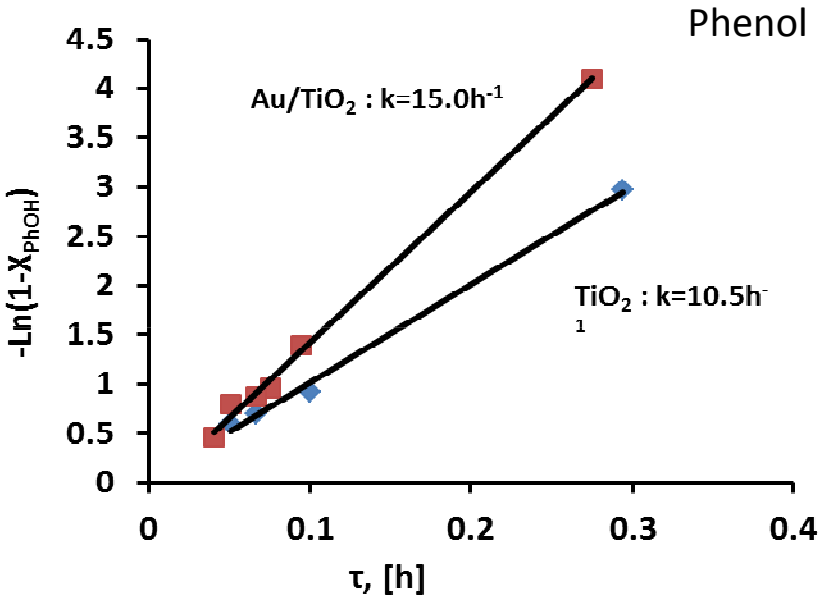
The TOC conversion in CWPO of phenol is proportional to The TiO_2 surface area

TiO_2 materials	Surface area, m^2/g	Pore Diameter nm	Pore Volume cm^3/g	Crystal size, nm	Performance in CWPO of phenol*	
					PhOH conversion, %	TOC conversion, %
TiO_2-I Saint-Gobain NorPro Co	30	17.9	0.17	30	82	52
TiO_2-II Saint-Gobain NorPro Co	150	4.6	0.42	15	99	66
TiO_2-III BGU	240	3.4	0.09	4.5	>99	76
TiO_2-IV BGU	310	3.0	0.27	8.5	>99	85

*Testing conditions: T = 80°C, H_2O_2/PhOH = 1.5 Stoich., LHSV = $3.8h^{-1}$, P_a = 1atm, pH_{in} = 2.5, TOS = 25 h.

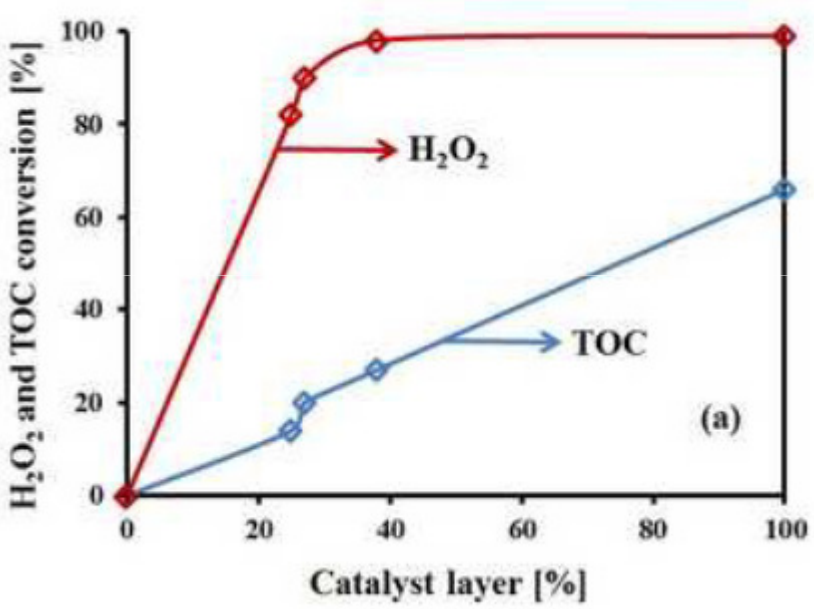
CWPO on TiO_2 and Au/TiO_2 follows first order kinetics relative to Phenol and TOC removal

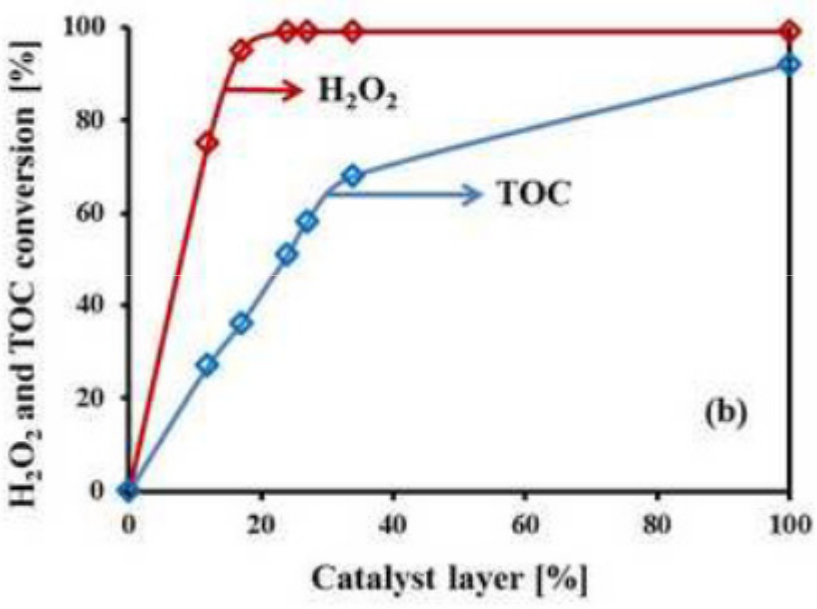




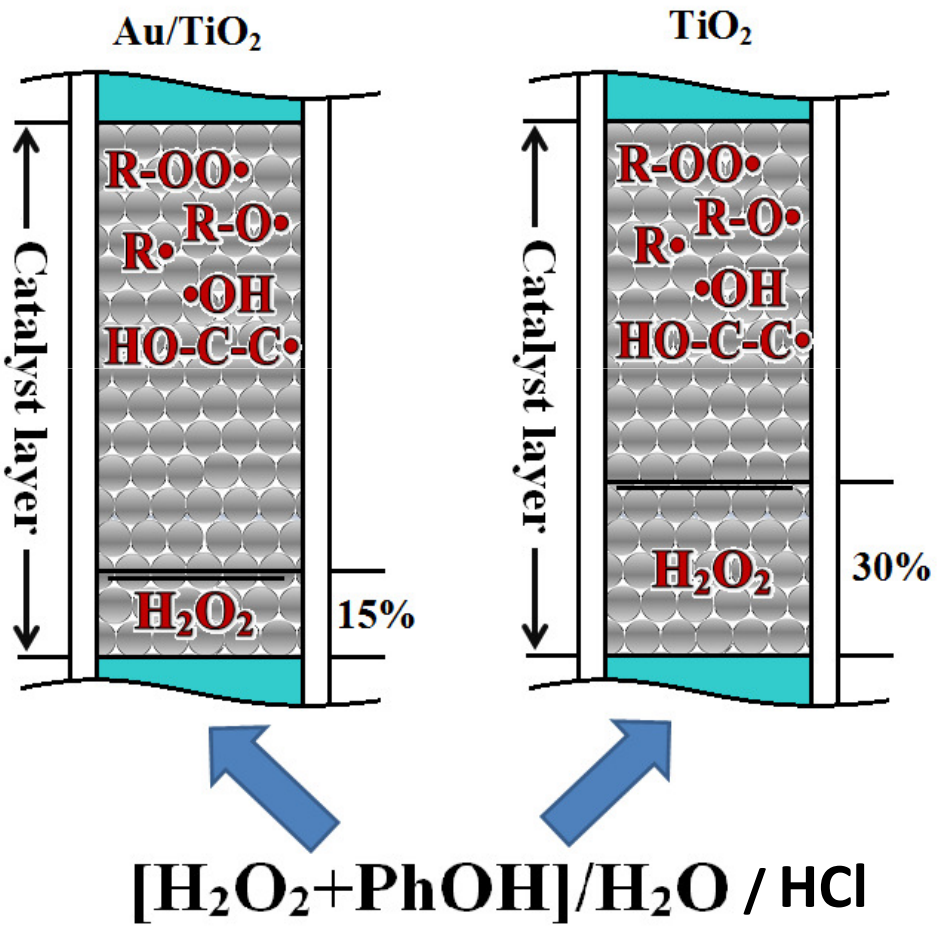
Deposition of Au nanoparticles increases the catalytic activity of titania catalyst/support in TOC conversion by a factor of 2.5

Au nanoparticles are efficient catalysts for production of OH radicals from H_2O_2





Radicals formed from H_2O_2 in the bottom of catalysts layer proceed to be reactive in the upper catalysts layers

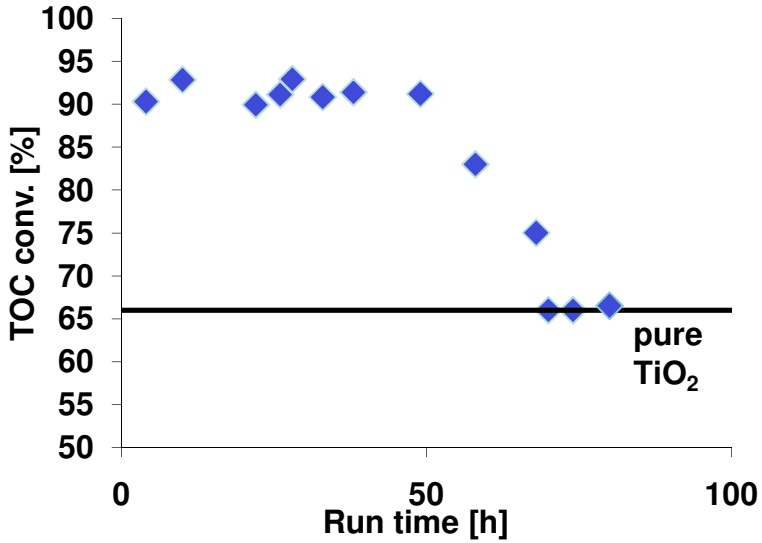


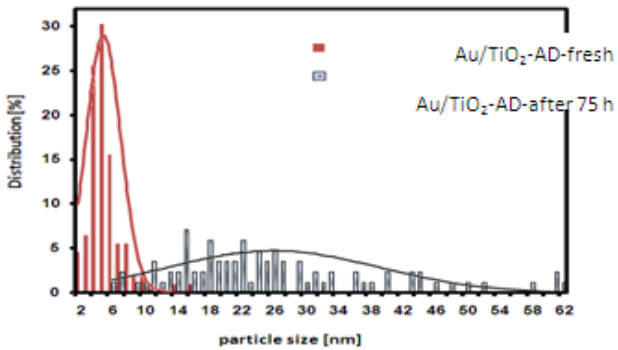
Aggregation of Gold nanoparticles causes catalysts deactivation

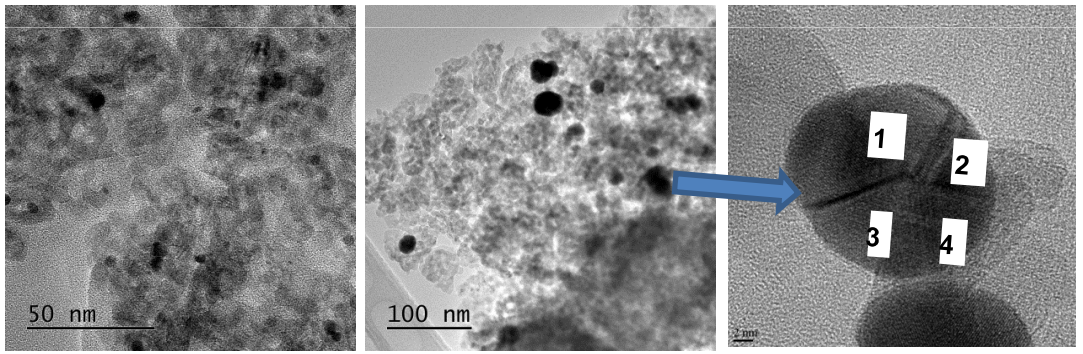
Treatment conditions:

T = 80°C; LHSV = 3.5 h^{-1}; P = 1 atm,

H_2O_2/PhOH = 1.5stoich.

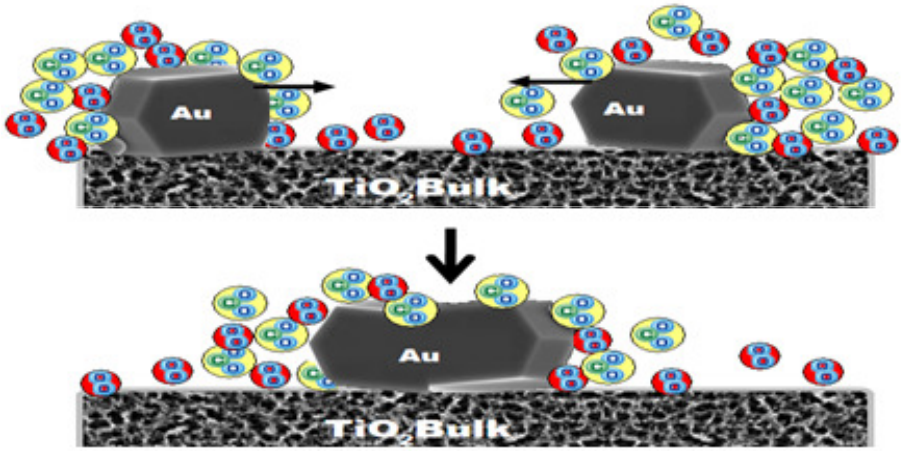






The possible reasons for aggreagation of Au nanoparticles and their deactivation

- **Ostwald ripening** (**Au concentration in water is <0.001 ppm**)
- **Propellant effect of gaseous CO_2/O_2 formed at nanocrystals grains with relatively high surface energy (increasing of external pressure up to 25 bar had no effect on catalysts deactivation)**



- **Blocking of Au surface with strongly adsorbed dicarboxilic acids with partial oxidation of gold**

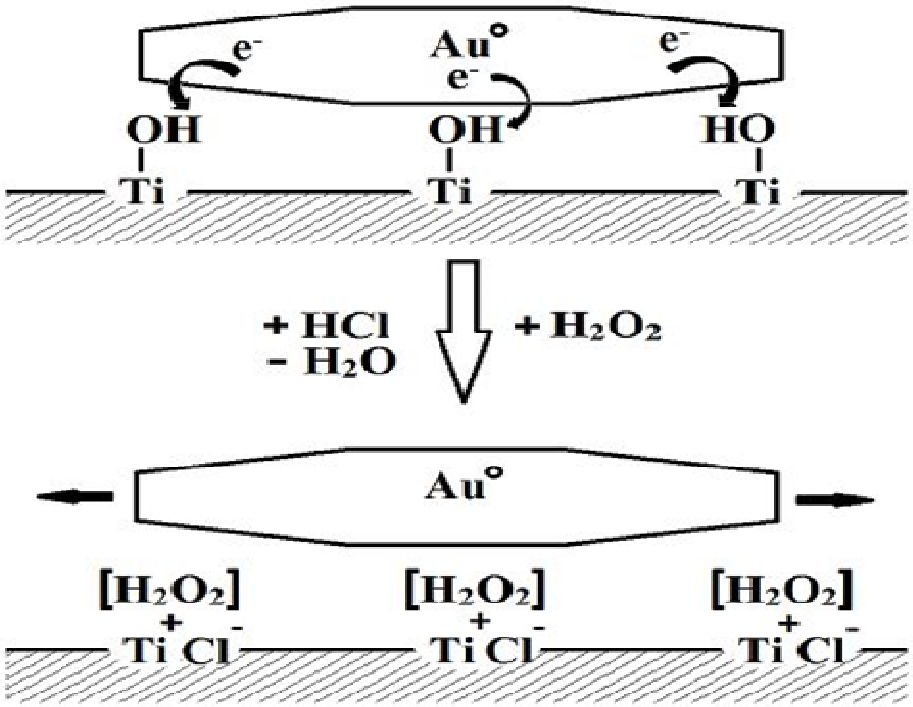
- **Mobility of Au nanoparticles at TiO_2 surface in presence of H_2O_2 due to complexation-decomposition of hydroperoxide molecules by surface titanium ions ("lubrication" effect)**

H_2O_2 is a reagent accelerating the aggregation of gold nanoparticles at titania surface

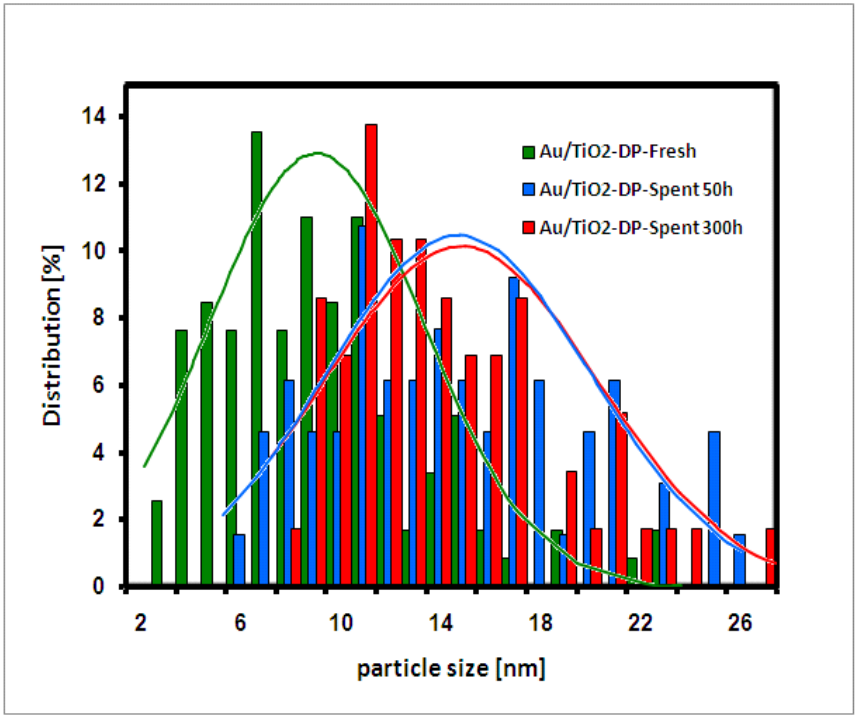
Treating conditions of Au/TiO_2-II-AD				Average Au crystal size (XRD)	
Water composition	Tempera-ture, °C	Treatment time, h	Water solution pH	Fresh catalyst	After treatment
H_2O_2(1250 ppm)-PhOH-HCl	80	100	2.5	3.5	25
PhOH-HCl	80	100	2.5	3.5	4.0
H_2O_2(1250 ppm)	80	100	7.0	3.5	3.5
Treating conditions of Au/TiO_2-II-DP				Average Au crystal size (XRD)	
H_2O_2(1250 ppm)-PhOH-HCl	80	300	2.5	8	13
Industrial wastewater H_2O_2(15000 ppm) – organics-HCl	80	70	2.5	8	45

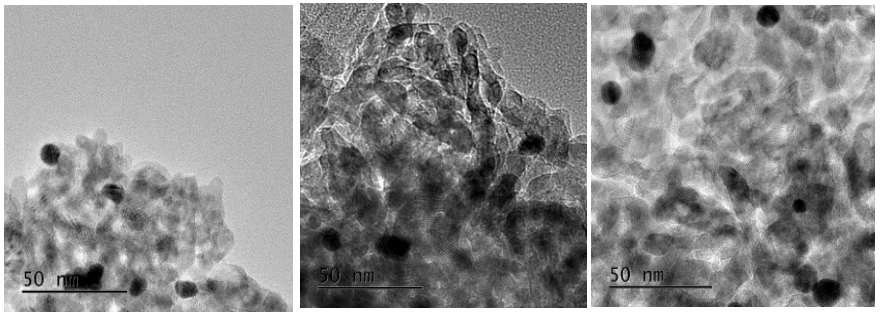
- **Mobility of Au nanoparticles at TiO_2 surface in presence of H_2O_2 due to complexation-decomposition of hydroperoxide molecules by surface titanium ions**

("lubrication" effect)



Increasing of Au particle size stabilized the catalytic activity with partial deactivation



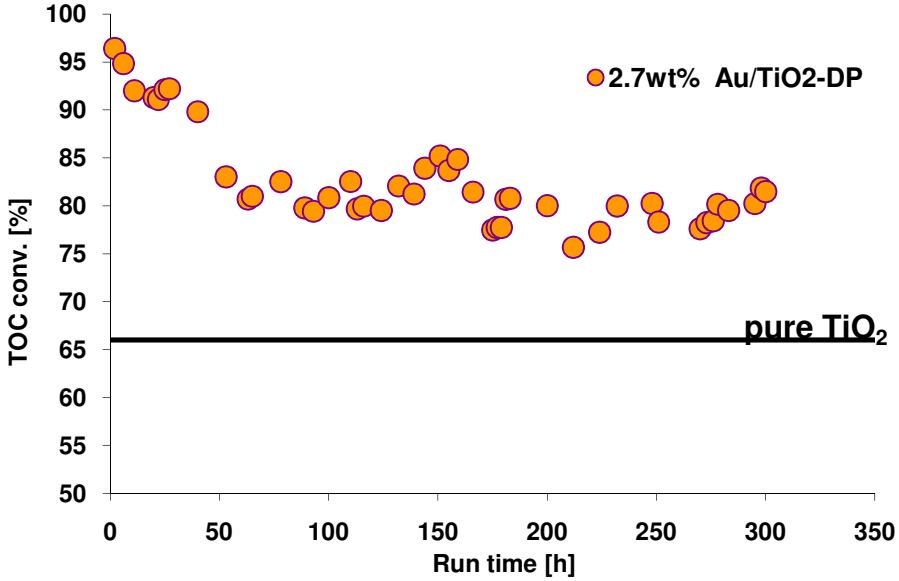


Fresh After 50h After 300h

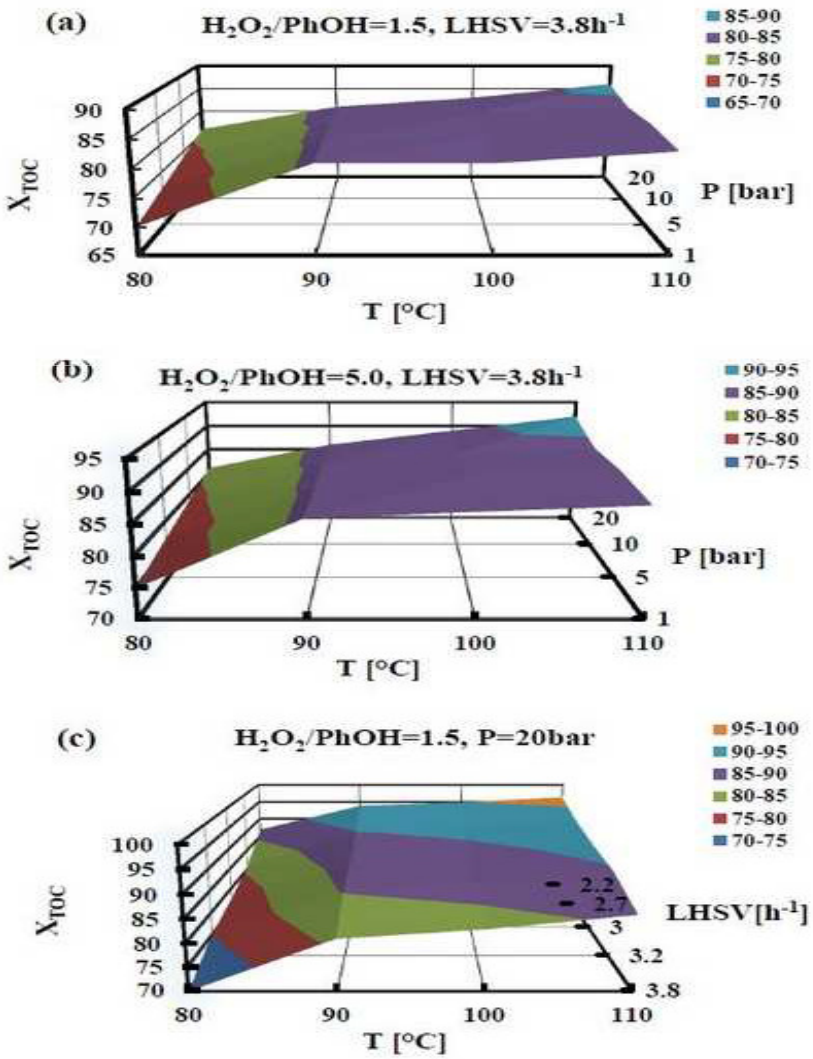
Treatment conditions:

T = 80°C; LHSV = 3.5 h^{-1}; P = 1 atm,

H_2O_2/PhOH = 1.5stoich.



Optimizing the reaction conditions allowed to get >90% TOC removal in CWPO of phenol even with pure TiO_2-II without gold deposition



Oxidative (CWPO) pretreatment strongly increases the biodegradability of DBNPG

Results of biological treatment of dibromoneopenthylglycol solution

Run Time [days]		0	1	7	30	60
AOX [ppm]	not treated	63	63	63	55	43
	after TiO_2	38	31	18	-	-
	after Au/TiO_2	22	17	9	-	-
TOC [ppm]	not treated	507	-	175	70	65
	after TiO_2	490	301	70	-	-
Br^- [ppm]	not treated	5	5	17	70	100
	after TiO_2	69	81	102	-	-

Biodegradability studies were conducted by M. Zangy, A. Kushmaro and A. Brenner, BGU Environmental Engineering Department

Blechner Center acknowledges the financial and technical support:

- *ISF*
- *BMBF-MOST German-Israeli Fund*
- *Blechner Fund*

- *Dr. A. Erenburg*

  XRD studies
- *Dr. V.Ezersky*

  HRTEM-EELS-STEM-EDS
- *S. Koukouliev*

  Catalysts testing
- *M.Vigovsky*

  Catalysts preparation



Ben – Gurion University of the Negev

