Use of magnetized nanosized P-25 TiO_2 particles in water treatment

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Nowelties
European Joint Doctorate

MARIE SKŁODOWSKA-CURIE ACTIONS
Innovative Training Networks (ITN)
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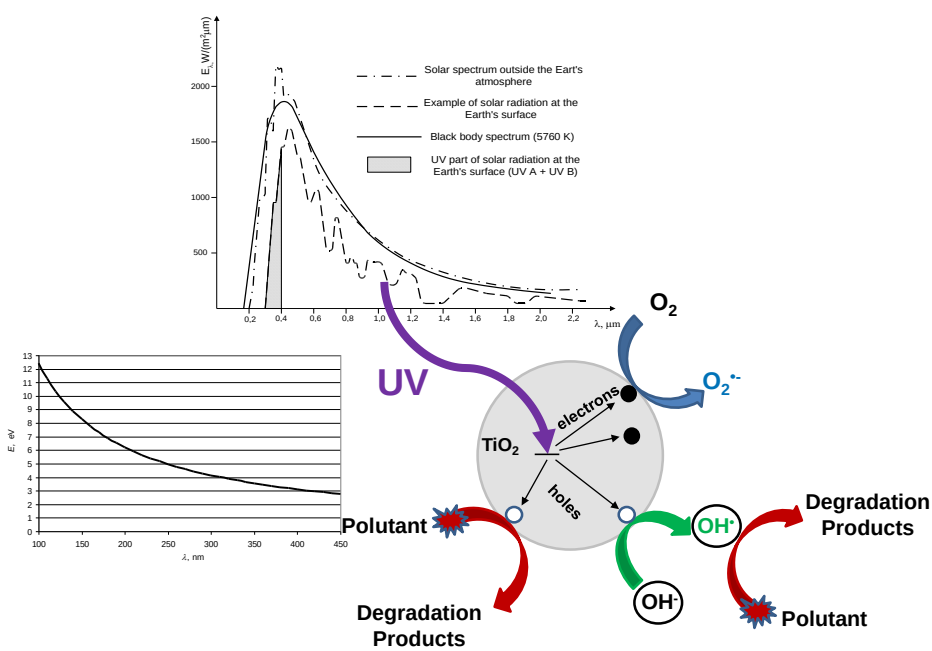
Topics:

- Main mechanisms of photocatalytic oxidation process (Advanced Oxidation Process – AOP)
- TiO_2 as a most suitable photocatalytic material for use in water treatment
- Magnetizing of TiO_2 particles
- Use of irradiated magnetized TiO_2 particles as a water treatment step - for degradation of different organic materials dissolved in water

- Photocatalytic oxidation process, with heterogeneous photocatalysts, as one of the Advanced Oxidation Processes (AOPs), can be effective technology in the oxidation/degradation of different water pollutants

- For the activation of the process, TiO_2 particles should be irradiated by UV radiation… and to be more environmental friendly, we tried to use natural solar radiation (3-5% UV)

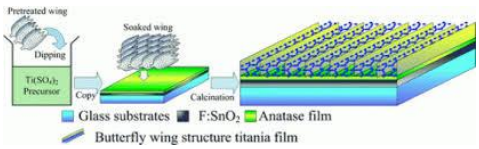


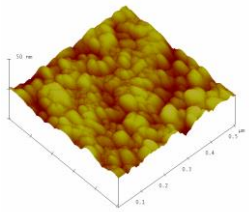
- This study deals with the production of a magnetic photocatalyst using a new magnetizing technique – growth of magnetite crystals onto P-25 TiO_2 particles from Degussa Co. (Today – Evonik Co., **AEROXIDE® TiO_2 P-25**)

- Degussa (Evonik) P-25 contains about 75-80% anatase TiO_2 with a minor amount of rutile (about 25%) and a small amount of amorphous phase…

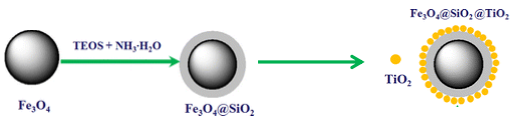
- **Degussa P-25 TiO_2 is in most cases superior in photoactivity to other produced TiO_2 particles, it is practical a reference material for photocatalytic experiments**

- **The main problem with manipulation with TiO_2 particles (20-30 nm!) is the need to separate them after the photocatalytical oxidation process**
  - One of the solutions: - making the thin TiO_2 films on different materials. Drawback – low mass transfer!





  - Other solutions – particles of TiO_2 with magnetic core. Drawbacks – need for separation layer (SiO_2) to slow the recombination of electrons-holes, TiO_2 not efficient as P-25, bigger particles = smaller active photocatalytic area…



So, our team decided to attempt to produce magnetic P-25 TiO_2. We had to answer the following questions:

Why? - to influence non-magnetic substances, as TiO_2 is, to move in magnetic fields, to separate magnetic particles from water

New? - aggregates with grown Magnetite

Demands? - to retain the surface properties of the particles (important for substances where the surface properties should not change e.g. catalysts or sorbents)

How? - Green Rust as a precursor substance for the formation of Magnetite

„Our team”:

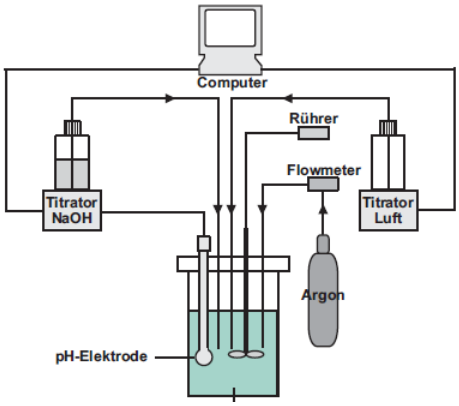
- Dr. Davor Ljubas, University of Zagreb
- Dr. Hans Christian Bruun Hansen, University of Copenhagen
- Dr. Matthias Franzreb, KIT – Karlsruhe Institute of Technology KIT
- Dr. Peter Weidler, KIT

But, also the following persons had a great influence for the whole process (all from KIT, former Forschungszentrum):

- Dr. Ernst Gilbert
- Dr. Rolf Nüesch
- Dr. Christina Vogt
- Sylvia von Hodenberg
- Marita Heinle

KIT

- Magnetite (MT) was synthesized via green rust, a layered double hydroxide (LDH; $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4$), by controlled oxidation, of 20 mmol/L iron(II) sulfate solution within total volume of 250 mL MilliQ® water.
- The production of magnetic MT/P-25 particles was carried out in two steps and both of them took place in the same magnetite-production reactor

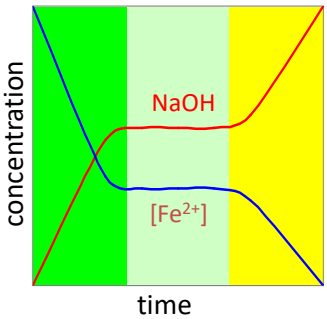


Phases During Formation of Green Rust

$Fe^{2+} \rightarrow Fe^{3+}$

$\rightarrow$ „$Fe(OH)_3$“

$\rightarrow$ Green Rust

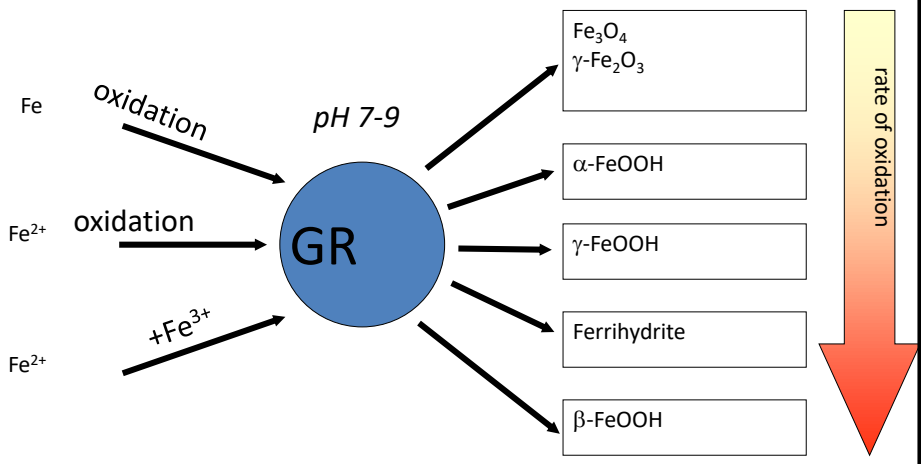


formation of Iron(hydr)oxides

equilibrium between GR und $[Fe^{2+}]$ in solution

oxidation of Fe^{2+} in the GR ($Fe(^{2+})$: 20-70%)

Transformations



Magnetite Synthesis

$6Fe^{2+} + O_2 + 8OH^- + SO_4^{2-} + 2H_2O$

Addition of P-25 TiO_2

1.

- slow oxidation of Fe^{2+} with air
- solution at pH~7
- 4-6 hours

$Fe^{2+}_4Fe^{3+}_2(OH)_{12}SO_4$ (Green Rust)

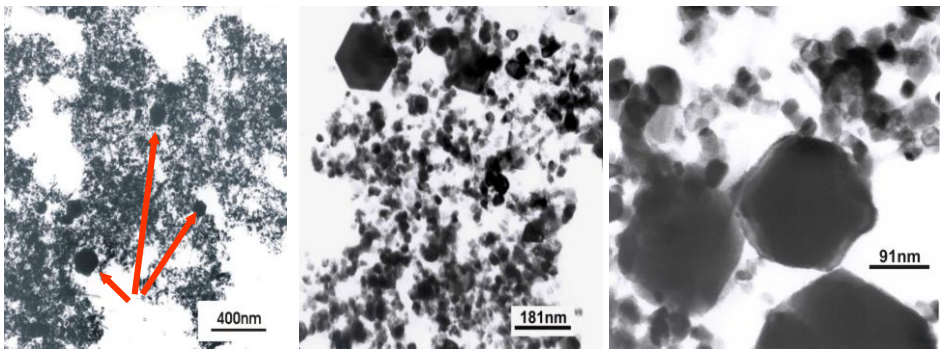
Green Rust

2.

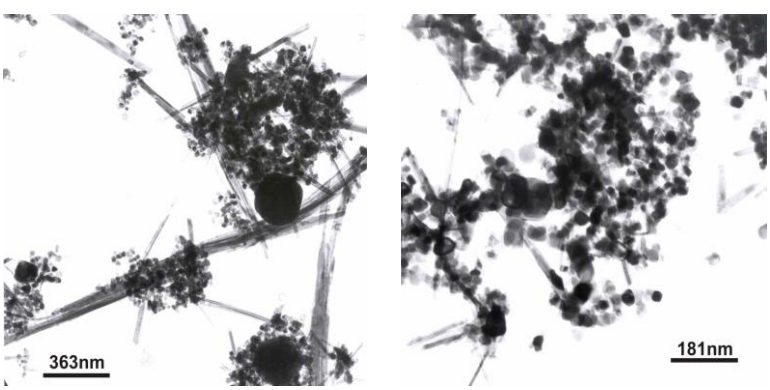
- slow oxidation with air (120 hours)
- ratio: 0.06 – 0.1 [ml air/min]
- pH 7-10

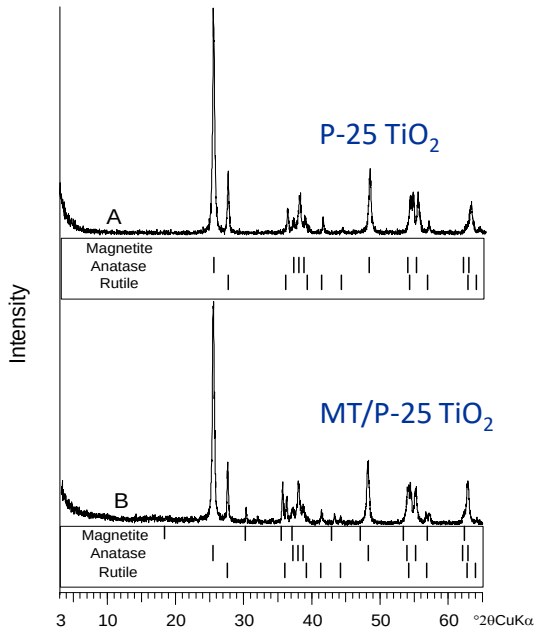
Magnetite

TEM: TiO_2 with Magnetite



Unsuccessful generation of magnetized particles (TEM):

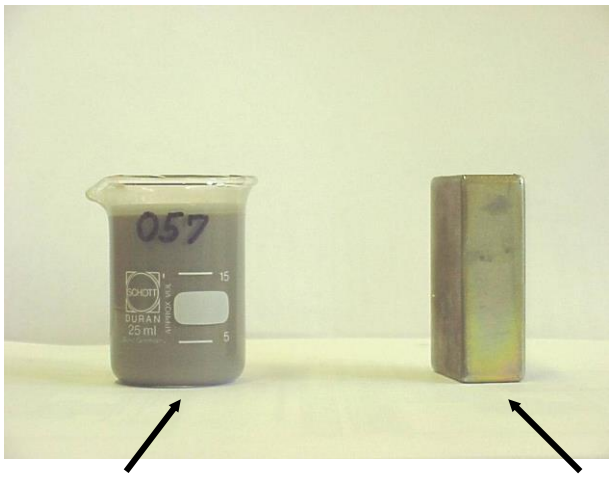




- This technique enabled formation of magnetic nanoparticles without destruction of the P-25 TiO_2's structure and noteworthy coverage of the active TiO_2 surface, since this process of magnetite crystal formation and growth takes place at room temperature and normal pressure

- During the experiments no drastic reduction of the photoactivity of the MT/P-25 aggregates had been observed, even though aggregates consist of directly connected particles of grown magnetite on the P-25 TiO_2

Magnetic Separation – „Hand magnet"



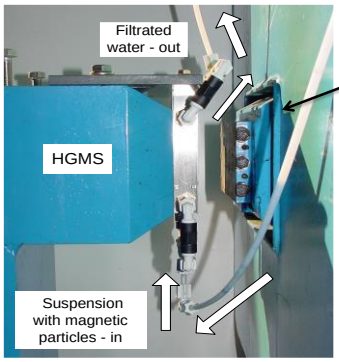
Suspension with the aggregates,
t = 0 sec.

Magnet
B = 0.6 T

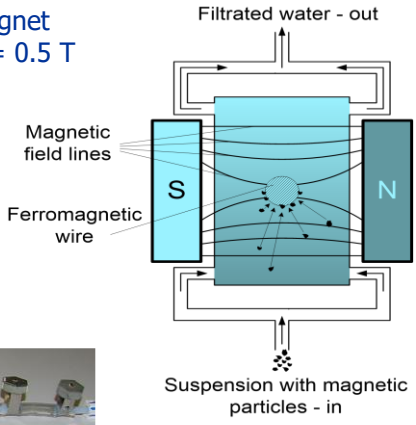
Suspension with the aggregates,
t = 10 sec.

Suspension with the aggregates,
t = 5 min.

Magnetic Separation – HGMS – high gradient magnetic separator, KIT

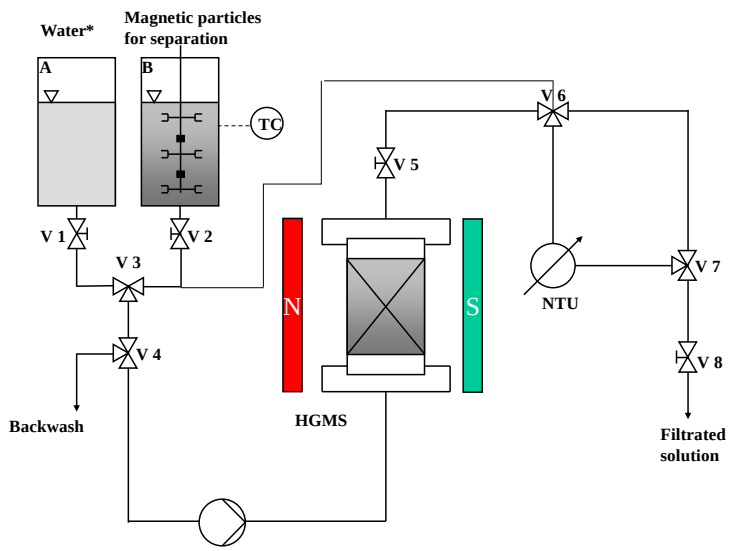


Magnet
B = 0.5 T

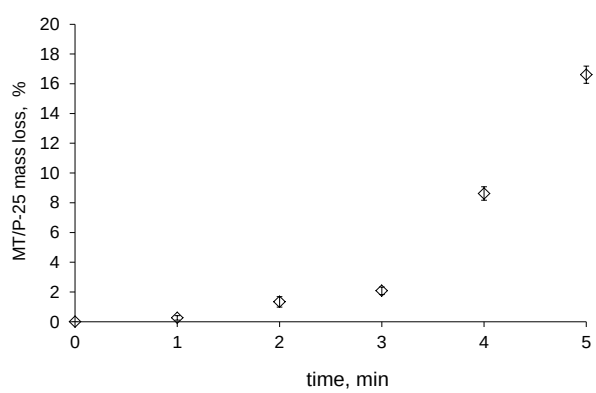


- filter chamber filled with magnetizable stainless steel nets

Magnetic Separation – HGMS – high gradient magnetic separator, KIT

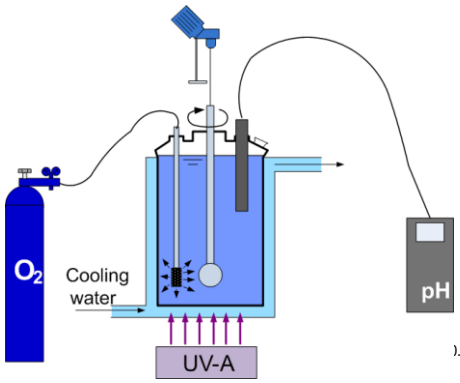


Magnetic Separation – HGMS – high gradient magnetic separator, KIT

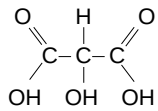


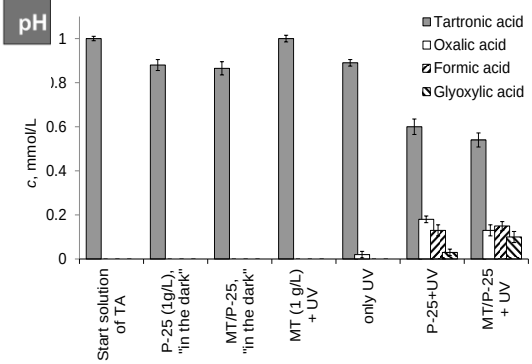
MT/P-25 mass loss versus time of dosing into the HGMS. The flow of suspension with MT/P-25 aggregates was 250 mL/min, and the magnetic field strength was 0.5 T. (Error bars refer to standard deviations).

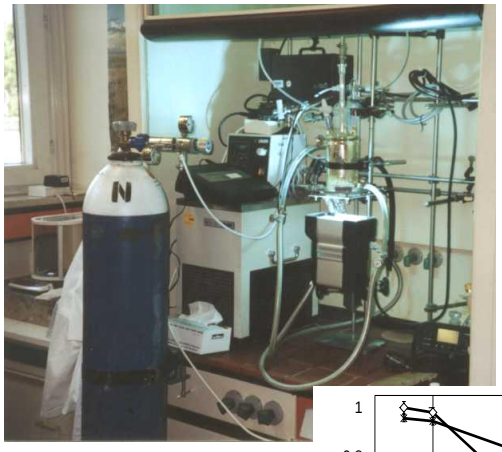
Degradation of Tartronic acid, 1 mmol/L solution

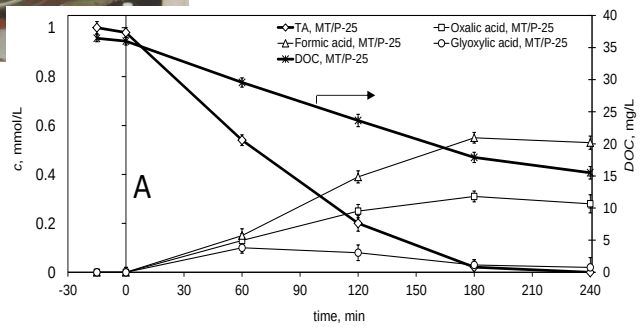


Tartronic acid (2-hydroxypropanedioic acid, hydroxymalonic acid) (TA), $C_3H_4O_5$

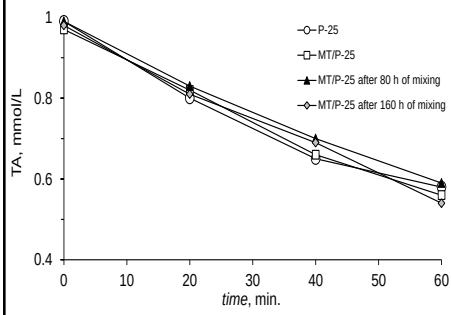


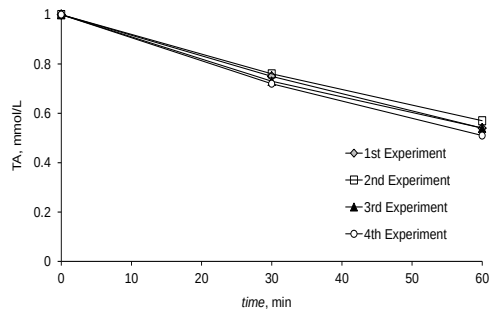






Stability of the aggregates to stirring and magnetic separation





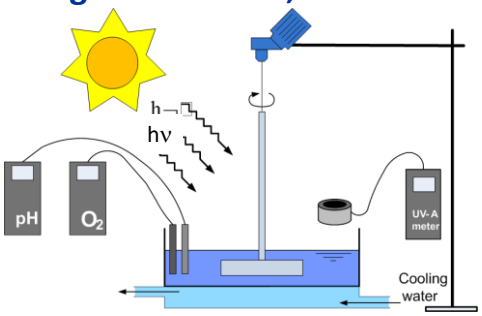
*The comparison of the photocatalytic activity of the MT/P-25 aggregates after **0, 80 h and 160 h of stirring** "in the dark" with the photocatalytic activity of pure P-25 TiO_2*

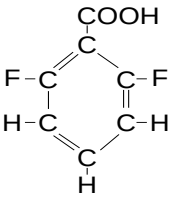
Repeated photocatalytic experiments with the same MT/P-25 aggregate particles suspended in fresh solution of TA.

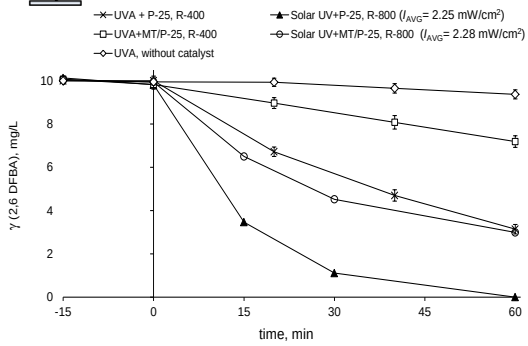
Stability of the aggregates to ultrasonication

- The stability of the MT/P-25 aggregates applied to ultrasonication - using an ultrasonic laboratory unit Sonorex RK 100 H, running at 35 kHz and HF-power of 80 W. The duration of the treatment was 60 minutes. The suspension was kept in a 500 mL Erlenmeyer flask and exposed to the ultrasonication at 20 ± 1 ºC.
- After ultrasonication, the MT/P-25 aggregates were separated onto their basic components which demonstrate that the aggregates are not stable when ultrasonicated.

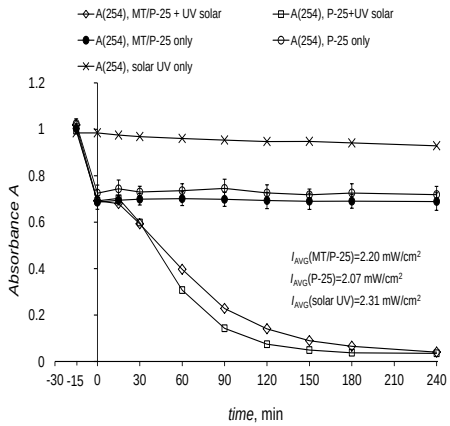
Degradation of 2,6 difluorobenzoic acid, 10 mg/L solution

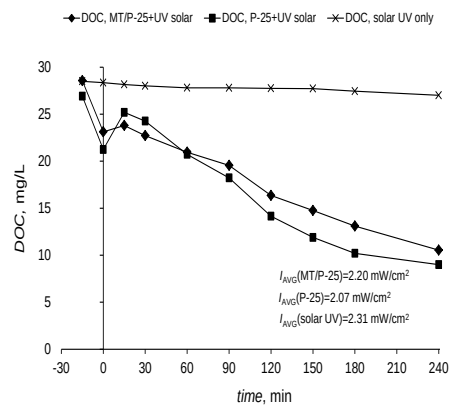






Degradation of NOM from Hohloh lake (Schwarzwald, Germany)





A comparison of the process of the NOM degradation in HLW in reactor R-800 with P-25 and MT/P-25 aggregates, irradiated with the natural solar radiation:

- left- followed by the A(254);
- right - followed by the DOC degradation.

Photonic efficiencies (not Quantum Yield!)

📖Photonic efficiencies of the photolytic oxidation process of TA with P-25 and MT/P-25 aggregates over 60 min in reactor system R-400

Experiment:	R-400, TA + (P-25) + (UV-A)	R-400, TA + (MT/P-25) + (UV-A)
Initial TA concentration, mmol/L	1.00	1.00
Concentration after 60 min, mmol/L	0.60	0.54
Degradation rate, mmol/(L·min)	0.0067	0.0077
Degraded in reactor, mmol/min	0.0027	0.0031
Photonic flow, mol/s	$3.7 \pm 0.7 \times 10^{-6}$	$3.7 \pm 0.7 \times 10^{-6}$
Photonic efficiency	**$1.20 \pm 0.02 \times 10^{-2}$**	$1.38 \pm 0.03 \times 10^{-2}$

Photonic efficiencies

📖Photonic efficiencies for the degradation of 2,6 DFBA in the R-400 and in R-800 experimental systems

Experiment:	R-400: 2,6 DFBA + (P-25) + (UV-A)	R-400: 2,6 DFBA + (MT/P-25) + (UV-A)	R-800: 2,6 DFBA + (P-25) + (Solar UV)	R-800: 2,6 DFBA+ (MT/P-25)+(Solar UV)
Starting conc., mg/L (mmol/L)	10.0 (0.0632)	10.0 (0.0632)	9.82 (0.0621)	10.05 (0.0635)
Degradation rate, mmol/(L·min)	0.0007	0.0003	0.0018	2.99 (0.0189)
Degraded in reactor, mmol/min	0.0003	0.0001	0.0015	0.0006
Photonic flow to reactor, mol/s	$(3.7 \pm 0.7 \times 10^{-6})^a$	$(3.7 \pm 0.7 \times 10^{-6})^a$	$(2.54 \times 10^{-6})^b$	$(2.54 \times 10^{-6})^b$
Photonic efficiency, -	**$(1.30 \pm 0.3) \times 10^{-3}$**	**$(5.34 \pm 0.1) \times 10^{-4}$**	**9.6×10^{-3}**	**3.9×10^{-3}**

a-measured
b-calculated according to literature data

Conclusions – 1/2

📖The production of the magnetic aggregates from the nanoparticles of TiO_2 and magnetite (MT) using a synthetic approach via green rust was successful.

📖This new technique keeps the original crystallinity and the similar photoactivity of the widely used photocatalyst P-25 TiO_2 from Degussa Co.

📖The aggregates were mechanically stable and kept their photochemical efficiency during the high gradient magnetic separations and mechanical mixing; only ultrasonication caused separation of the MT from the TiO_2 particles.

Conclusions – 2/2

- The MT/P-25 magnetic aggregates exhibited the similar photochemical oxidation rates for tartronic acid (TA) as the P-25 TiO_2
- The photocatalytic degradation of two additional aqueous organic substances - 2,6 DFBA and natural organic matter (NOM) in Hohloh Lake water (HLW) - proved that the MT/P-25 particles are photoactive under both artificial UV-A and natural solar radiation
- No significant dissolution of the Fe was observed over 60 minutes of the experiments with MT/P-25 TiO2 aggregates. However, additional research work is needed on the possible problem with chemical dissolution of the Fe from MT over longer period of use (or outside of pH interval between 6.5-9.0)

Thank you for your attention!

Questions…

(also per e-mail: davor.ljubas@fsb.hr)