AOPs for Environmental Applications: An overview (or sthg like this)

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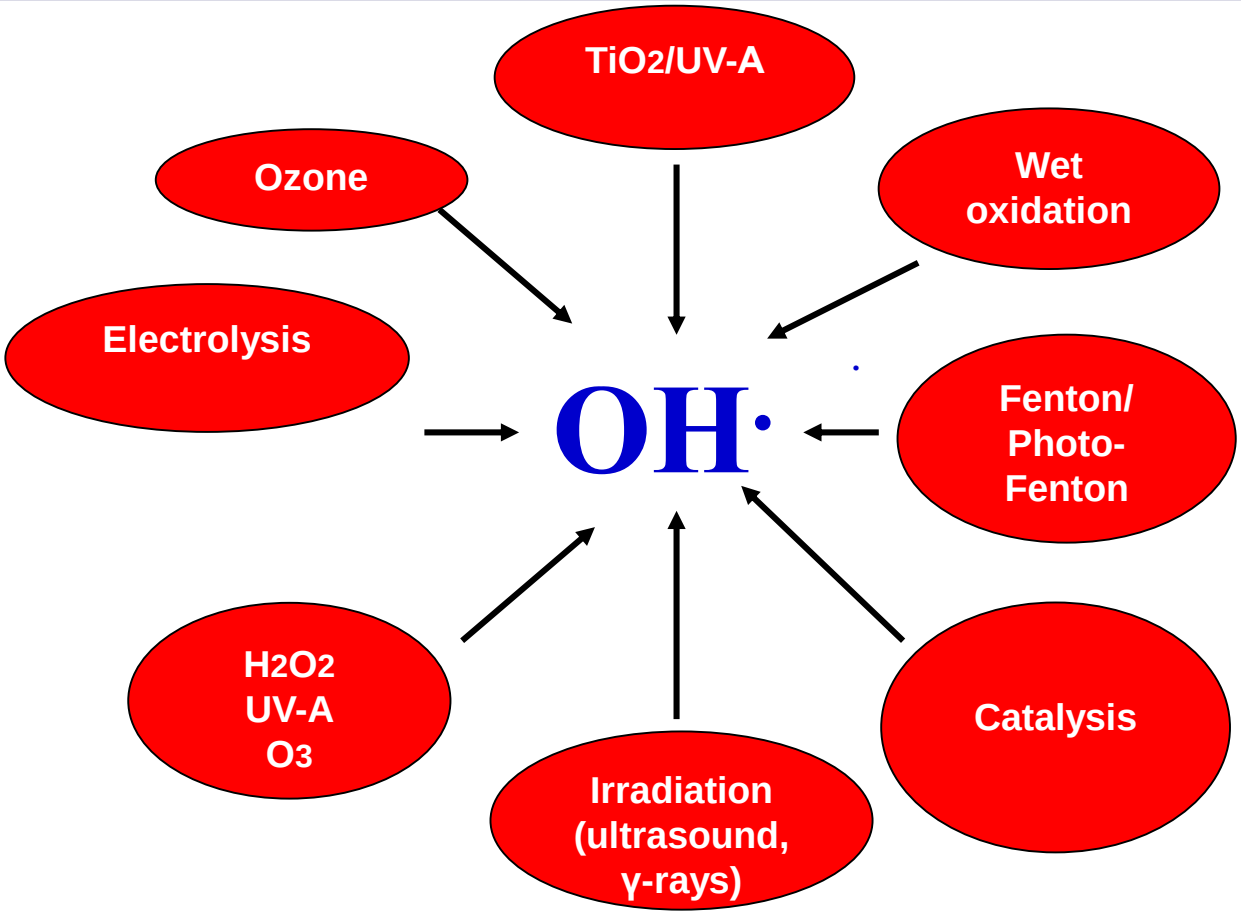
ChemEngUP

Tips to sustain a smiley face during your PhD

A bunch of young PhD students in London of the last century (October 1993 !)

This is me

AOPs: How things have changed since the launch of this schematic ?



Feature: **Processes yielding and based on OH radicals and other ROS**

Tip #1: Process integration

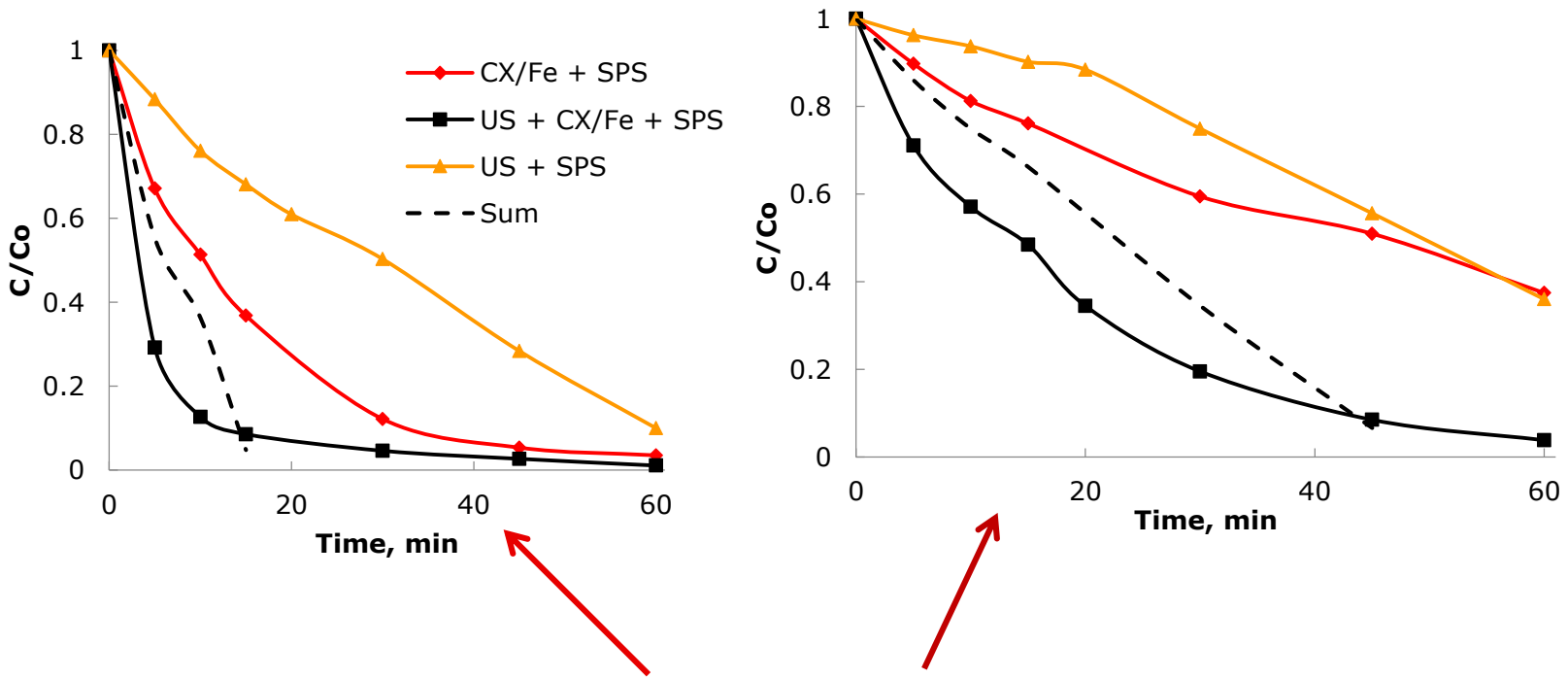
Scenarios of Process Integration

- **Simultaneous application of AOPs**
- **Coupling AOPs with physicochemical processes (to improve selectivity/treatability)**
- **AOPs as pre-treatment to biological post-treatment (to save money)**
- **Various combinations of the above**

Additive or synergistic action ? (by visual inspection)

Endocrine disruptor: 420 µg/L propyl paraben

Magnetic carbon xerogel (CX/Fe) + persulfate (SPS), Ultrasound (20kHz US) + persulfate

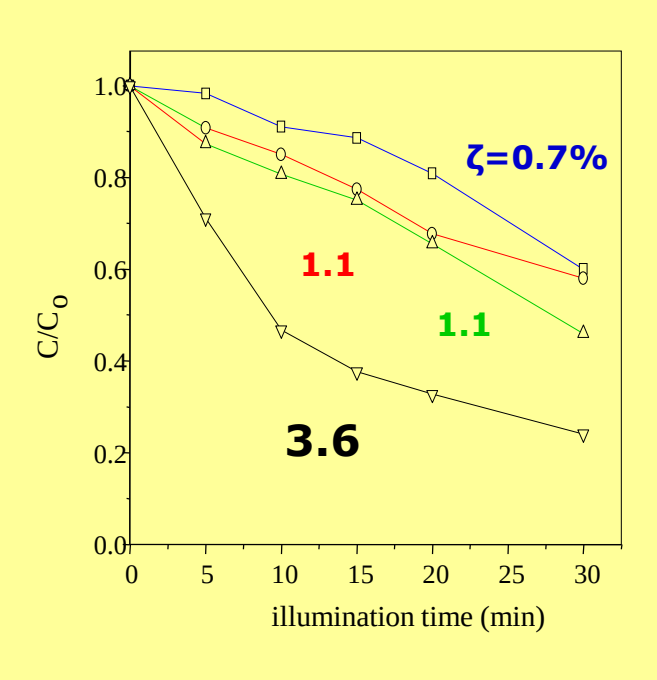


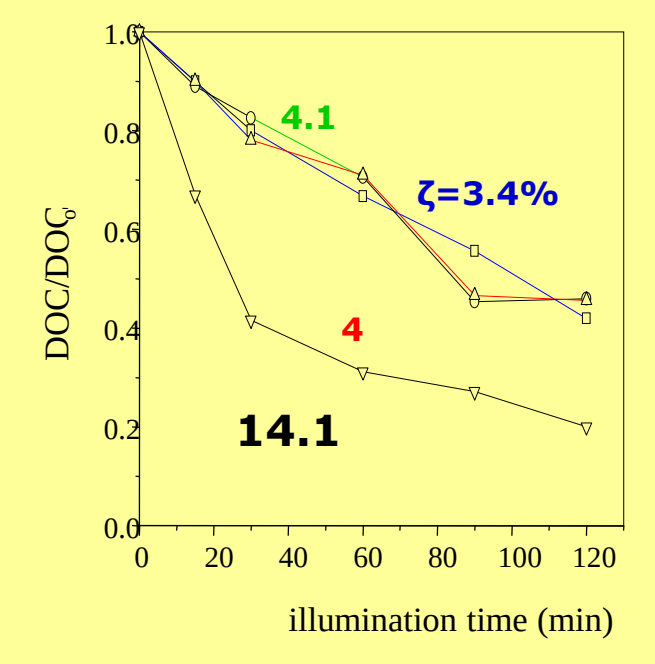
Pure water wastewater

Additive or synergistic action ? (based on initial rates)

Pesticide imidacloprid: 20 mg/L (it looks and actually is huge !)

UV-A degradation: TiO_2, TiO_2/H_2O_2, TiO_2/Fe^{3+}, $TiO_2/Fe^{3+}/H_2O_2$





(■) TiO_2 (0.5 g/L), (●) TiO_2 (0.5 g/L) + Fe^{3+} (7 mg/L), (▲) TiO_2 (0.5 g/L) + H_2O_2 (50 mg/L), (▼) TiO_2 (0.5 g /L) + Fe^{3+} (7 mg/L) + H_2O_2 (50 mg/L)

ζ=f(initial rate, photon flux)=apparent photonic efficiency

Quantifying synergy (based on kinetics)

$$S(\%) = 100 \frac{k_{combined} - \sum_{1}^{n} k_i}{k_{combined}}$$

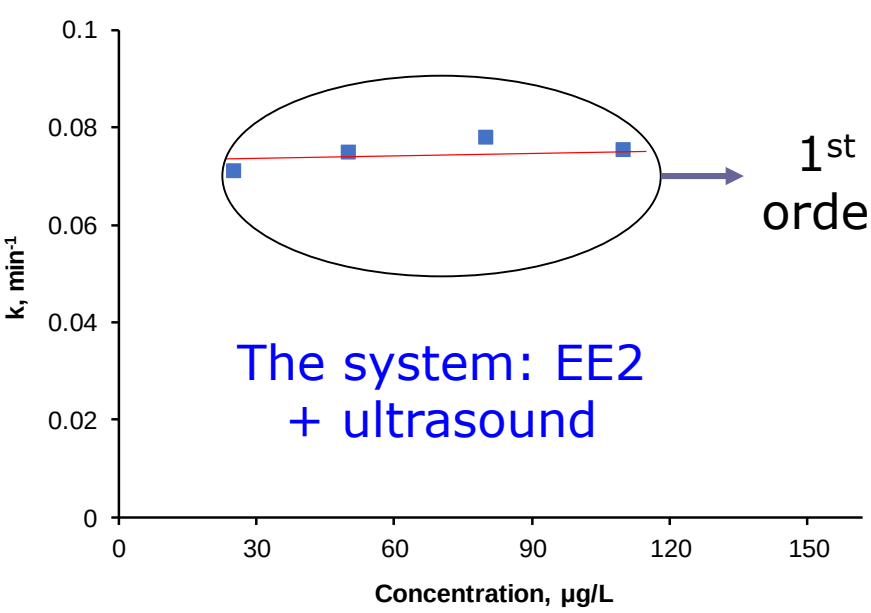
$$S \begin{cases} > 0 & synergistic\ \ effect \\ = 0 & cumulative\ effect \\ < 0 & antagonistic\ \ effect \end{cases}$$

* Defining the individual processes may be tricky
* Which are the individual pieces in sonophotocatalysis (US+UVA/TiO_2) ?
* Sonolysis + Photocatalysis ?
* Sonocatalysis + Photocatalysis ?
* Sonocatalysis + Photolysis ?

…the approach requires knowledge of k values

Tip #2: Kinetics at a simple level

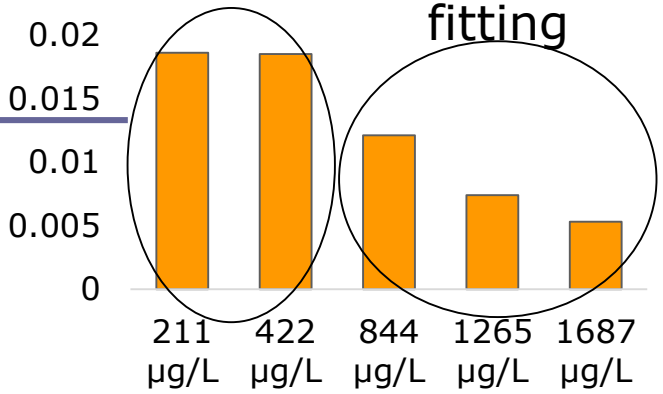
* Kinetics, even at the level of a power-law expression, can be confusing
* Runs at a single concentration and data fitting to $R_A=-kC_A$ is the norm
* Confusion between data fitting and kinetic modelling
* Confusion between first and pseudo-first order
* It's more likely to get 0^{th} order rates at unrealistic concentrations
* Reactor design is a function of R_A



The system: EE2 + ultrasound

1st order

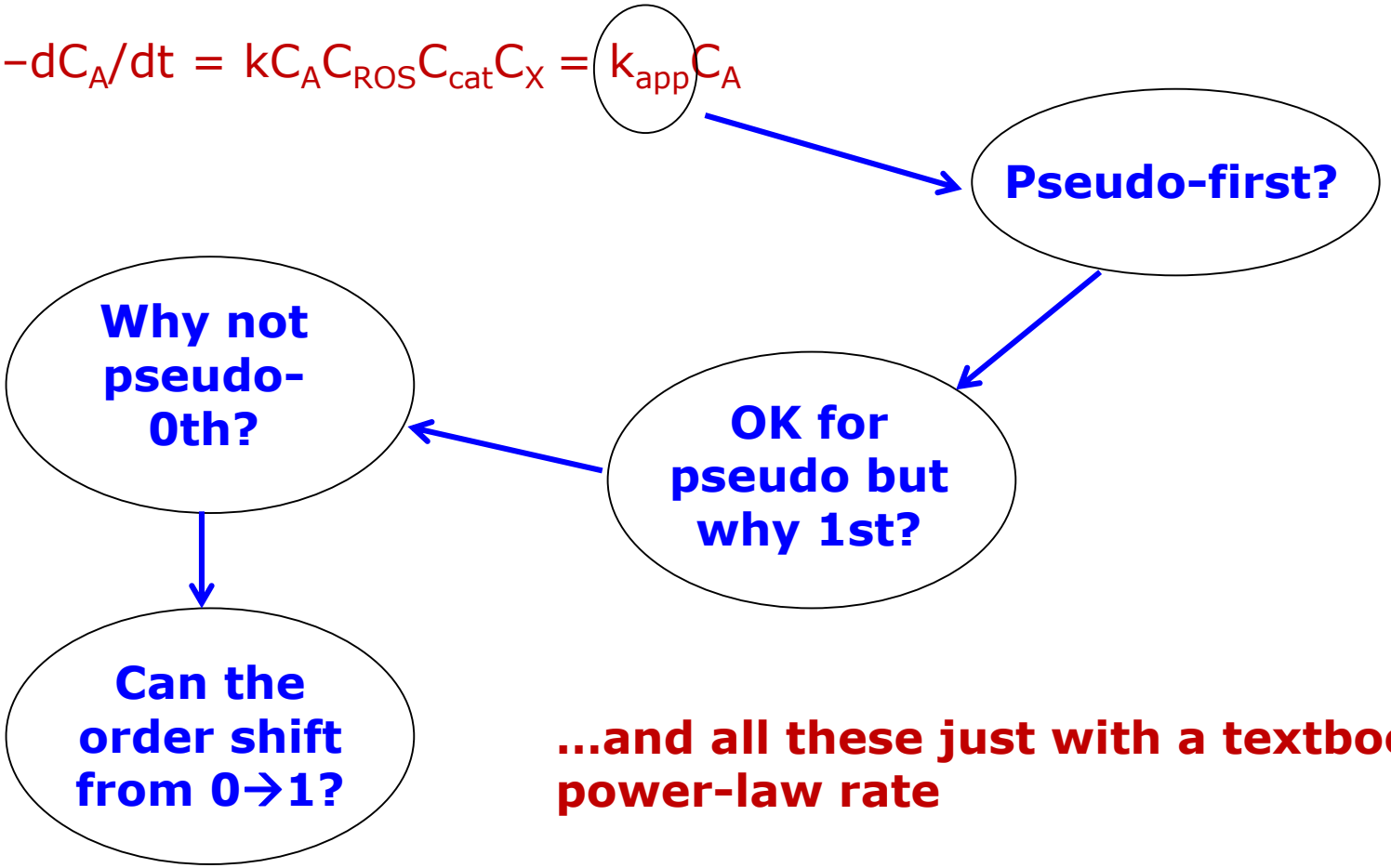
Data fitting



The system: Propylparaben + Al/TiO_2 + solar light

Tip #2: Kinetics at a simple level

Assume $-dC_A/dt = kC_AC_{ROS}C_{cat}C_X = k_{app}C_A$



…and all these just with a textbook power-law rate

Tip #2: Kinetics at a simple level

* Factorial design and alike statistical tools are very popular nowadays since they "minimize" research effort, e.g. to study 4 variables requires 2^4 experiments between a low and a high value

* Process variables → response → simple (simplistic) model → physical meaning occasionally questionable

* If C_o is a variable, DO NOT use % removal as the response; instead, try g/L of whatever is removed

* Avoid using pH as a variable even if the system is buffered; pH is a logarithmic expression but the model is usually linear

Tip #3: The water matrix

* Naturally occurring substances, e.g. anions, cations, natural organic matter, effluent organic matter, extracellular polymeric substances, solids

* Substances associated with industrial pollution (incl. agrochemical pollution)

* Substances needed to operate a given AOP, e.g. catalysts and activators, dissolved gases, electrolytes, oxidants

* Microorganisms

* The degree of complexity

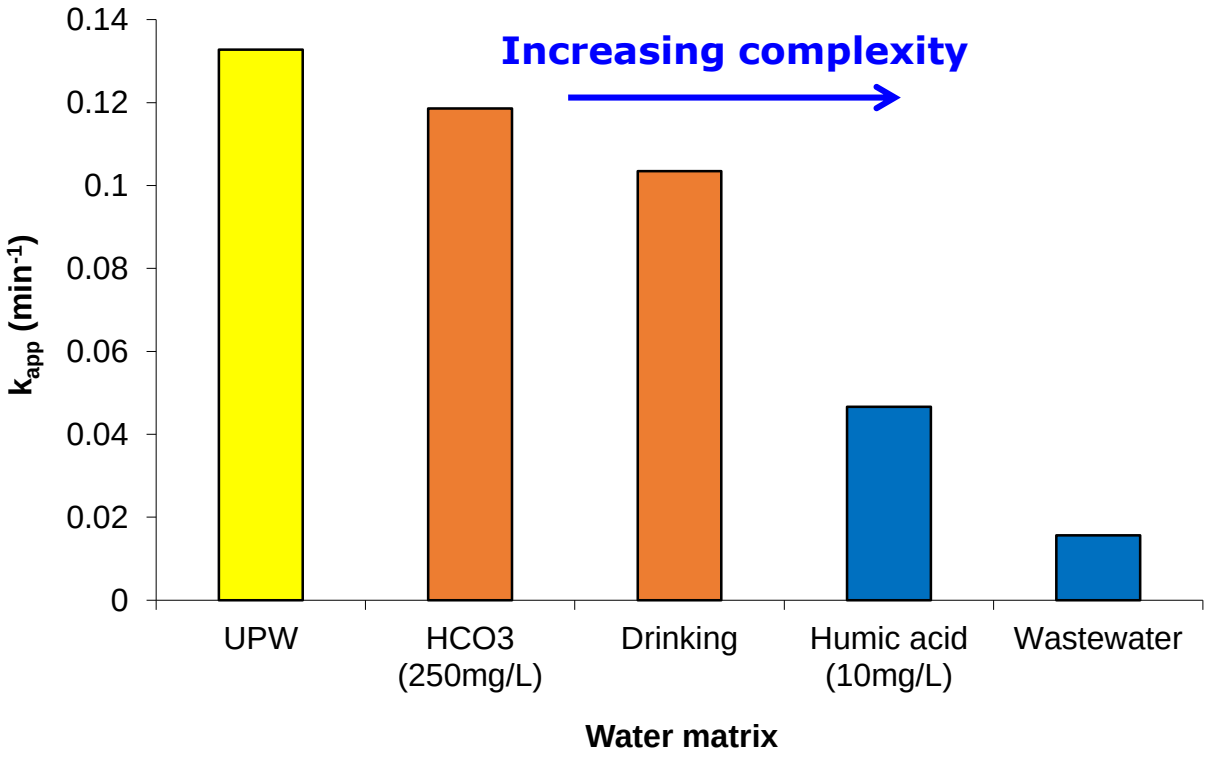
* **Define the basis to define the matrix !**

The dominant opinion

Rule of thumb: The more complex the matrix is, the slower the rate is

* Non-target organics and inorganics scavenge ROS but produce others
* Concentration of target contaminants <3 orders than non-target species

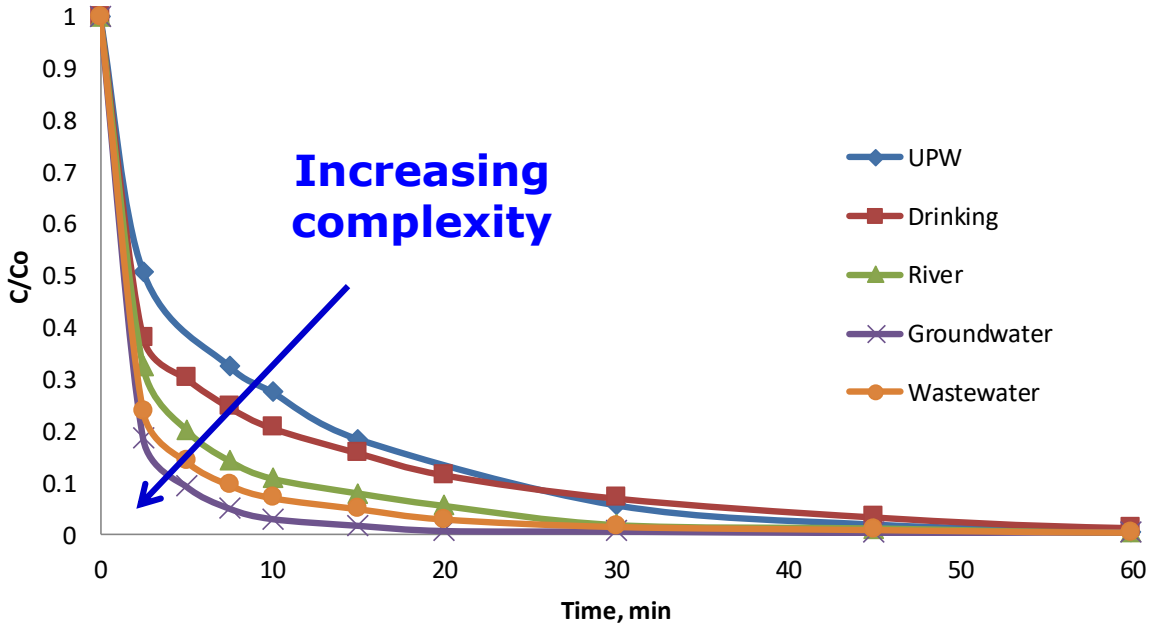
The system:
SMX (ppb) +
WO_3/TiO_2 +
solar light



The “rule of thumb” re-visited

Question: Is it just an interplay between ROS and the matrix?
Answer: Straight No
Hypothesis: Very system-specific incl. type of contaminant, source of ROS, catalysts/activators, operating conditions

The system:
Bisphenol (BPA) (ppb) + $Na_2S_2O_8$ (ppm) + CX/CoFe



Bicarbonate – The general perception

What generally happens:

$HCO_3^- + {}^\bullet OH \rightarrow {}^\bullet CO_3^- + H_2O$

$2{}^\bullet CO_3^- \rightarrow CO_2 + CO_4^{2-}$

$2{}^\bullet OH \rightarrow H_2O_2$

…and its implications:

$^\bullet OH$ stronger than $^\bullet CO_3^-$ (2.3 vs 1.8 V)

$^\bullet CO_3^-$ may be more selective than $^\bullet OH$

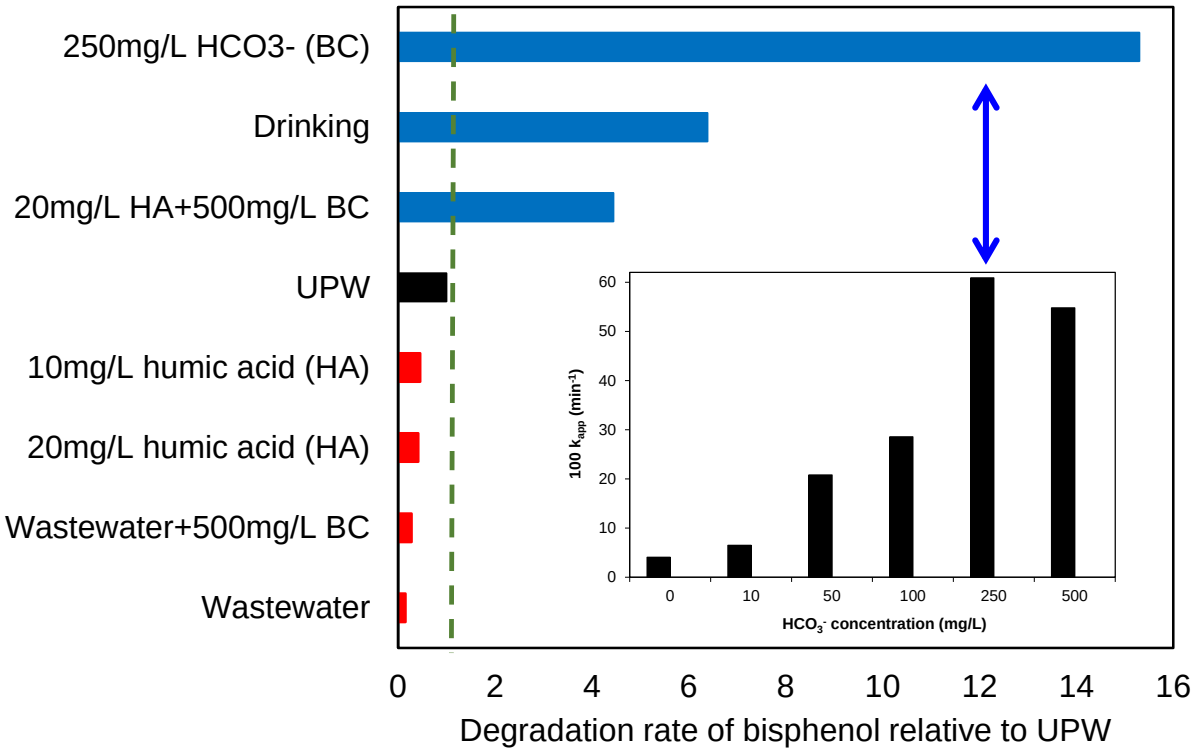
$^\bullet OH$ recombines 100X faster than $^\bullet CO_3^-$

The net result:

can go either way but changes in rates are not dramatic

Bicarbonate – Dr Jekyll or Mr Hyde ?

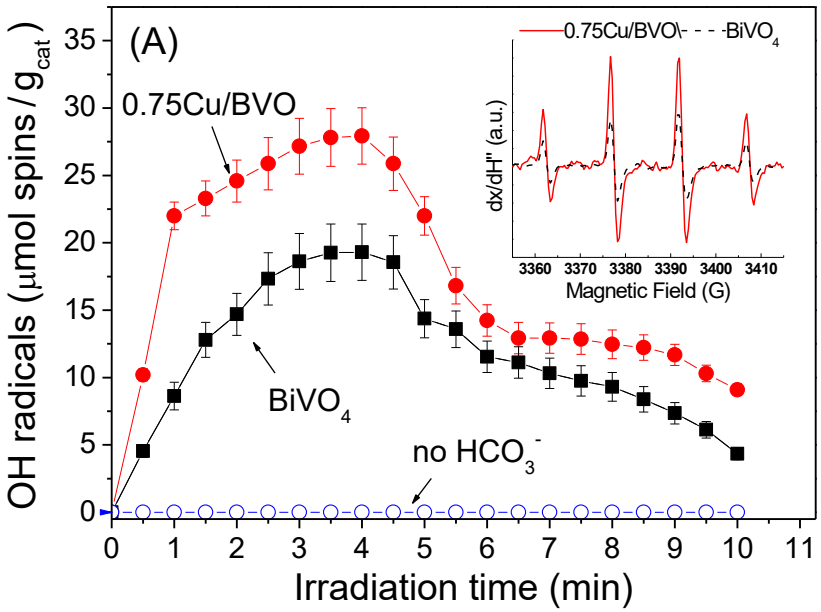
The system:
BPA (ppb) +
0.75$CuO_x/BiVO_4$
+ solar light

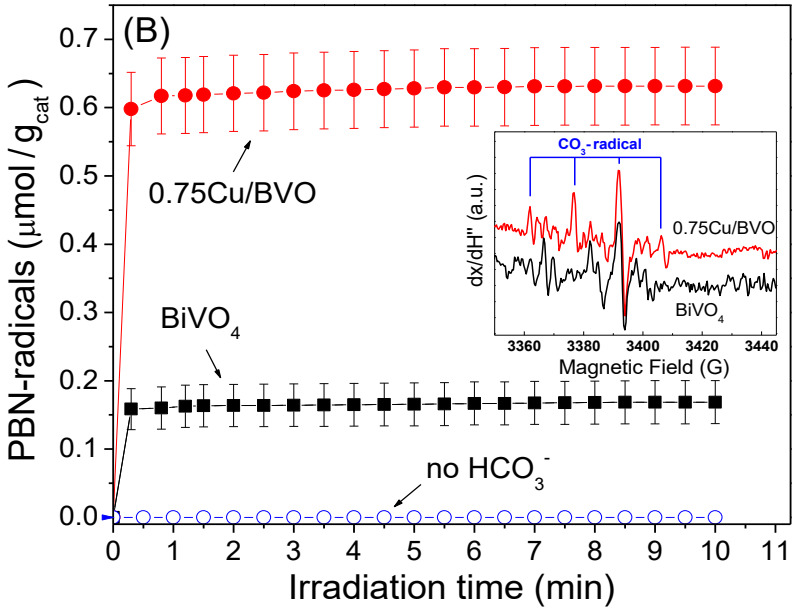


Chemical Engineering Journal, 318, (2017), 39-49

The mechanism of “acceleration”

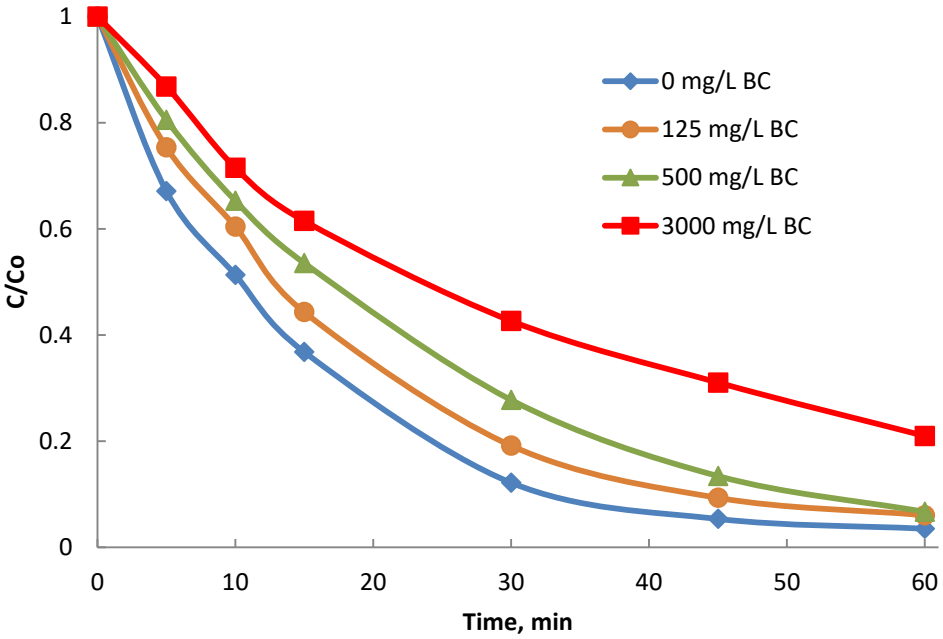
EPR (DMPO & PBN spin-trapping) shows that **(A)** OH radicals diffuse from the catalyst surface to the solution only in the presence of bicarbonate, while **(B)** carbonate radicals stay on the surface

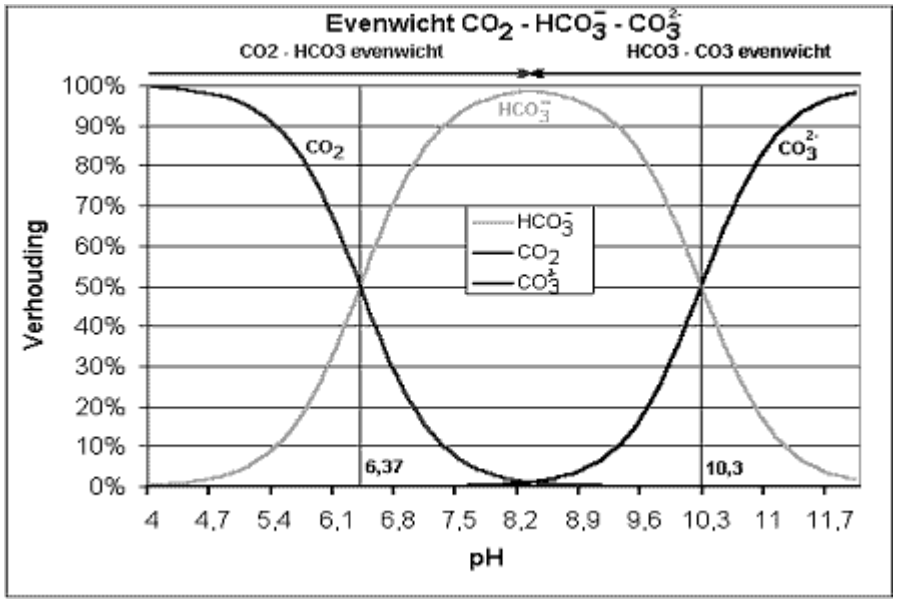




Bicarbonate – Beware of Greeks bearing gifts ☺

* Bicarbonate can be damaging although it's not supposed to be there
* Check for the operating conditions (agitation, purging etc)





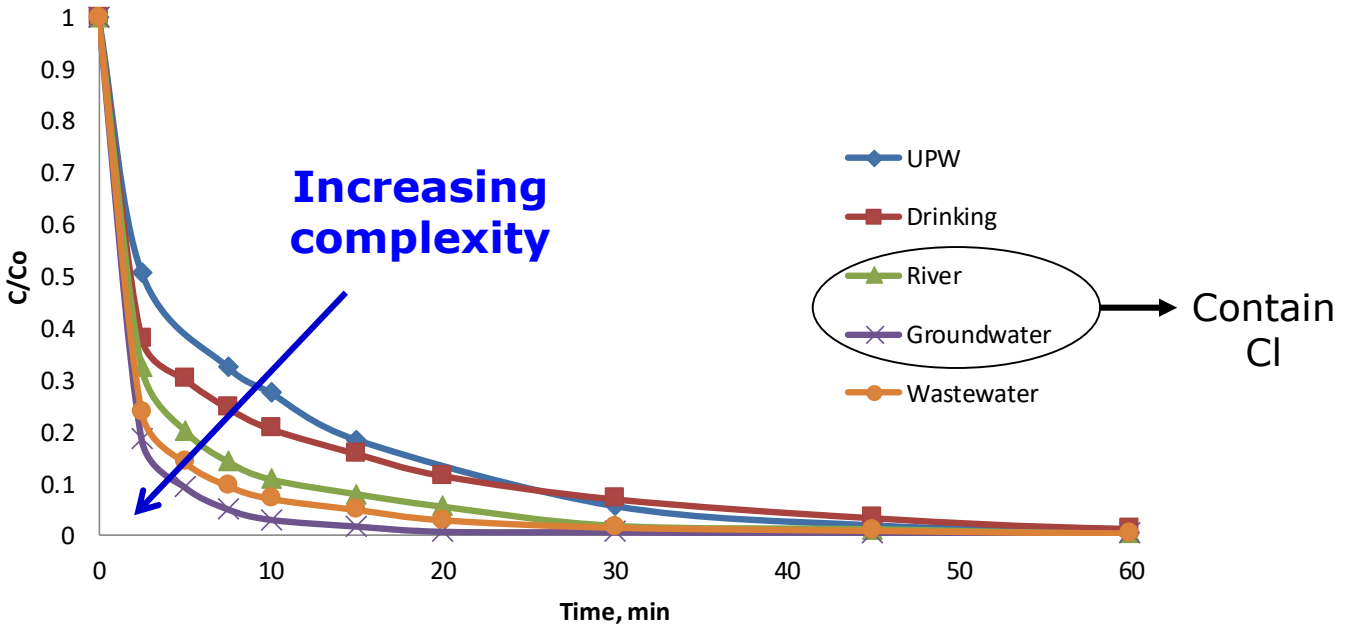
Source: http://www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm

The system: Propylparaben (ppb) + $Na_2S_2O_8$ (ppm) + CX/Fe + buffered pH=3

☺ *Timeo Danaos et dona ferentes,*
Aeneid (II, 49), Virgil, 29-19 BC

The effect of chloride on kinetics (or mechanisms ?)

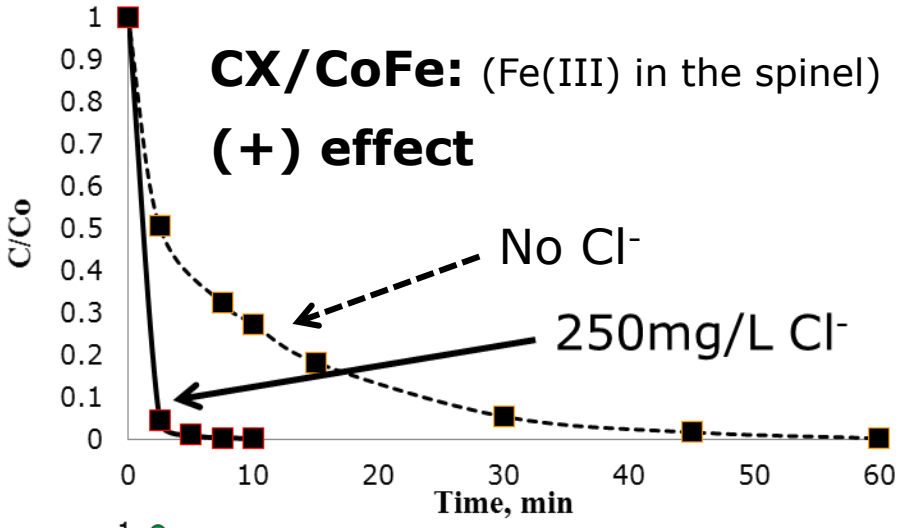
The system:
BPA (ppb) +
$Na_2S_2O_8$ (ppm)
+ CX/CoFe



Individual effects:

Bicarbonate (detrimental)
Alcohols (detrimental)
Humic acid (detrimental)
Chloride (?)

The effect of chloride



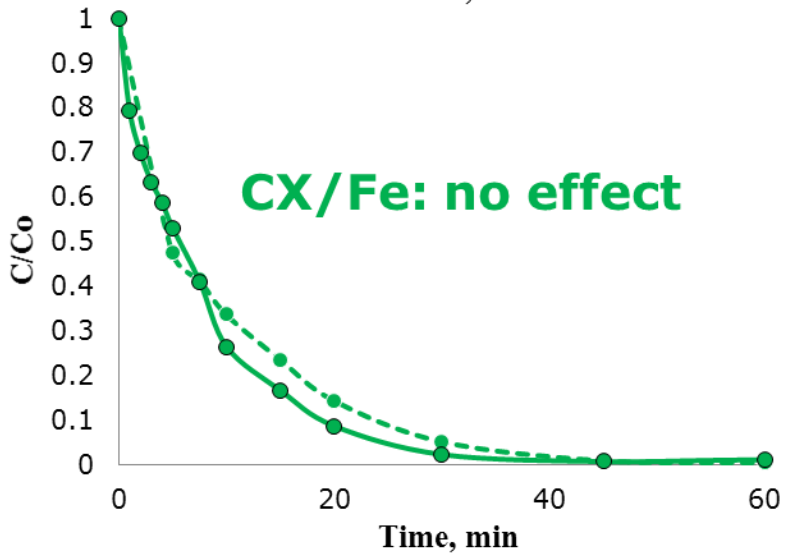
$\bullet SO_4^- + Cl^- \rightarrow SO_4^{2-} + \bullet Cl$

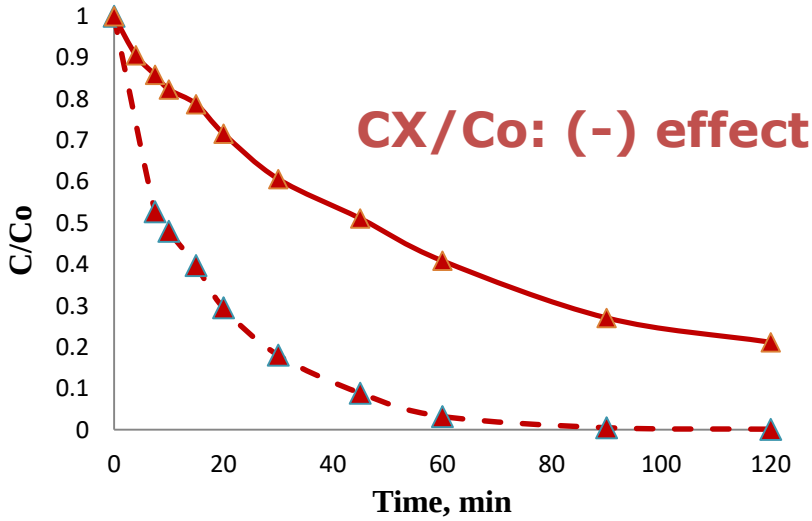
$\bullet Cl + Cl^- \rightarrow \bullet Cl_2^-$

Several Cl-TBPs (LC-MS-TOF)

$Fe^{2+} + \bullet Cl \rightarrow Fe^{3+} + Cl^-$

$Fe^{2+} + \bullet Cl_2^- \rightarrow Fe^{3+} + 2Cl^-$





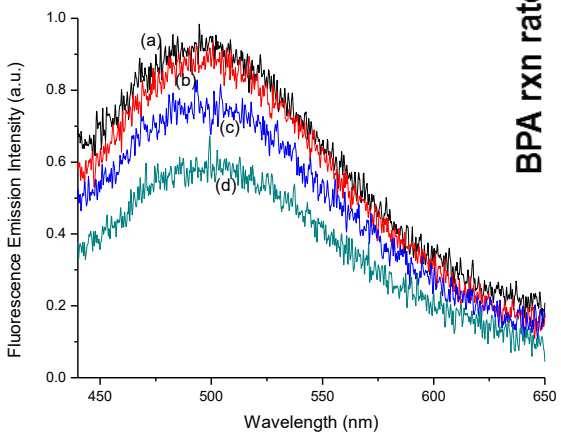
Organics behaving badly

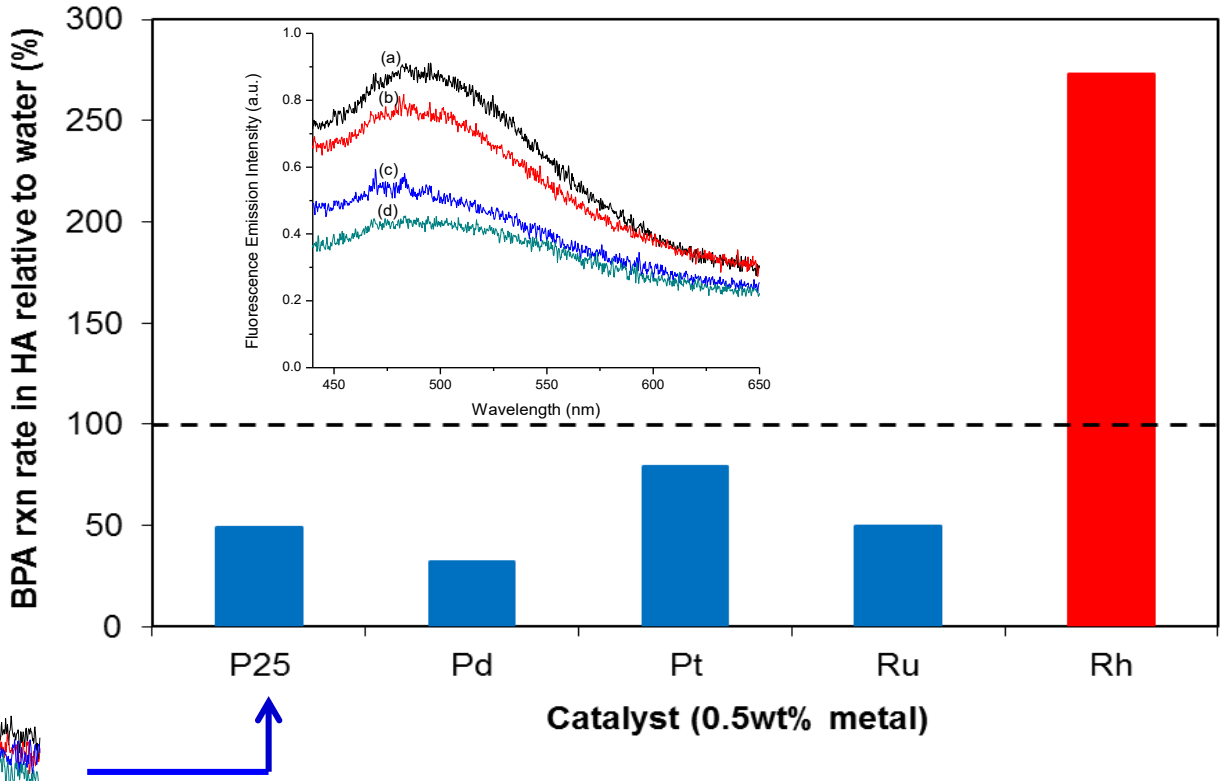
* NOM, EfOM, EPS in waters/wastewaters
* Macro-molecules modelled by humic, fulvic acids
* Concentrations 3+ orders of magnitude relative to (micro-)contaminants
* As ROS are non-selective, the effect on rates is expectedly negative
* Perhaps, the most predictable behavior of all effects

Exceptions that prove the rule…

HA photosensitizes Rh/TiO_2. Inset graph shows fluorescence spectra (410nm) of HA at various Rh/TiO_2 concentrations (a-b-c-d=100-200-500-1000 mg/L)

The system:
BPA (ppb) +
Me/TiO_2 +
solar light





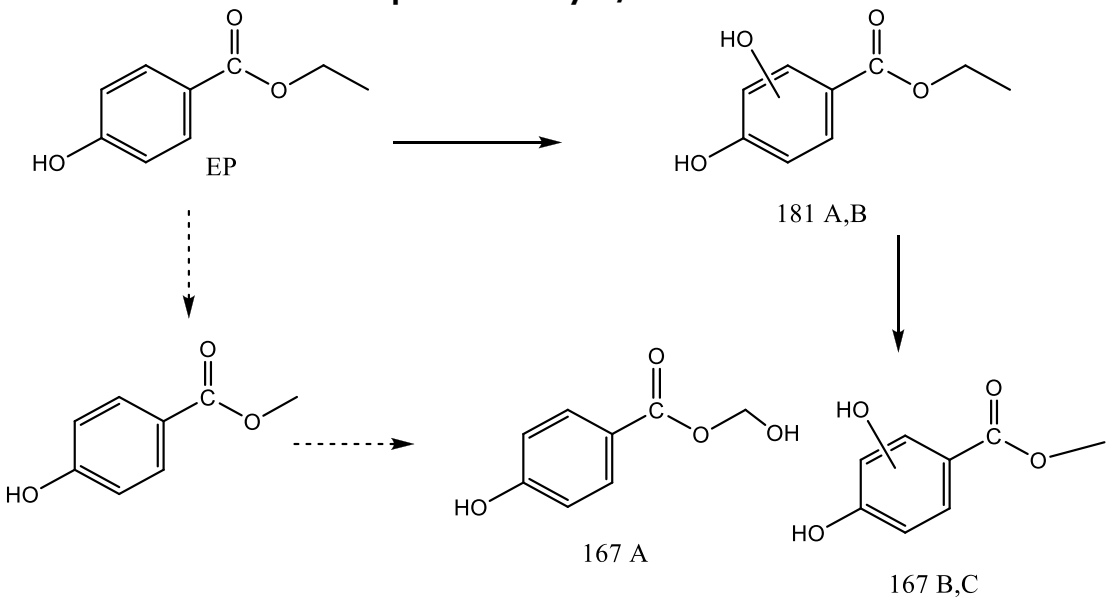
Catalysis Today, 284, (2017), 59-66

Matrix goes beyond the inherently present species

* Chloride is a favorite electrolyte in the electrochemical community
* Indirect oxidation through Cl radicals, Cl_2, ClO_2, HOCl

* Liquid bulk rxns can yield current efficiencies $= \frac{COD_o - COD_t}{8It} FV >> 100\%$

* More impressive can be the effect on pathways/mechanisms

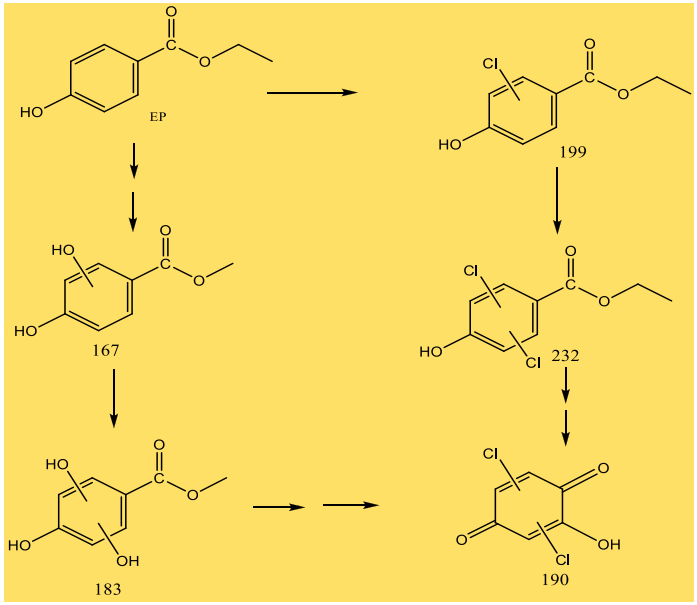


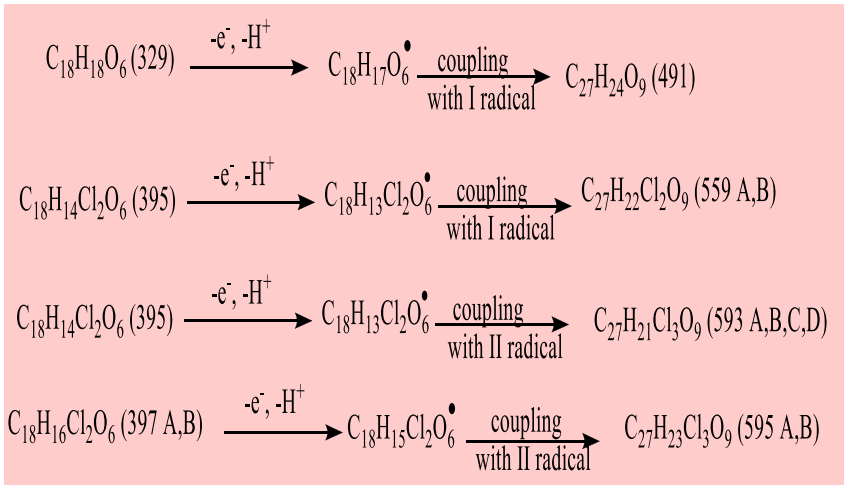
The system:
Ethylparaben (ppb) +
BDD anode + Na_2SO_4

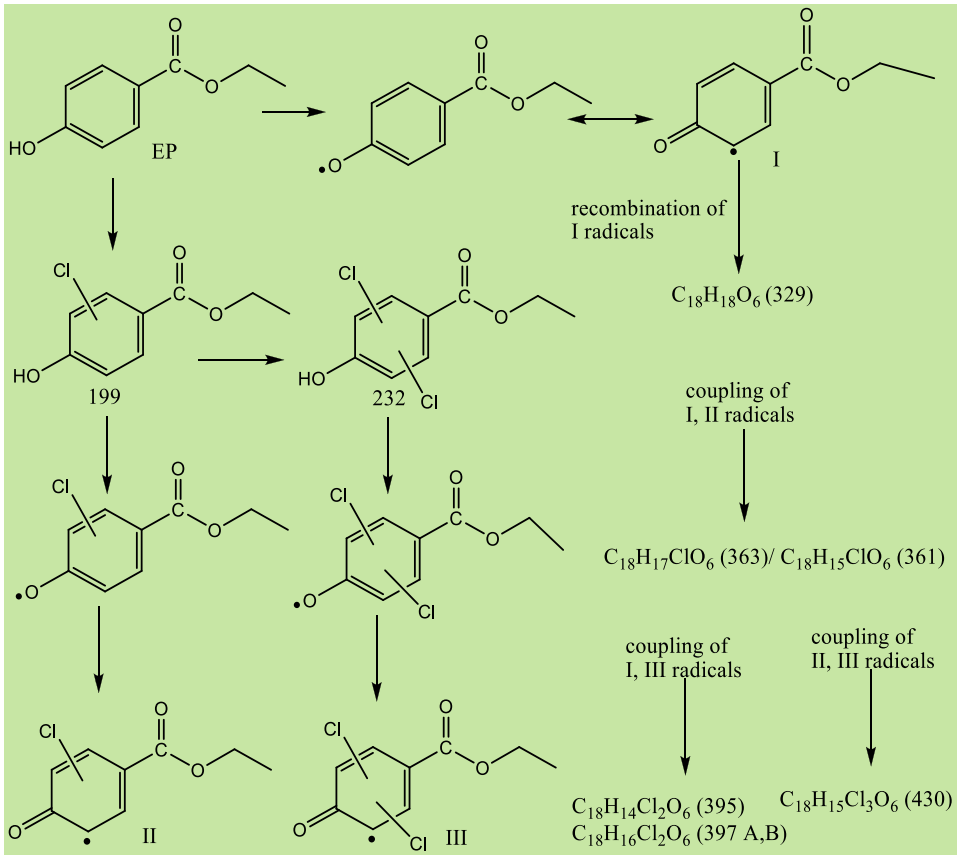
***Journal of Environmental Management*, 195, (2017), 148-156**

* Hydroxylation -> Dealkylation rxns through •OH
* Nothing really fancy occurs

Switching to NaCl…







Chlorination, hydroxylation, dealkylation

Dimerization rxns

Trimerization rxns

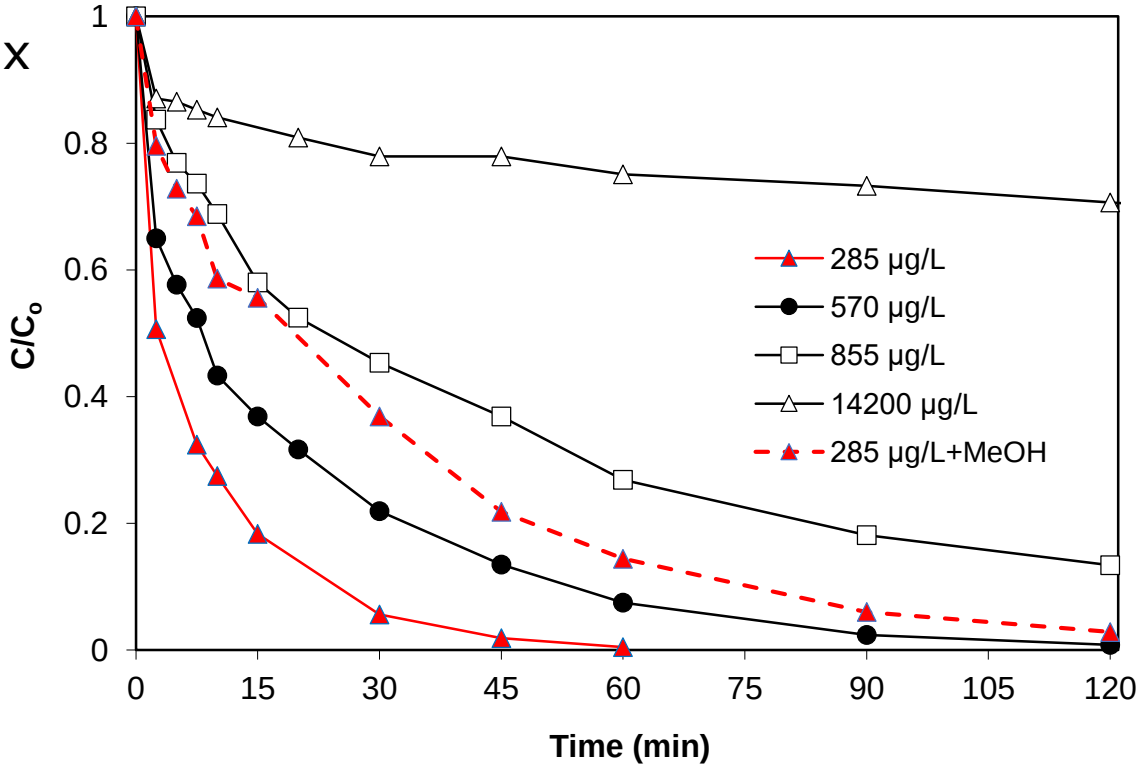
Unrealistic concentrations: an equivalent matrix effect

* Micro-contaminants (ng/L-µg/L) are typically studied at mg/L levels

Authors' reply: "…to overcome analytical constraints associated with very low concentrations and achieve realistic time-scale treatments…"

* This introduces a matrix effect in terms of:
- kinetics (for sure)
- TBPs distribution (?)

The system:
BPA (ppb) +
$Na_2S_2O_8$ (ppm)
+ CX/CoFe



Bits and pieces of thoughts (instead of conclusions)

* Matrix effects are known, unknown and suspected * Dyes and visible PAOPs need caution * Dyes and O_3 is great combination * Polymerization is under-looked * 1st order * Batch or continuous operation * Integration * Chlorine-based oxidants * Fenton and temp. * Ultrasound and temp. * H_2O_2 method of addition * Synergy * Scale-up * Cost and LCA * L-H model (or dark vs light adsorption) * Control and blank runs * Discuss with others * Write-up (chapters, papers etc) during research * Disappointment is part of the process * Non-TiO_2 photocatalysts * Sample pre-treatment * Pressure costs (for WAO) * COD usually (2-3) times TOC * Different perspectives for micro- and mega-contaminants * Detection of TBPs makes nice papers * Bio- and toxicity tests for mega-contaminants

* Nearly everything can be explained in this live !

* …and more importantly: **DO NOT LET ADVISORS TOUCH THINGS**

Summing up…

PROCESSES

- "Old-Fashioned" Process integration
- Novel Hybrid Process development

ENVIRONMENT

- Carbon footprint reduction
- Emerging pollution abatement

Working at the interface of

ENGINEERING

&

SCIENCE

APPLICATIONS

- Effective exploitation of:
  - Water (Reuse as Potable)
  - Resources (Valorization)
  - Energy (Renewable & Alternative)

MATERIALS

- Selective catalysts
- (Photo-) active catalysts