NTUA

SOLAR SAFE WATER

Puerto Iguazú - Misiones - República Argentina

Photocatalytic Treatment of Humic and Fulvic Substances in Solar Cocentric Parabolic Concentrator

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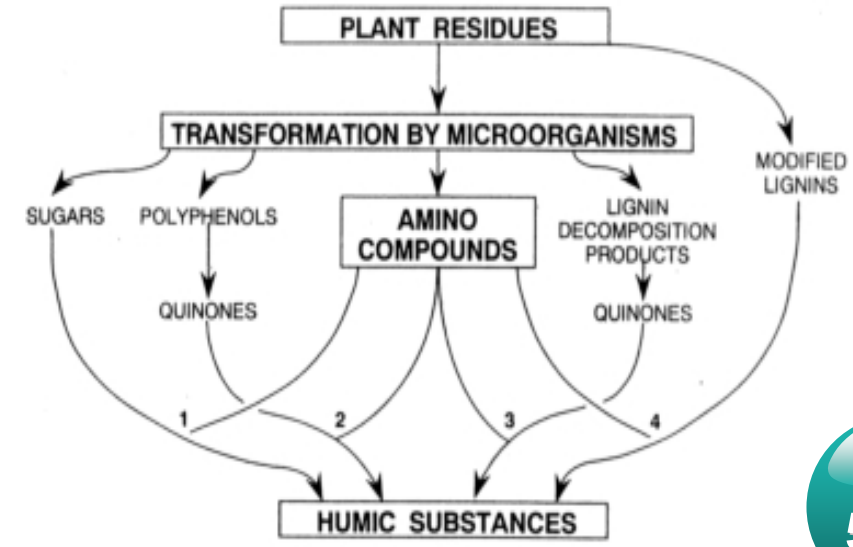
Dissolved Organic Material (DOM) in natural waters

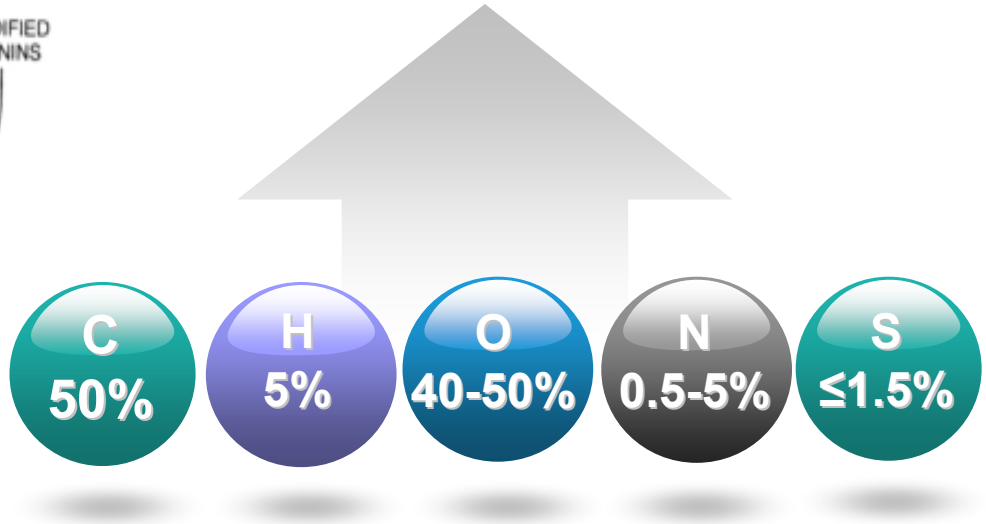
- The largest pool of organic material in the water column is dissolved organic material (DOM).
- Aquatic humus accounts for 40-60% of the DOM.
- Humic substances are formed during the degradation of plant and animal material, and both microbiological and abiotic processes contribute to their production.

Origin – Composition of HAs

Formation pathways of Humic Substances



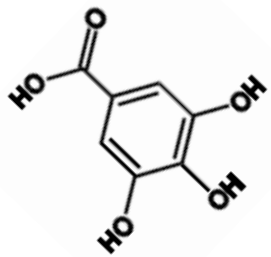
Elemental Composition



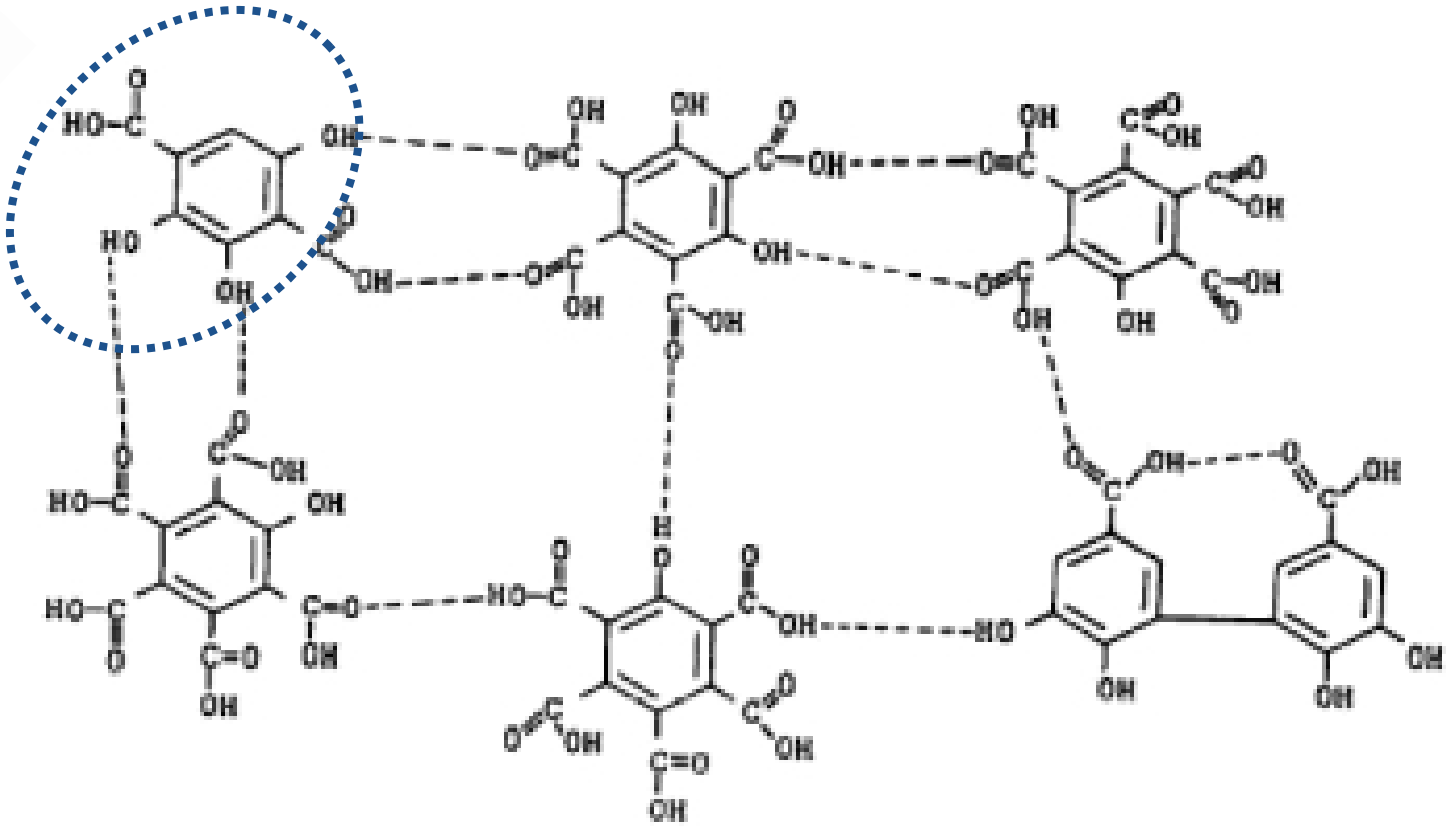
Humic Substances (HS)

- Heterogeneous polymeric organic acids: aliphatic and aromatic character.
- Rich in oxygen-containing moieties : carboxyl, phenolic, alcoholic, and ketonic.
- HS impart a brown/yellow colour to the water.
- They complex with metals and organic pollutants.
- They affect the mobility and bioavailability of aquatic contaminants.
- They are precursors of mutagenic halogenated compounds in water formed after chlorination.
- HS play also the role of photosensitizers in aquatic photochemical processes.

Proposed Molecular Structure of Fulvic Acid



Gallic Acid



Effects of UV radiation on Humic Substances

- **UV provide the most energetic radiation available for photochemical reactions in surface waters**

  - Reduction of dissolved organic carbon average molecular weight
  - Changes in water optical properties
  - Production of a complex mixture of reactive oxygen species
  - Production of carbon photoproducts:
    - CO_2 production from photodecarboxylation
    - Low molecular weight compounds including carbonyls and organic acids → biologically available compounds generated by photochemical reactions → growth enhancement of heterotrophic bacteria

Photolysis

Excitation by light of HA molecules

$$HA_{aq} \xrightarrow{hv} HA_{aq}^{*}$$

The molecules are photosensitizers producing free radicals $OH^{\bullet}$ which contribute to further oxidation of the molecule

Semi-conductor Photocatalysis
TiO_2 Photocatalysis

TiO_2 : Stable, non toxic, low energy band gap

One of the most suitable semiconducting materials for photocatalysis

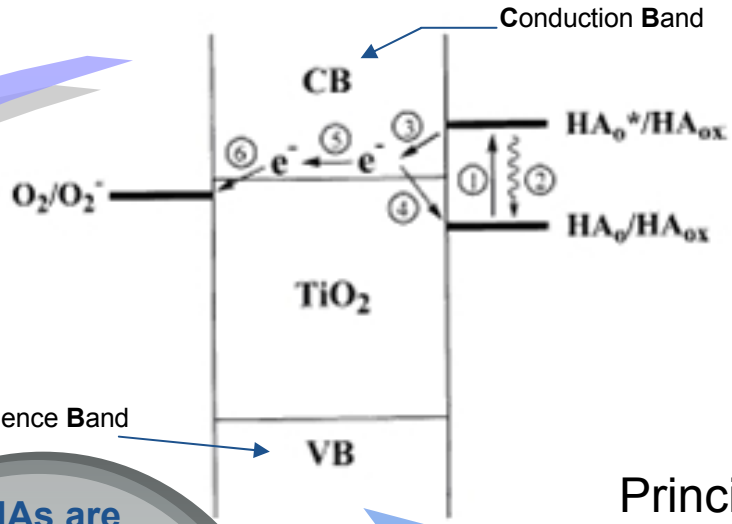
STEPS

1. Transfer of the reactant in the fluid phase to the catalyst surface
2. Adsorption of the reactant
3. Reaction in the adsorbed phase
4. Desorption of the products
5. Removal of the products from the interface region

Semi-conductor Photocatalysis
TiO_2 Photocatalysis

HA act as a natural photosensitizer in heterogeneous as well as homogeneous solutions

HA adsorbed on TiO_2 are excited by absorbing visible light and subsequently inject electrons to CB of TiO_2



HAs are oxidised upon electron injection. The injected electrons can transfer to substrates at the semiconductor/water interface to initiate sensitised reduction processes

Principle of photosensitised degradation of HA in TiO_2 under visible light

Semi-conductor Photocatalysis
TiO_2 Photocatalysis

- $TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB}$
- Organic molecule + O_2 …. $\xrightarrow{TiO_2,\ h\nu \geq E_{bg}}$ $CO_2 + H_2O$
- $h^+_{VB} + OH^- \rightarrow OH^\bullet$
- Organic radicals + $O_2 \rightarrow CO_2 + H_2O$
- $e^-_{CB} + O_2 \rightarrow O_2^-$
- $2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2$
- $H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + OH^-$

Elementary reaction steps of HA on the TiO_2/water interface

Adsorption on the catalyst surface

$HA_{aq} + TiO_2 \rightarrow HA\text{-}TiO_2$

Excitation by light of free-in solution non adsorbed HA molecules

$$HA_{aq} \xleftrightarrow{hv} HA_{aq}^*$$

Excitation of adsorbed HA molecules

$$HA\text{-}TiO_2 \xrightarrow{hv} HA^*\text{-}TiO_2$$

Adsorption of excited HA molecules on the catalyst and oxidation

$HA^*_{aq} + TiO_2 \rightarrow HA_{ox} + TiO_2 (e^-_{cb})$

Oxidation of the adsorbed excited HA molecules

$HA^*\text{-}TiO_2 \rightarrow HA_{ox}\text{-}TiO_2 (e^-_{cb})$

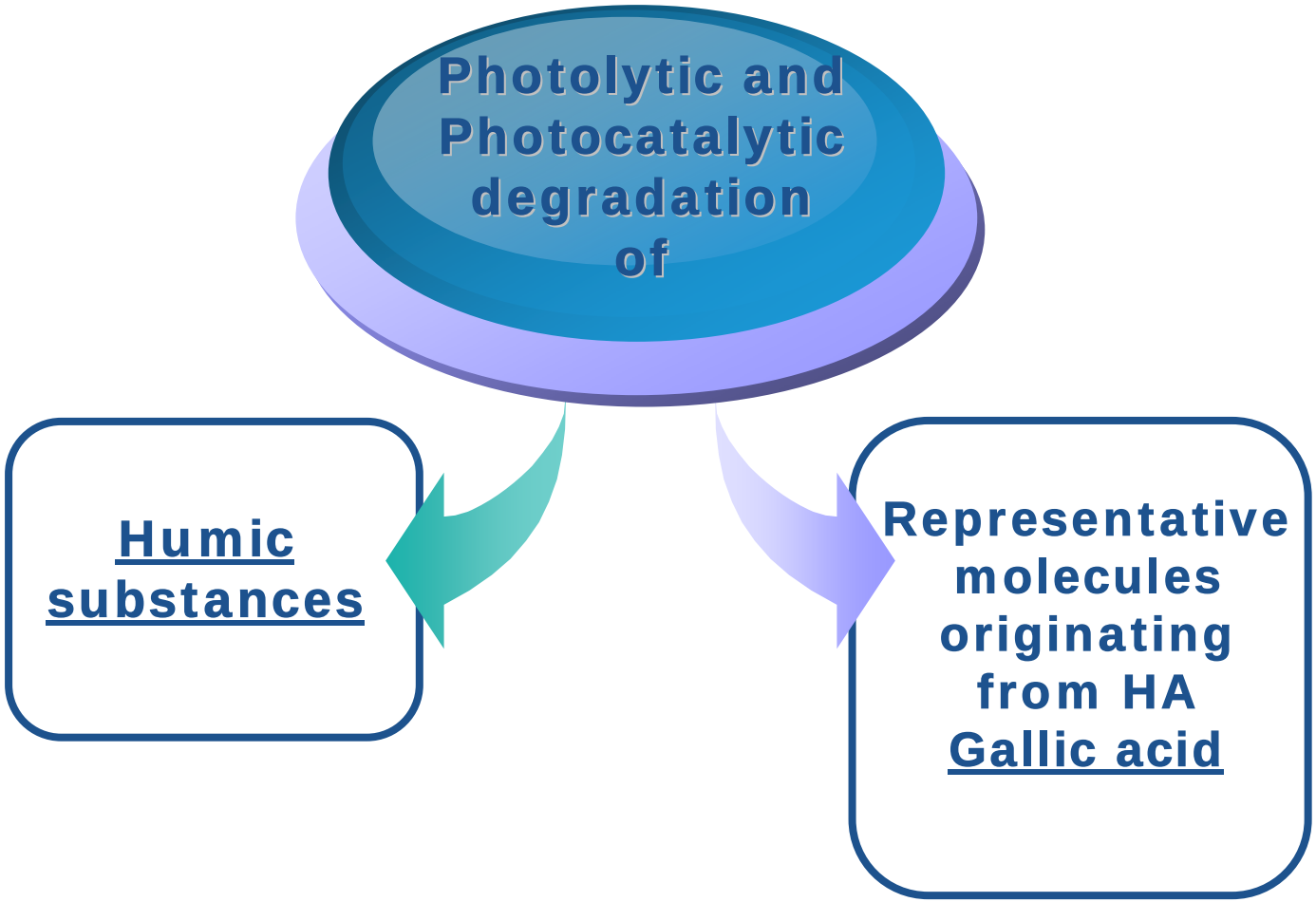
Electrons transfer to dissolved O_2, further oxidation of HA

$HA_{ox}\text{-}TiO_2 (e^-_{cb}) + O_2 \rightarrow HA_{ox}\text{-}TiO_2 + O_2^-$

Reduction of the oxidized HA molecules by recombination of electrons to HA_{ox}

$HA_{ox}\text{-}TiO_2 (e^-_{cb}) \rightarrow HA\text{-}TiO_2$

Target of the present study



Materials and Methods

1. Gallic Acid
2. Standard Fulvic acid purchased from International Humic Substances Society (IHSS)
3. Humic acid (Aldrich, Sodium salt)

Methodology followed

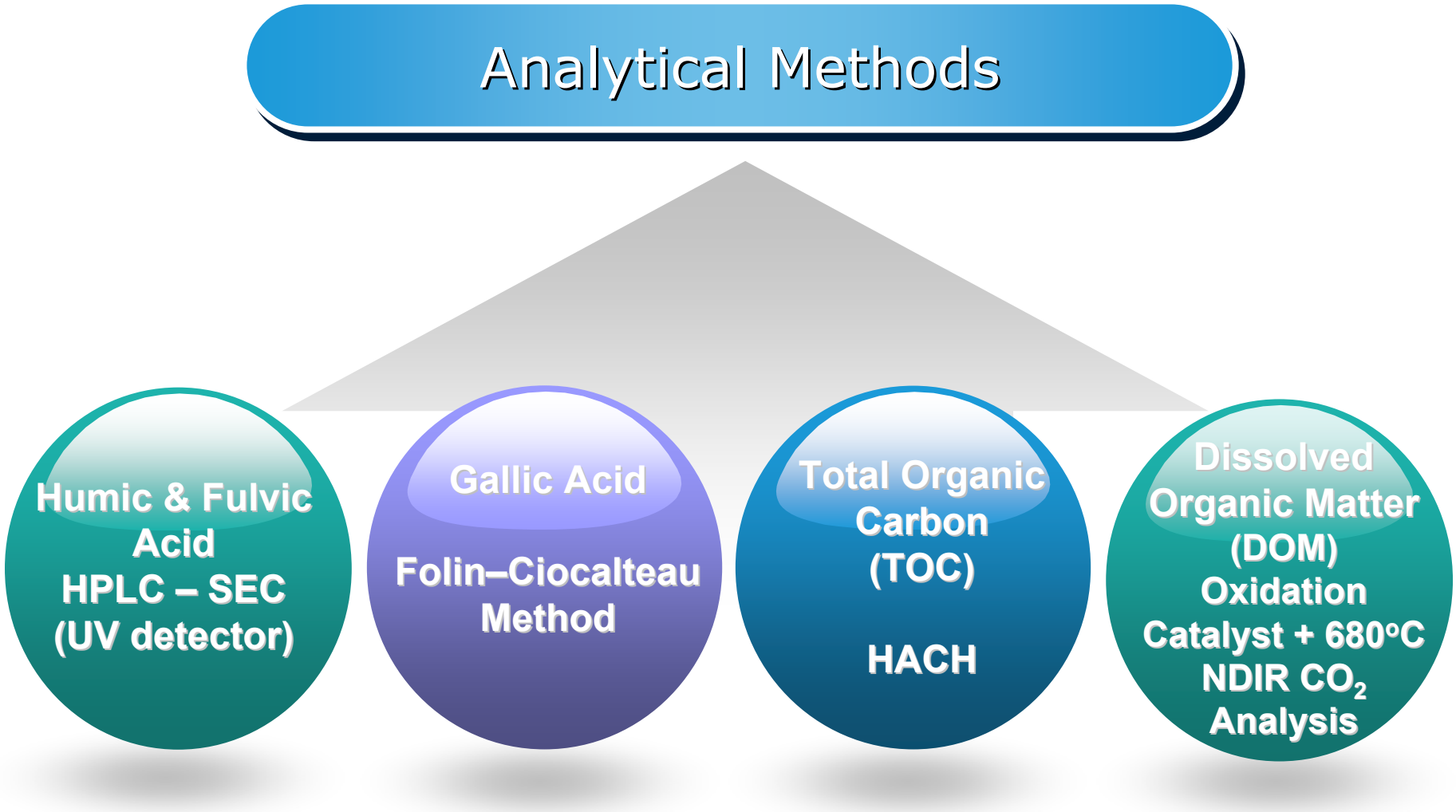
- Experiments without catalyst_: to study only the photolysis.
- Study of the adsorption of HA on the immobilized TiO_2. The CPC reactor operates initially for 15-20h in the dark.
- Experiments with 1049 AHLSTROM paper containing 20g/m^2 of TiO_2 Degussa P25. The solution is permanently in contact with 1.2 g/l TiO_2.
- The UV 254nm reactor is used for comparison and confirmation of the results obtained by the CPC reactor.

The photocatalytic reactors

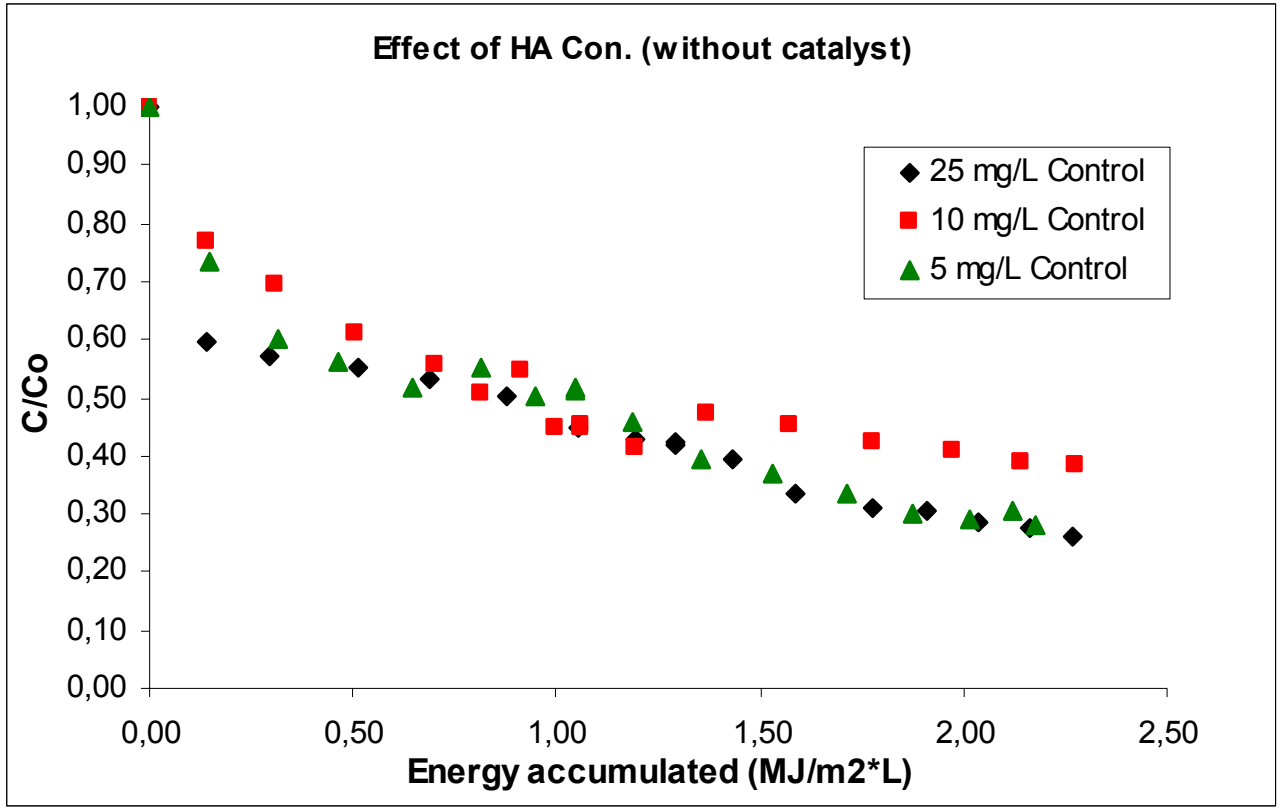
Solar Cocentric Parabolic Concentrator

UV 254 reactor

Materials and Methods



Results
HA Photolysis - CPC Reactor



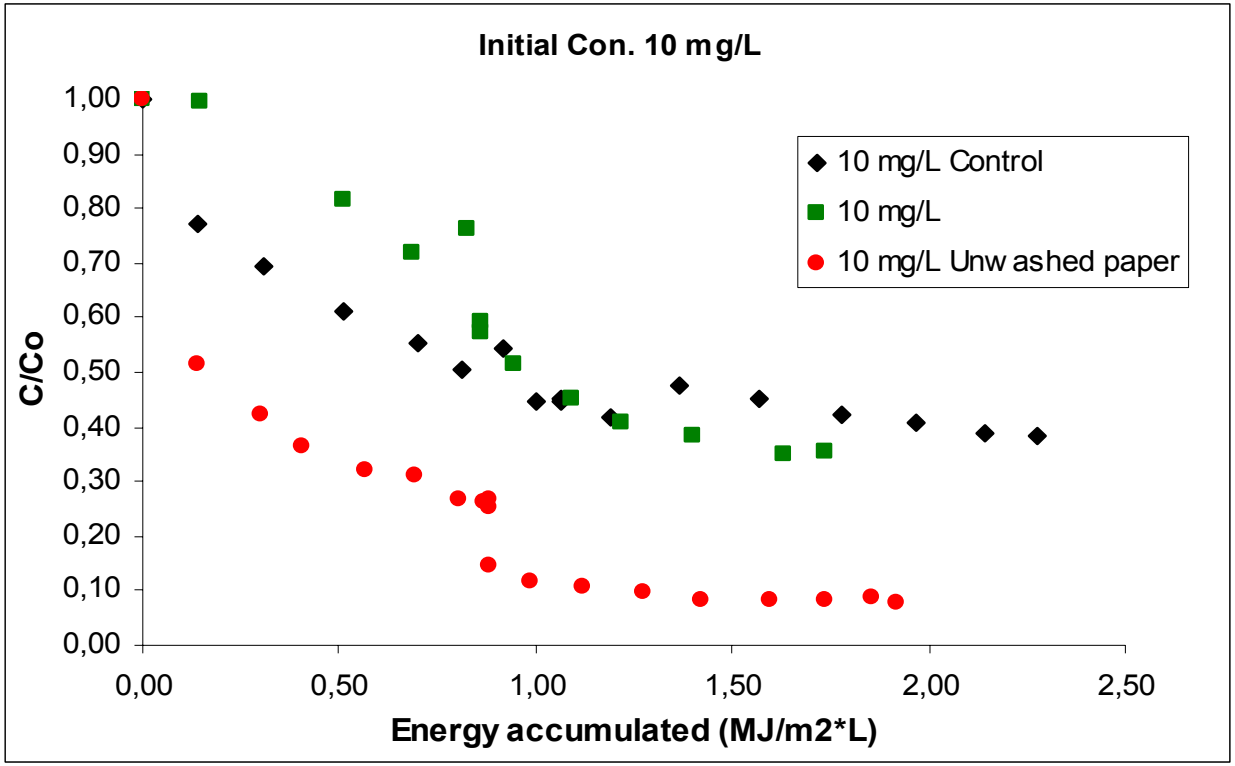
- ✓ 70 - 80% Phototransformation of HA → 2 - 2.5MJ/m^{2}L
- ✓ Photolysis: Zero order [HA]

Results
HA Photolysis & Photocatalysis

HS (Aldrich): 10 mg/l in HS ≅ 5 mg/l in C

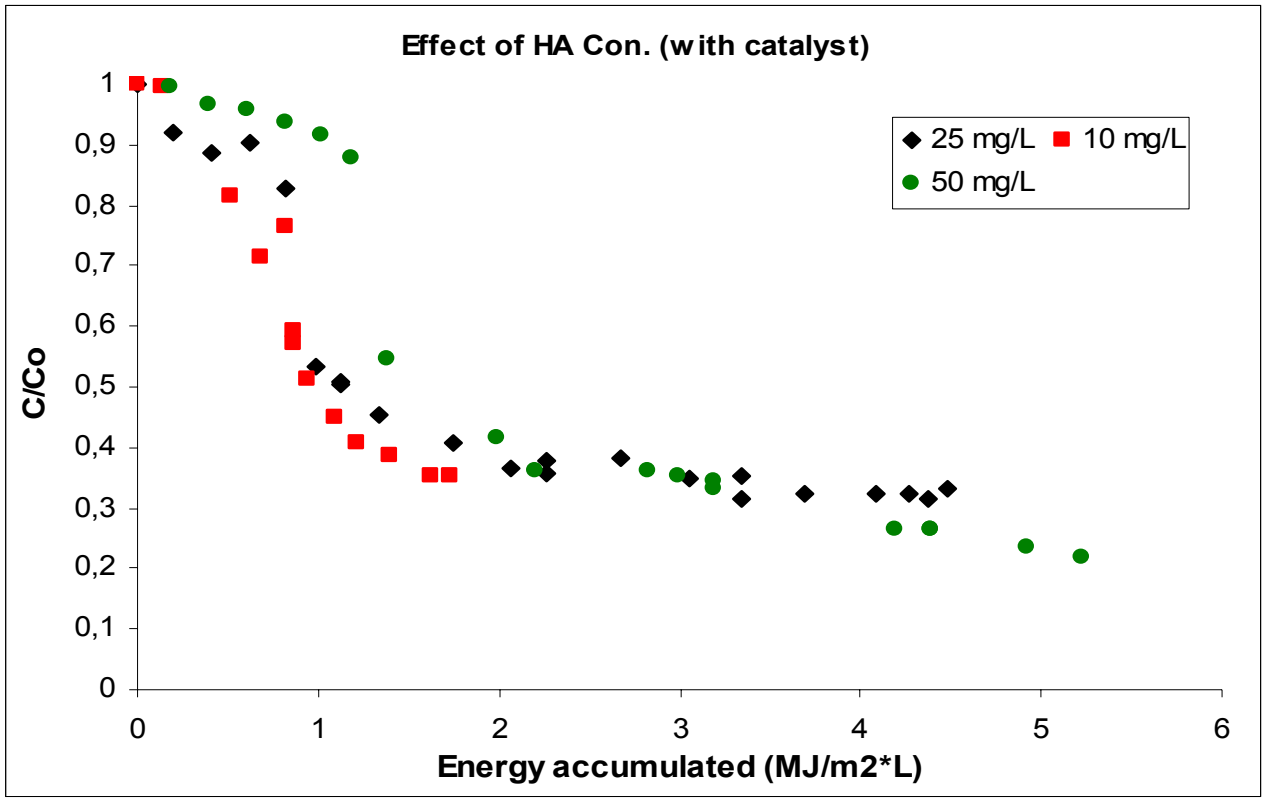
- Photolysis (Control)
- Photolysis + Photocatalysis : Immobilized TiO_2 (paper)
- Photolysis + Photocatalysis : Immobilized TiO_2 (unwashed paper)

Comparison between HA Photolysis & Photocatalysis CPC Reactor



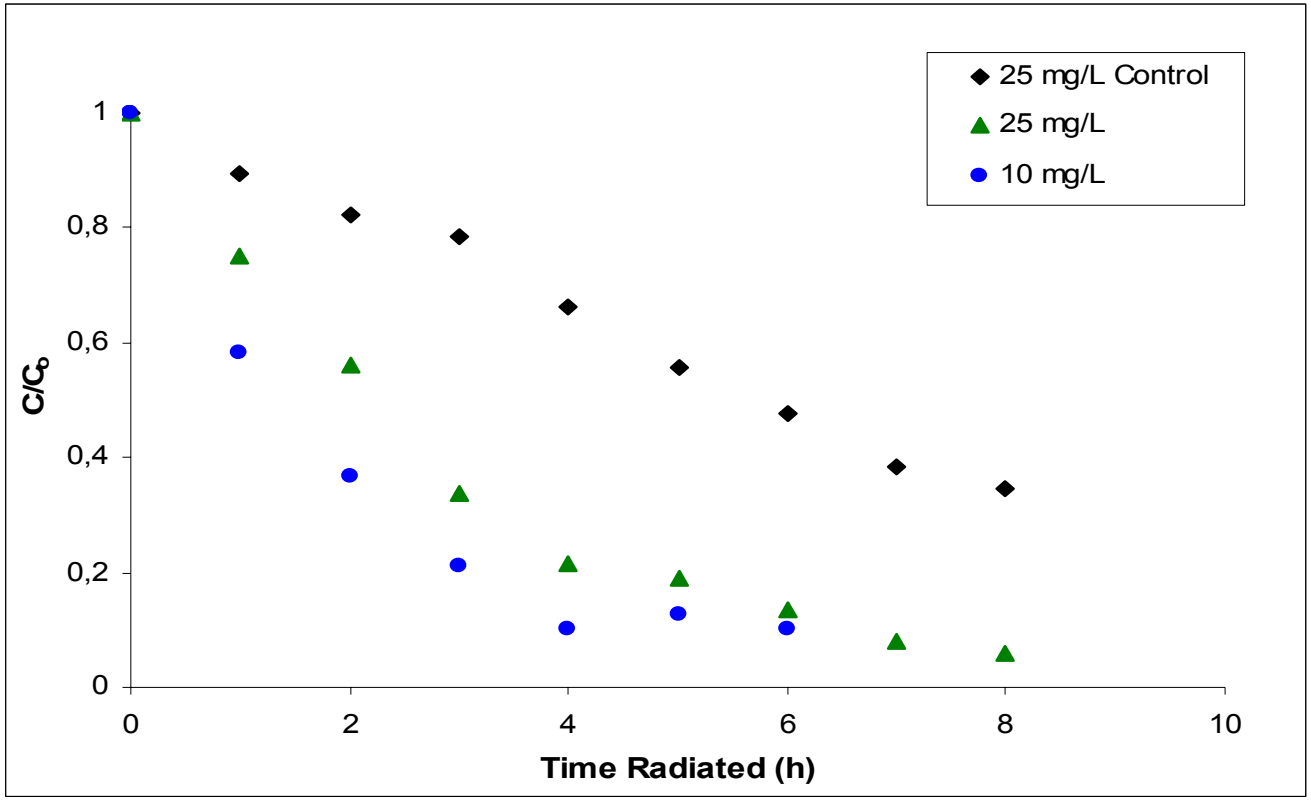
- ✓ About 50% adsorption of HA on immobilized TiO_2
- ✓ Photolysis – Self-Catalysis: 80% Phototransformation of HA, E=2-2.5MJ/m^2L
- ✓ Photocatalysis: >90% Phototransformation of HA → 2-2.5MJ/m^2L
- ✓ 30% Complete Mineralization

HA Photocatalysis: Effect of Initial Concentration CPC Reactor



- ✓ 70% Phototransformation of HA → 2 – 3 MJ/m^{2}L
- ✓ Photolysis: Zero order [HA]
- ✓ 30% Complete Mineralization

Gallic Acid : Photolysis & Photocatalysis CPC Reactor

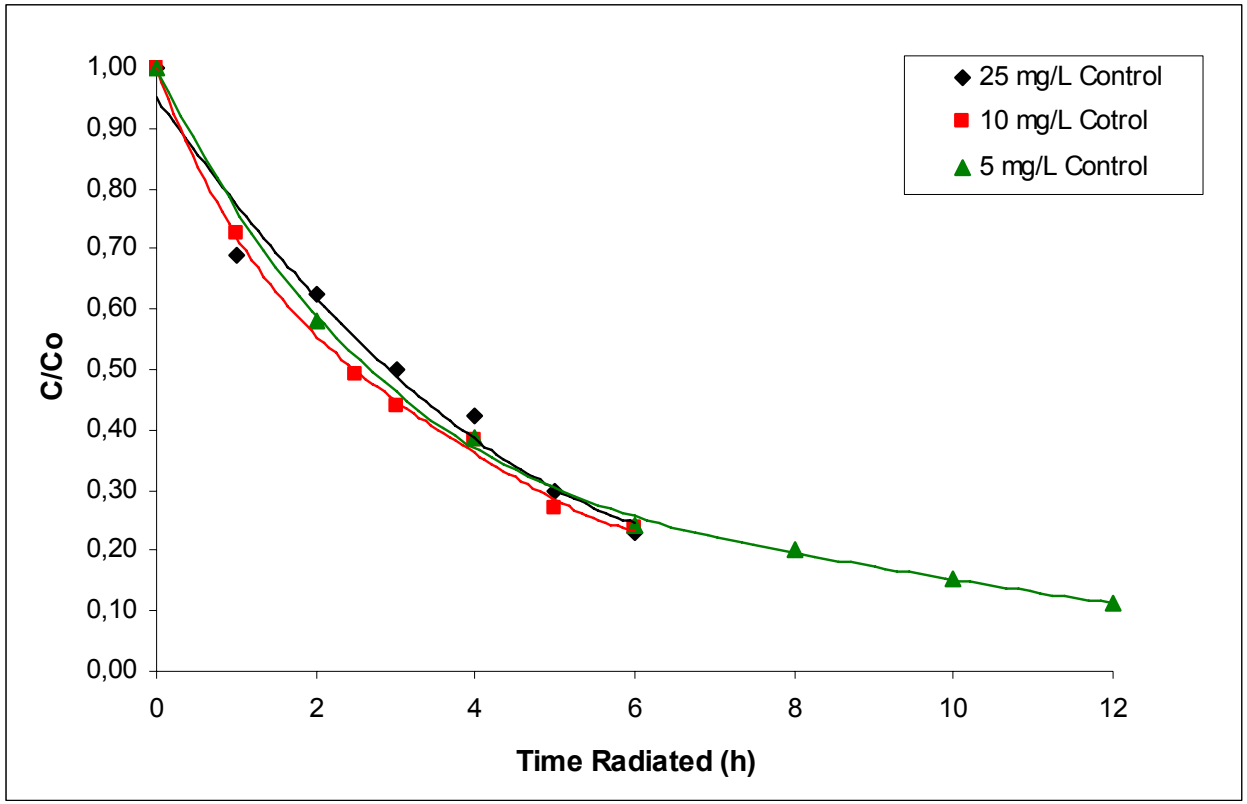


- ✓ Photolysis: 30 – 40% of the initial [GA]
- ✓ Photocatalysis: 90 – 95% of the initial [GA]
- ✓ Photocatalysis: Independent of initial [GA] (Zero order)

Summary : Photolysis & Photocatalysis CPC Reactor

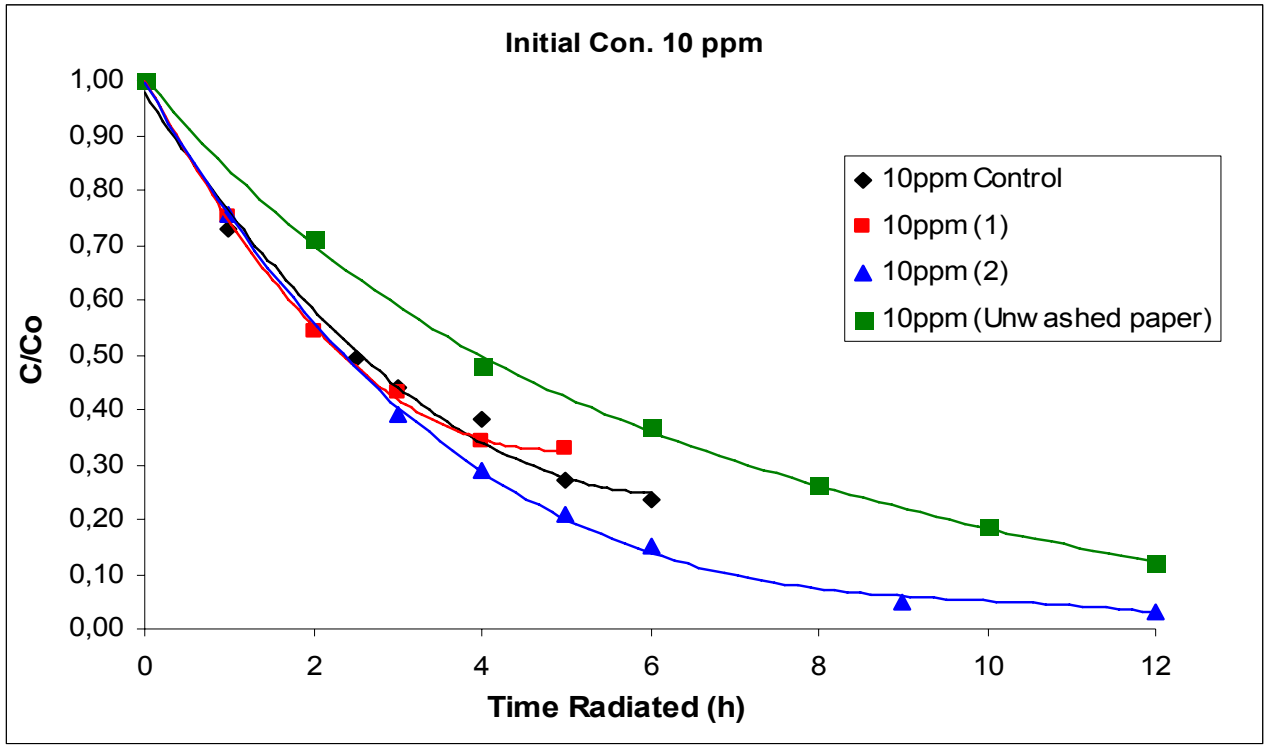
- HA Phototransformation: 70–80%, E=2–3 MJ/m^2L by photolysis. This means that HA molecules are efficient photosensitizers capable of self-catalyzing their oxidation.
- Immobilized TiO_2 contributes to a further 10 – 20% HA phototransformation.
- Complete mineralization of HA is estimated to be about 30%.
- GA Photolysis leads to a 40% degradation of the molecule.
- GA Photocatalytic degradation by immobilized TiO_2 may be complete.

Results
HA Photolysis - UV Reactor



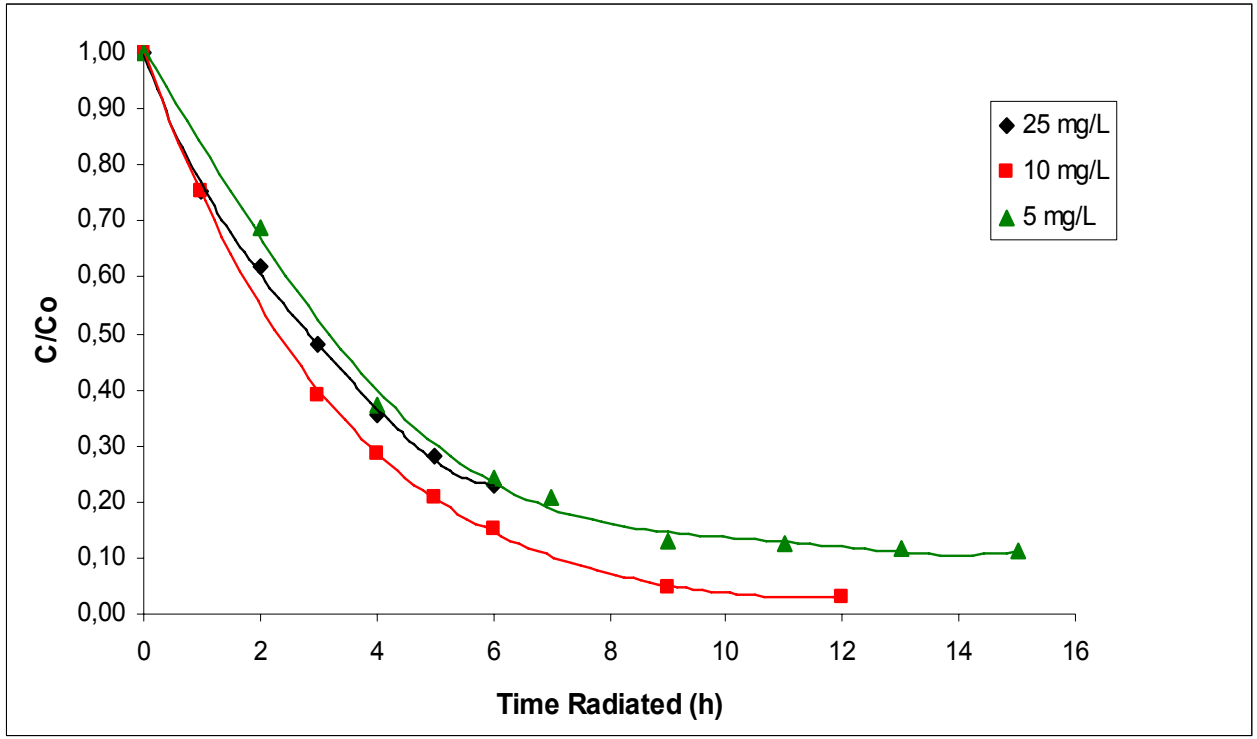
- ✓ 70 - 80% Phototransformation of HA
- ✓ Photolysis: Zero order [HA]

Comparison between HA Photolysis & Photocatalysis UV Reactor



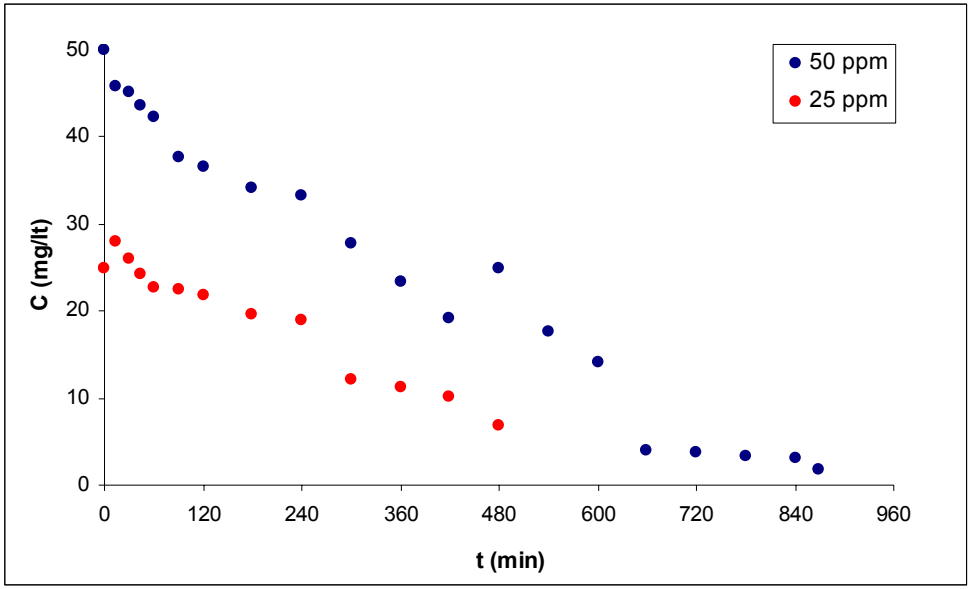
✓ At 254 nm the phenomenon of self-catalytic transformation of HA molecules is more pronounced and seems to be predominant.

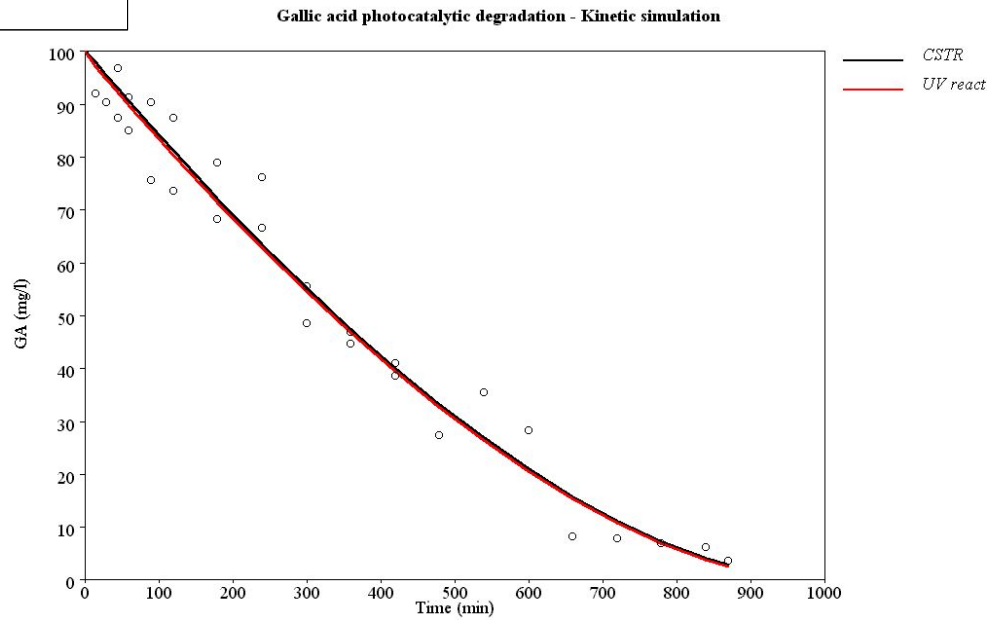
HA Photocatalysis: Effect of Initial Concentration UV Reactor



✓ Photolysis – Photocatalysis : Zero order [HA]

GA Photocatalytic Degradation UV Reactor





Solar Safe Water

Summary : Photolysis & Photocatalysis UV Reactor

- HA Phototransformation monitoring at 254 nm showed clearly that HA molecules are efficient photosensitizers capable of self-catalyzing their oxidation.
- Complete mineralization of HA is estimated to be about 30%.
- GA Photocatalytic degradation by immobilized TiO_2 may be complete.

Conclusions

- Fin-Type CPC reactor with immobilized TiO_2 is efficient for the photocatalytic treatment of DOM: HS and potential products of their degradation: e.g. Gallic Acid.

- HA Phototransformation: 70–80%, E=2–3 MJ/m^{2}L by photolysis $\Rightarrow$ HA molecules are efficient photosensitizers capable of self-catalyzing their oxidation.

- Immobilized TiO_2 contributes to a further 10–20% HA phototransformation.

Conclusions

- Complete mineralization of HA is estimated to be about 30%.
- GA Photolysis leads to a 40% degradation of the molecule.
- GA Photocatalytic degradation by immobilized TiO_2 may be complete.
- HA Phototransformation monitoring at 254 nm showed clearly that HA molecules are efficient photosensitizers capable of autocatalyse their oxidation.

Thank You !