

# Solar Photocatalytic Processes For Soil Washing Wastewater Treatment

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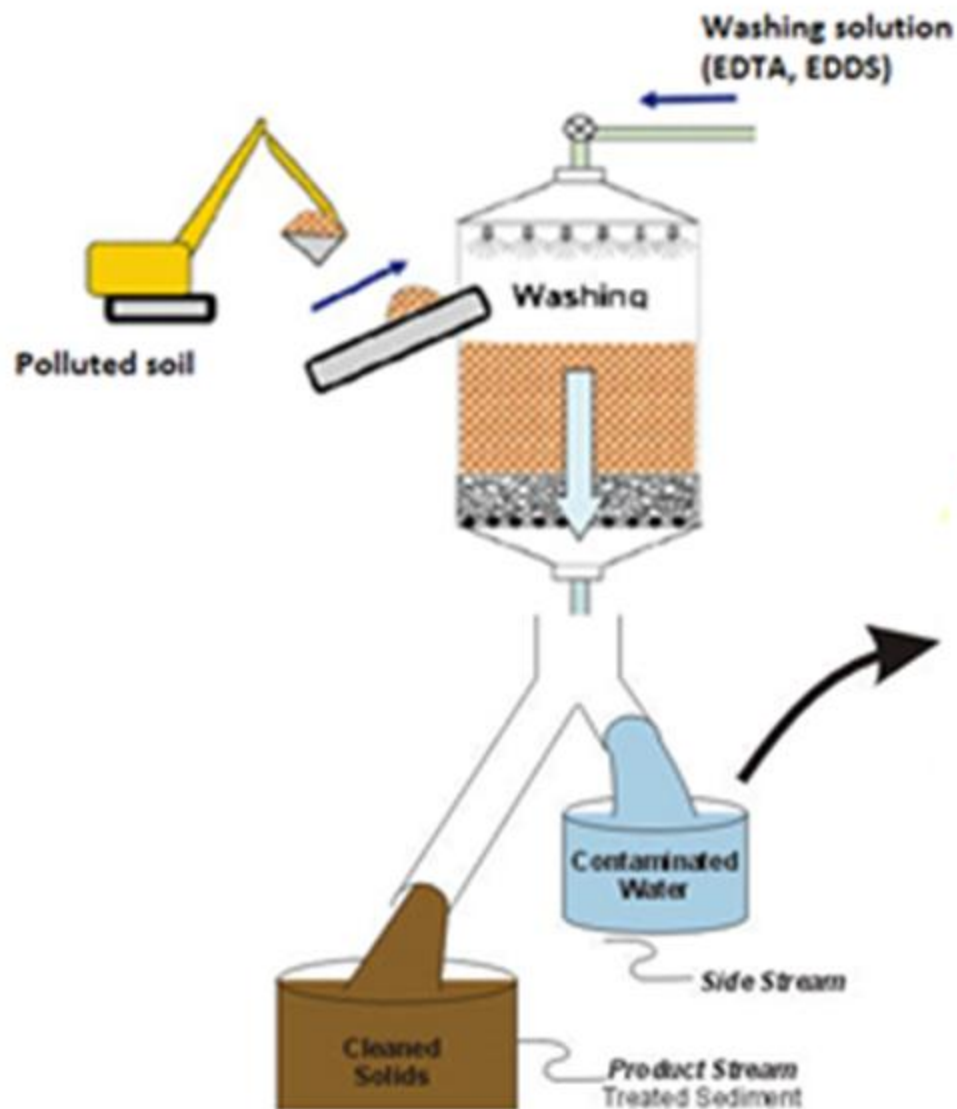
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Website 2: <http://scholar.google.it/citations?user=M3VH5ZMAAAAJ&hl=it>

# Soil washing procedure



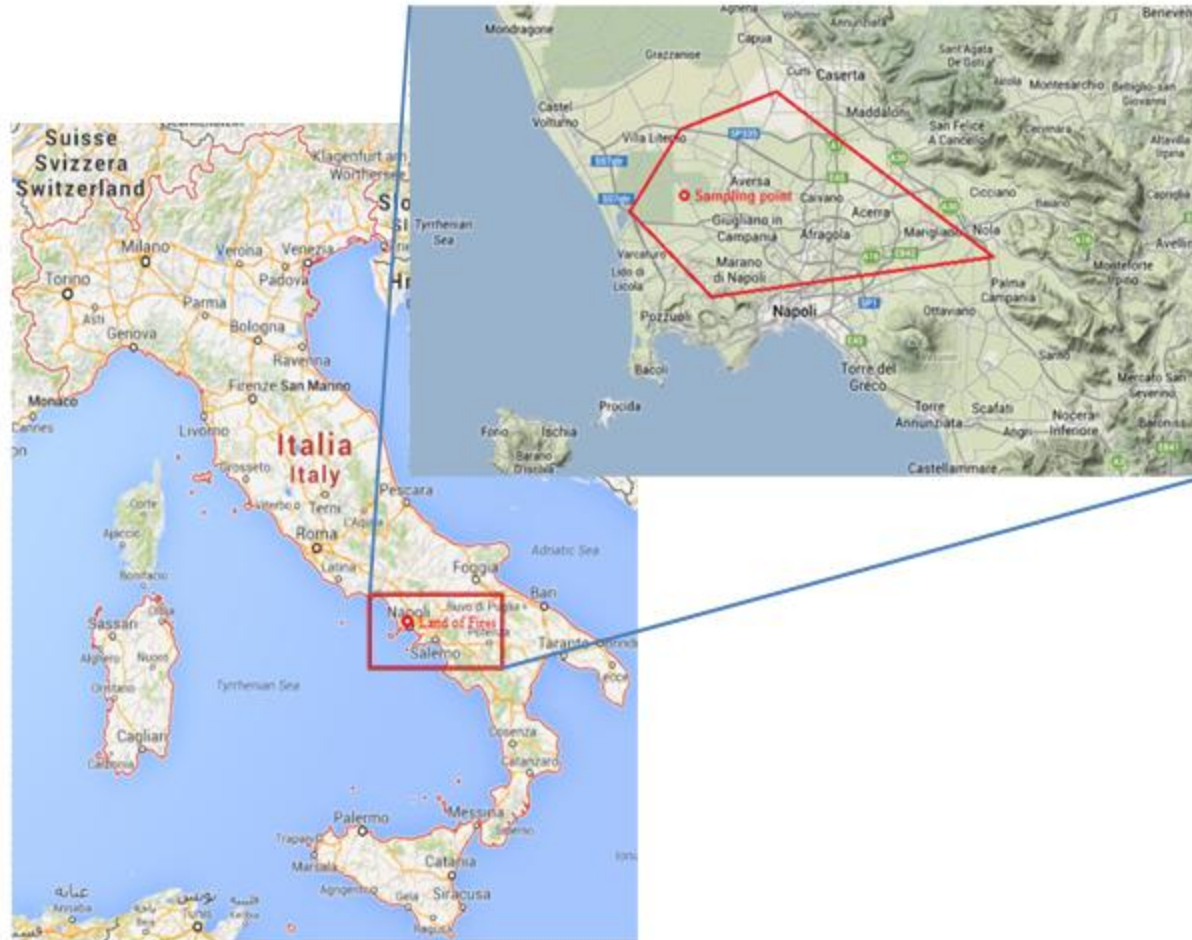
EDDS



Legal limits

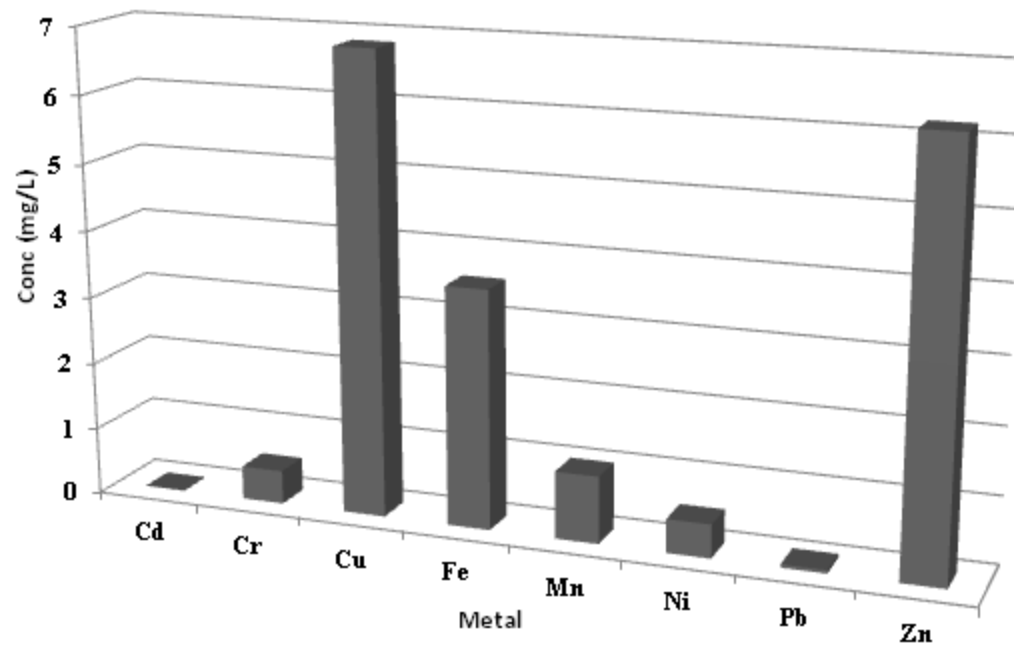


# Soil sampling: Land of Fires



...where illegal dumping of toxic waste has been continuously perpetrated, for decades, by criminal organizations. This area is known due to the high incidence of cancer mortality, which exceeds both the Italian national and European average values

After the soil washing process, the effluent contains **heavy metals** and **chelating agents**



For example **copper** and **zinc**, extracted from soil, are at concentration levels higher than the Italian regulatory limits for discharge in public sewers and consequently one or more post-treatment processes are required, before the discharge into the environment.

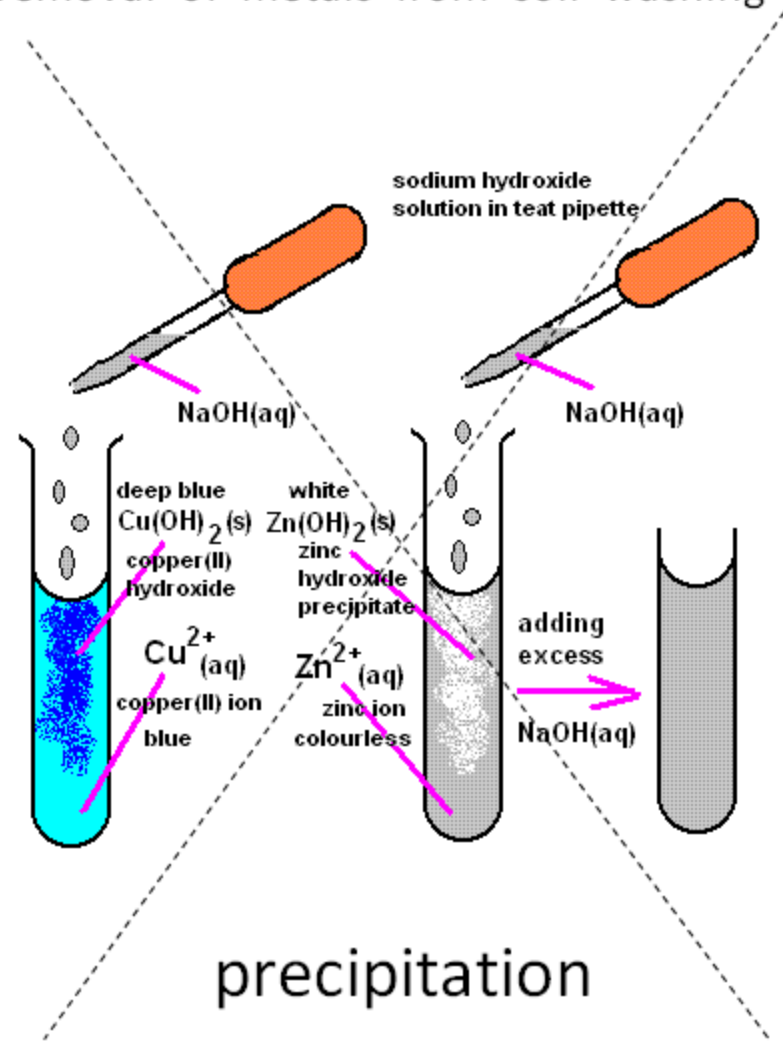
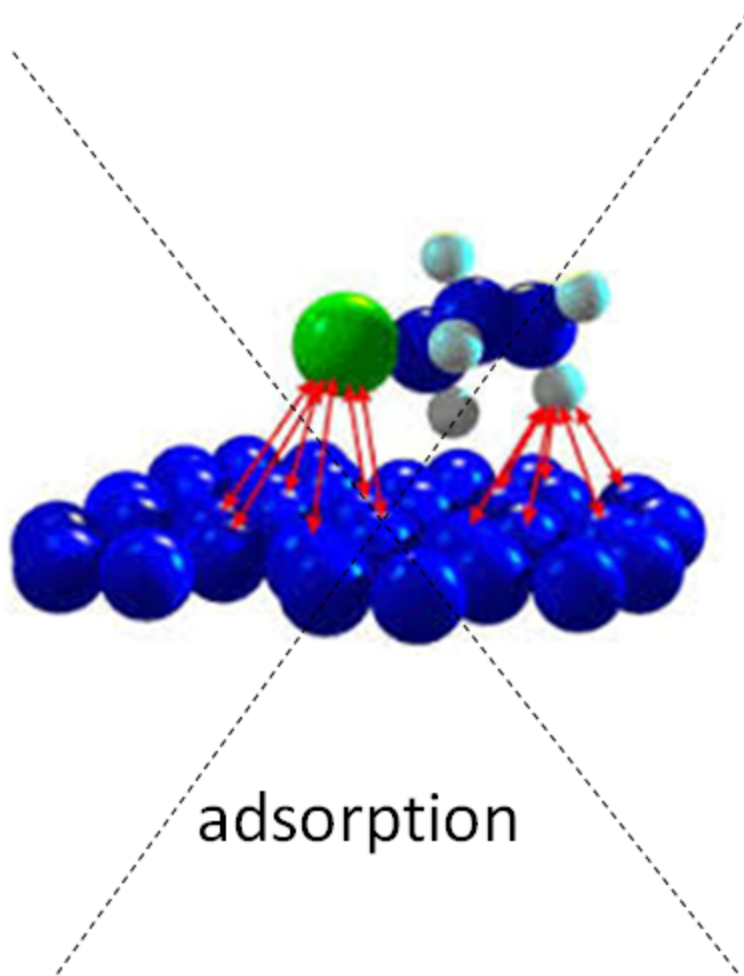
**Limits for sewage discharge in Italy: Cu (0.4 ppm); Zn (1.0 ppm)**

# Treatment soil washing effluents step

Due to the presence of metal-chelating agent chemical complexes.....

Cu(II)	Log K	Fe(III)	Log K
$Cu^{2+} + EDDS^{4-} \rightleftharpoons [CuEDDS]^{2-}$	18.6	$Fe^{3+} + EDDS^{4-} \rightleftharpoons [FeEDDS]^{-}$	20.6
$[CuEDDS]^{2-} + H^{+} \rightleftharpoons [CuHEDDS]^{-}$	3.6	$[Fe(OH)EDDS]^{2-} + H^{+} \rightleftharpoons [FeEDDS]^{-}$	7.9
$[CuHEDDS]^{-} + H^{+} \rightleftharpoons CuH_2EDDS$	2.3	$[Fe(OH)_2EDDS]^{3-} \rightleftharpoons [Fe(OH)EDDS]^{2-} + HO^{-}$	9.9
$[Cu(OH)EDDS]^{3-} + H^{+} \rightleftharpoons [CuEDDS]^{2-} + H_2O$	11.1		
$[CuEDDS]^{2-} + Cu^{2+} \rightleftharpoons Cu_2EDDS$	2.4		
$[CuEDDS]^{2-} + [HEDDS]^{3-} \rightleftharpoons [CuEDDS(HEDDS)]^{5-}$	2.5		
$[CuEDDS(HEDDS)]^{5-} + H^{+} \rightleftharpoons [Cu(HEDDS)_2]^{4-}$	7.1		
Zn(II)	Log K	EDDS	pK <sub>a</sub>
$Zn^{2+} + EDDS^{4-} \rightleftharpoons [ZnEDDS]^{2-}$	13.6	$H_4EDDS \rightleftharpoons H_3EDDS^{-} + H^{+}$	2.4
$[ZnEDDS]^{2-} + H^{+} \rightleftharpoons [ZnHEDDS]^{-}$	3.7	$H_3EDDS^{-} \rightleftharpoons H_2EDDS^{2-} + H^{+}$	3.9
$[ZnHEDDS]^{-} + 2H^{+} \rightleftharpoons [ZnH_3EDDS]^{+}$	5.9	$H_2EDDS^{2-} \rightleftharpoons HEDDS^{3-} + H^{+}$	6.8
$[Zn(OH)EDDS]^{3-} + H^{+} \rightleftharpoons [ZnEDDS]^{2-} + H_2O$	11.3	$HEDDS^{3-} \rightleftharpoons EDDS^{4-} + H^{+}$	9.8
$[ZnHEDDS]^{-} + HEDDS^{3-} \rightleftharpoons [Zn(HEDDS)_2]^{4-}$	5.5		

...the simple physical process of adsorption on activated carbon or metal precipitation as hydroxides can not ensure a satisfactory removal of metals from soil washing wastewaters.



Need to remove the chelating agent (i.e EDDS)



The soil washing effluent contains Iron too....

....Iron is naturally present in soils

Other “*ingredients*” economic and eco-friendly to be used are:

- 1) Sunlight
- 2) Air
- 3) Hydrogen peroxyde (*eventually*)
- 4) Titanium oxide

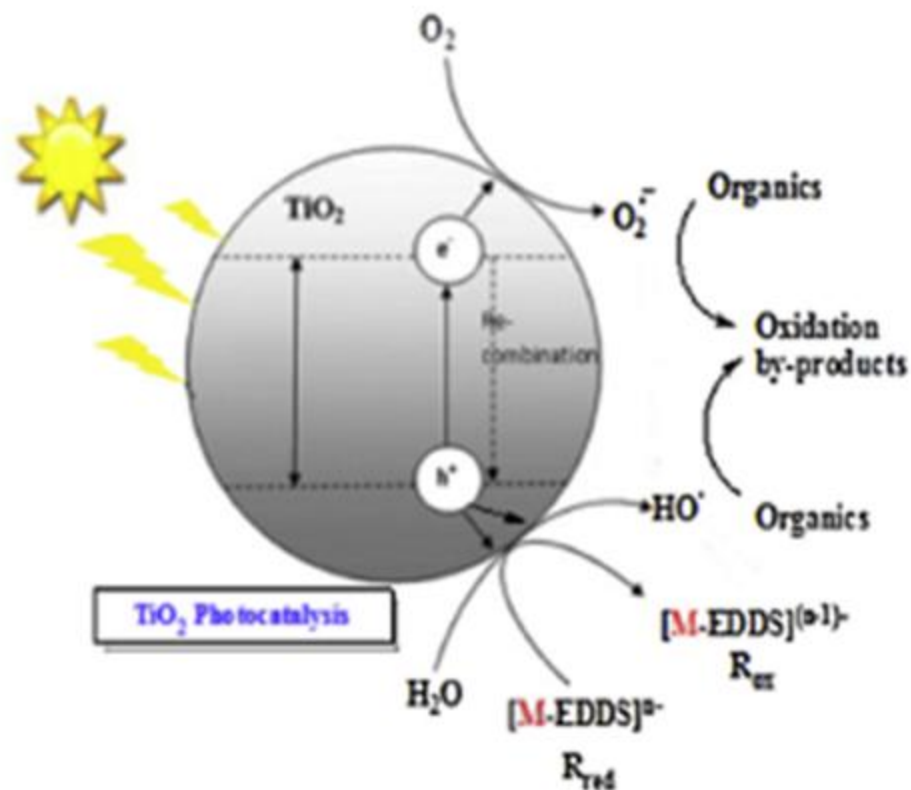
***Different*** ways to proceed for removing of copper and zinc .....



Air/TiO<sub>2</sub>:

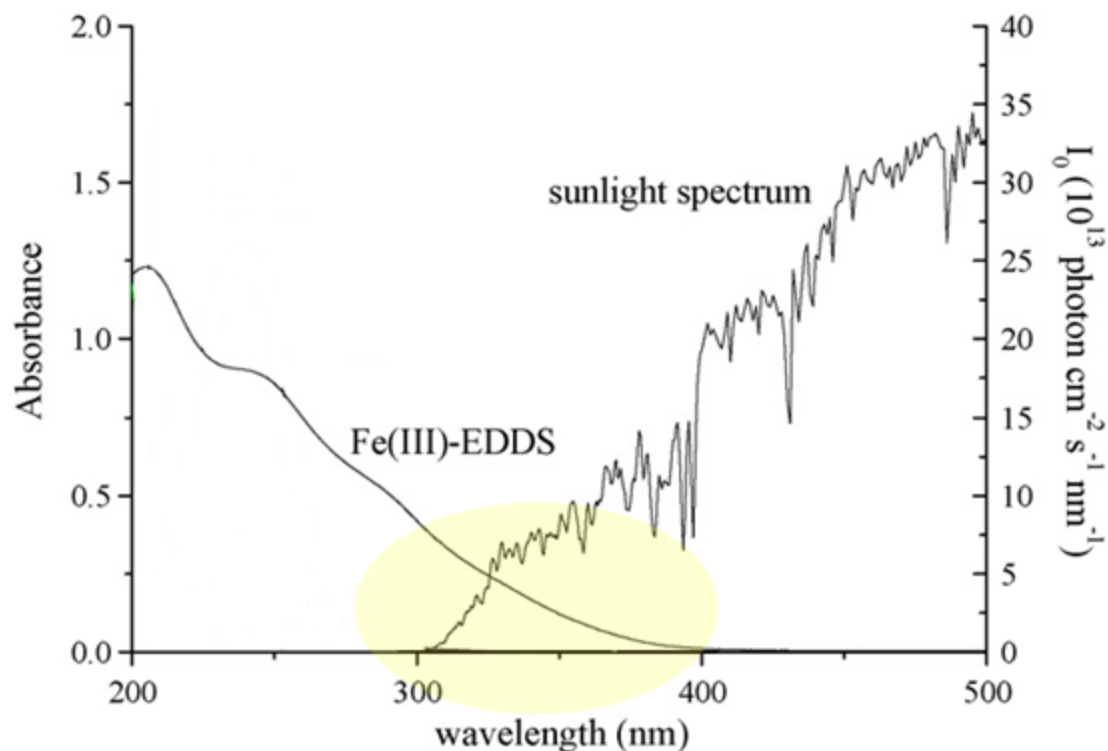
## Heterogeneous photocatalytic process

1) Production of HO radicals which attack and destroy the chelating agent

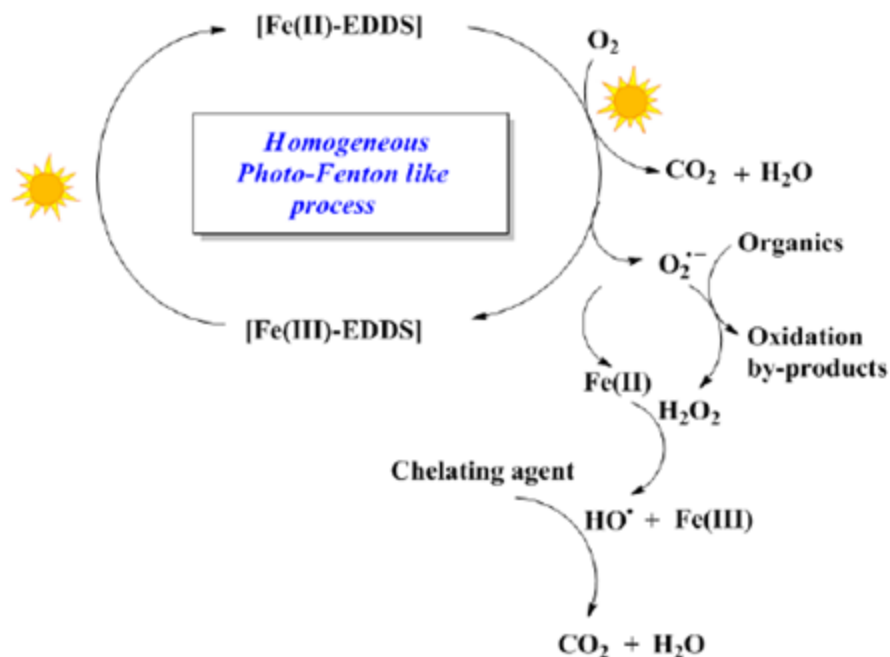


2) Some metals not longer complexed can precipitate as insoluble hydroxides

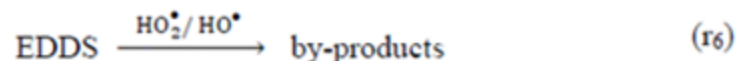
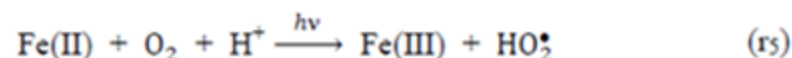
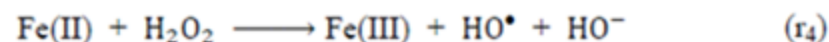
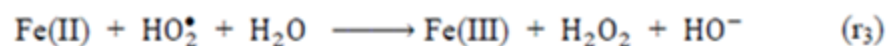
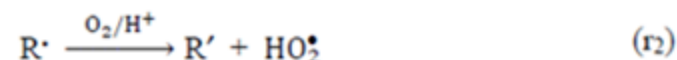
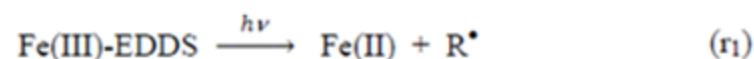
EDDS and its intermediate degradation products, form strong chelates with Fe(III).  
These species absorb in the UV-A range



## Homogeneous photocatalytic process



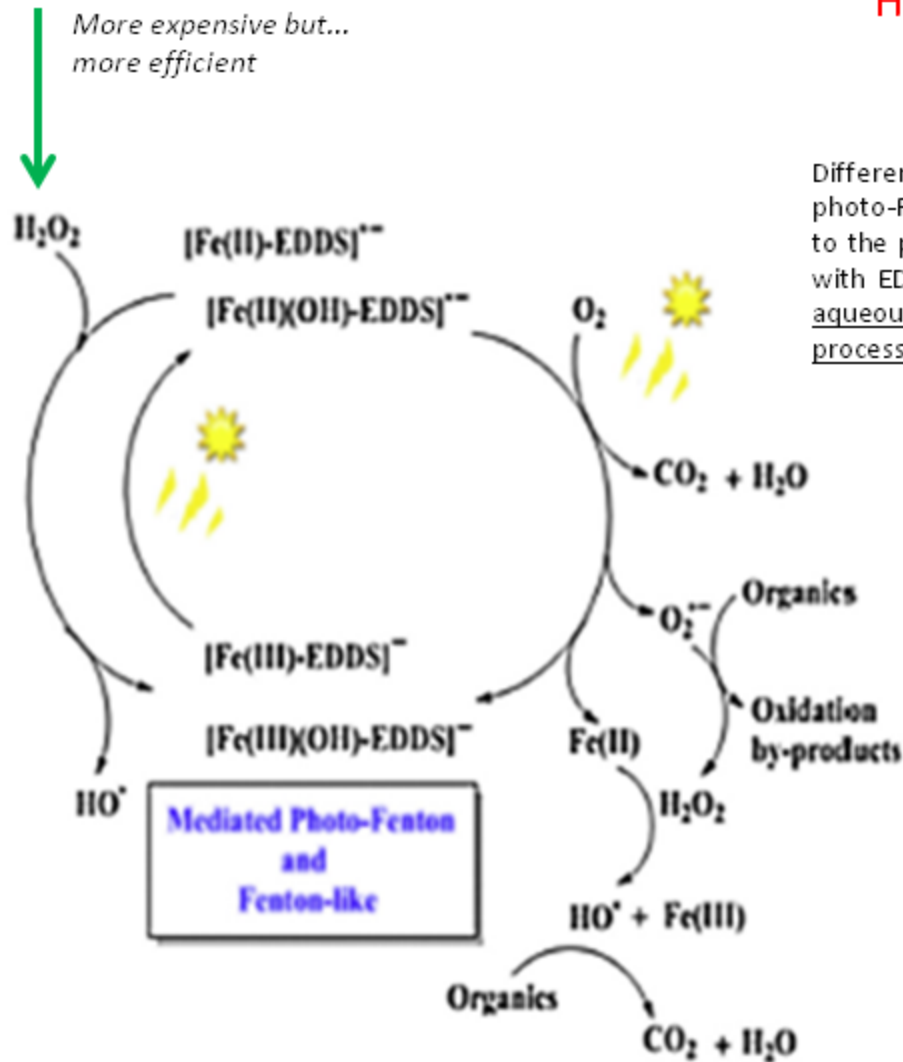
The photolysis of Fe(III)-EDDS species through intramolecular LMCT (ligand to metal charge transfer) transitions occurs with good quantum yields



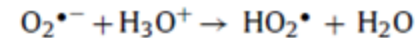
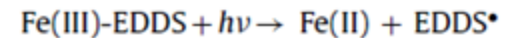
**NO adding of chemicals!**

Oxidant species, such as  $\text{HO}^\bullet$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^\bullet$  and  $\text{H}_2\text{O}_2$ , are formed during the photolysis of the iron(III)-EDDS complexes under aerated conditions

## Homogeneous photocatalytic process



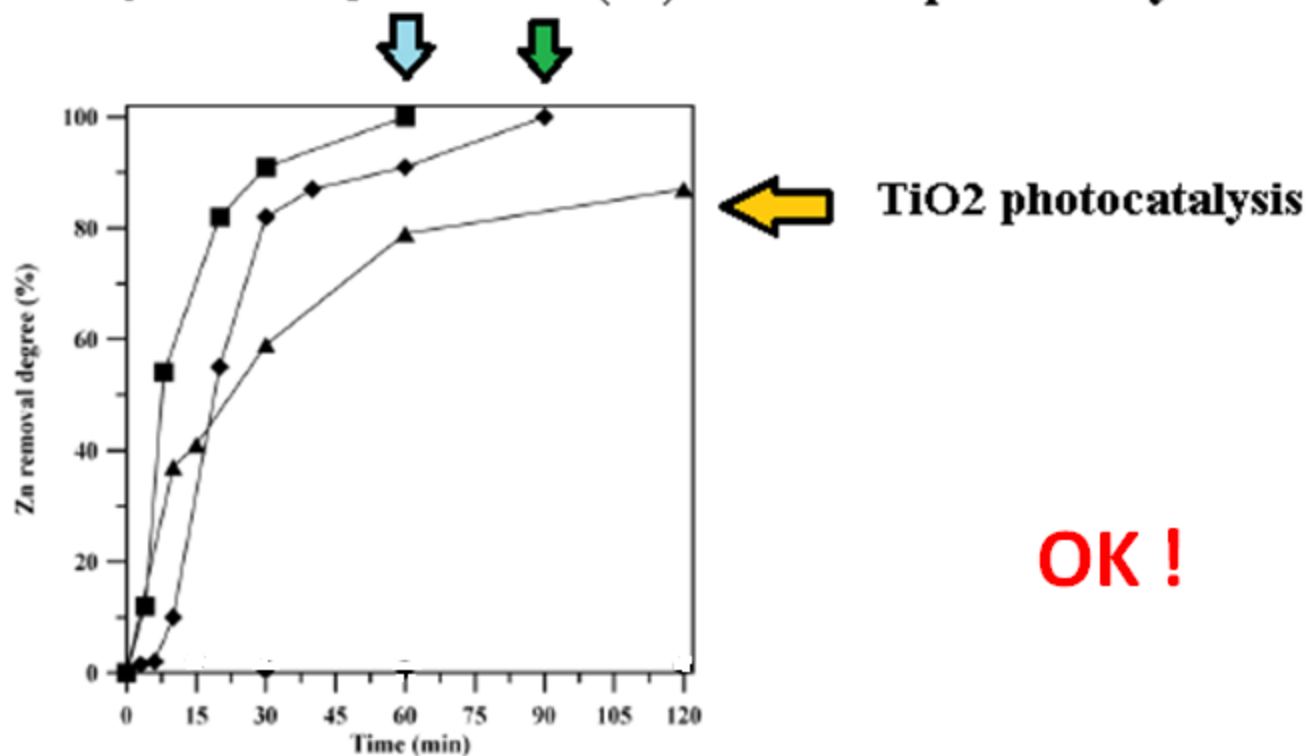
Difference with the "classic" photo-Fenton process: normally, the photo-Fenton reaction with Fe(III) is efficient in the pH range 2.0 – 4.0 due to the precipitation of iron at higher pH values. Whereas the complexation with EDDS produces a **double effect** by increasing the stability of iron in aqueous solution at higher pH and increasing the efficiency of the Fenton process by formation of hydroperoxyl/superoxide radicals:



For Zinc .....

**Fe(III)-EDDS/H<sub>2</sub>O<sub>2</sub> photocatalysis**

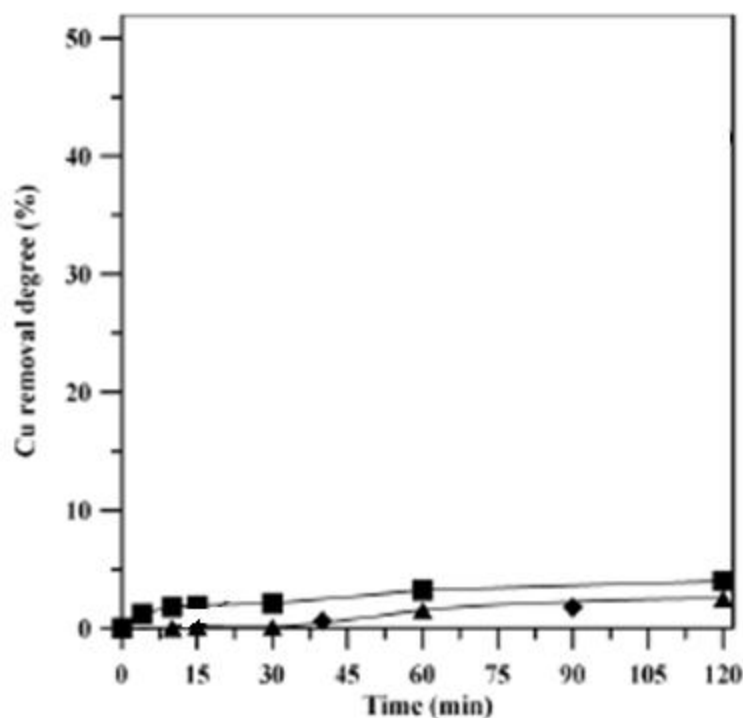
**Fe(III)-EDDS/Air photocatalysis**



**OK !**

But for copper.....

However, the previous photocatalytic processes are not all effective in removing copper species



**TiO<sub>2</sub> photocatalysis**

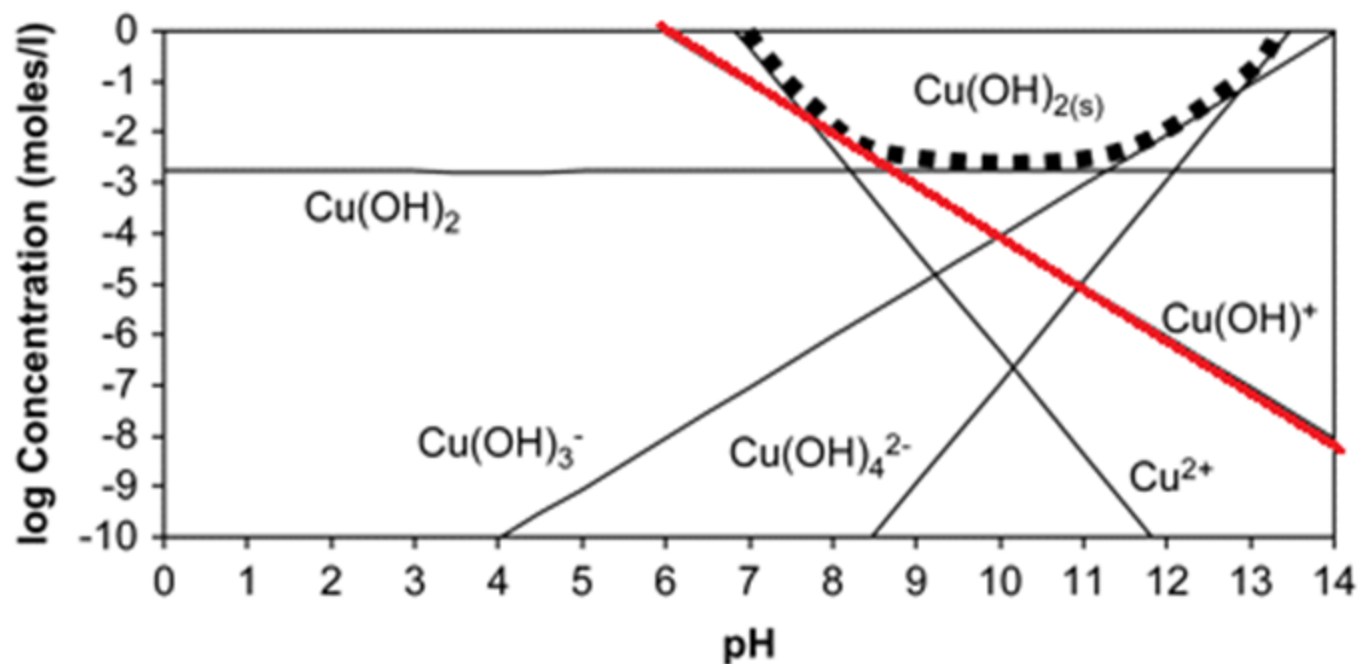
**Fe(III)-EDDS/Air photocatalysis**

**Fe(III)-EDDS/H<sub>2</sub>O<sub>2</sub> photocatalysis**

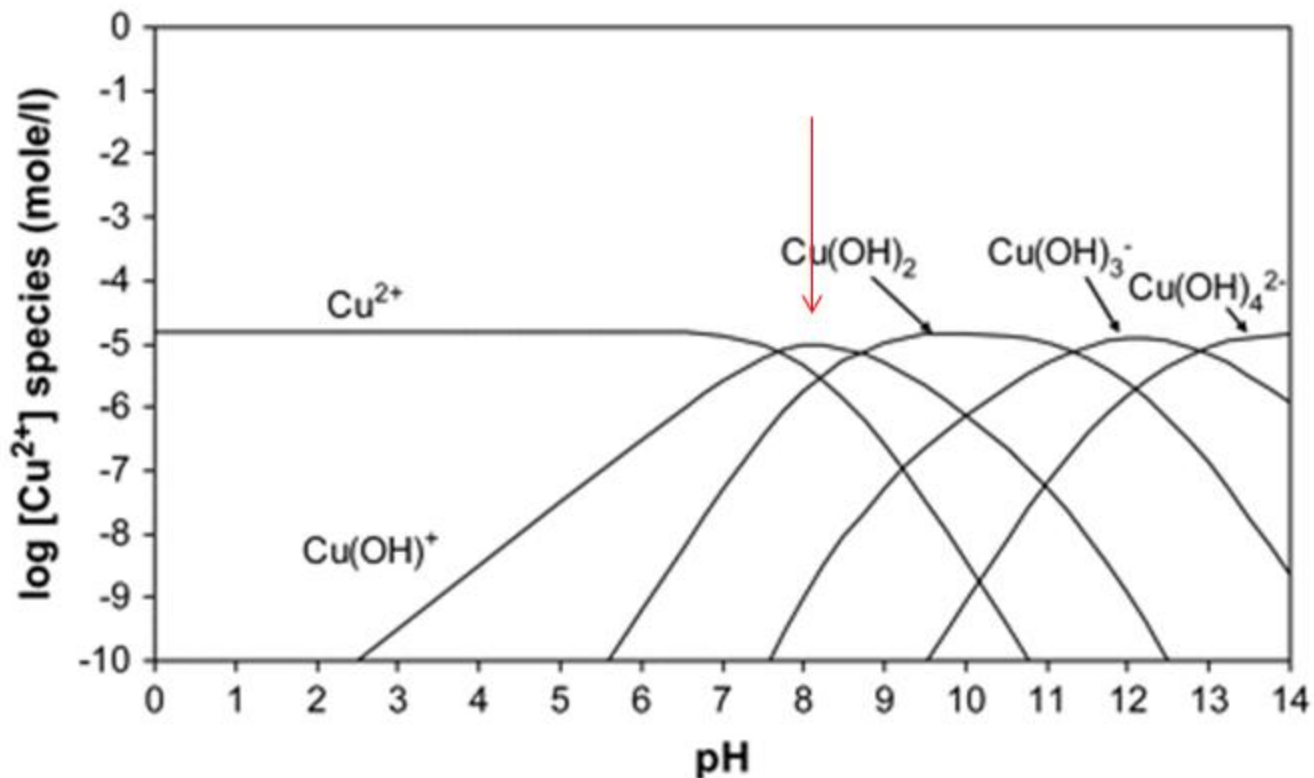
Why?



...probably due to the existence of soluble Cu-hydroxo-complexes such as  $\text{Cu}(\text{OH})^+$  at the adopted pH



inside dotted line shows zone where copper hydroxide solid will form



Theoretical copper speciation for hydroxy-complexes in pure water for a total copper concentration of 1 mg/l

How to remove Copper?

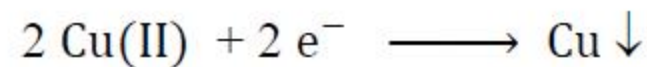
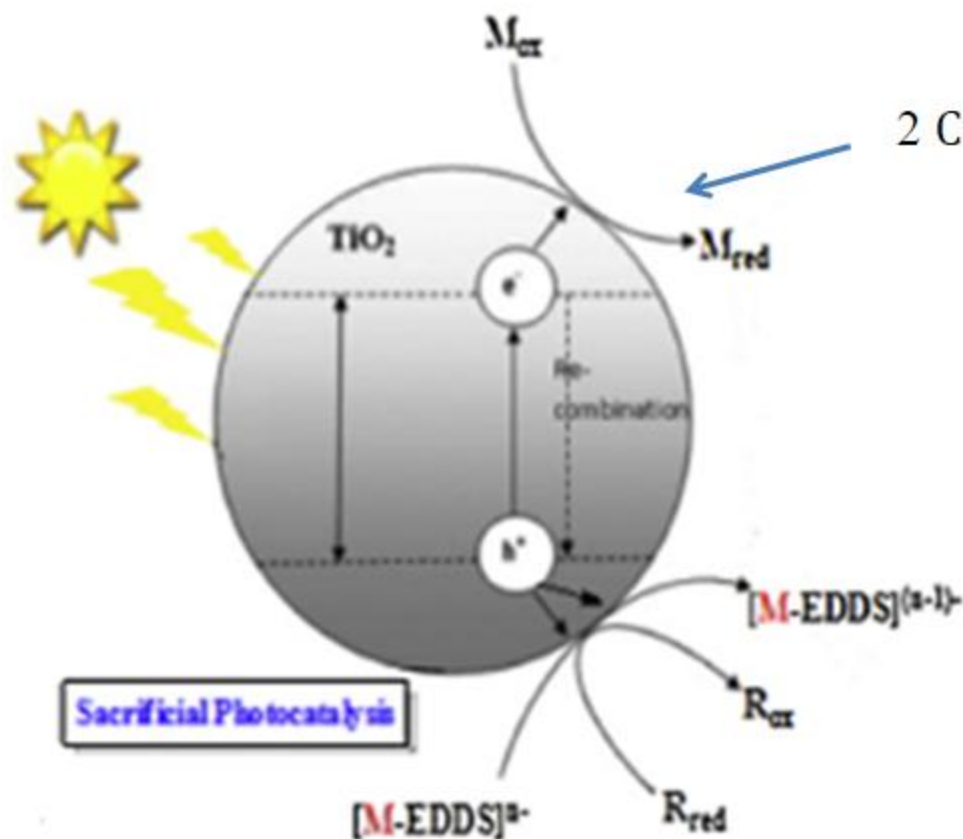




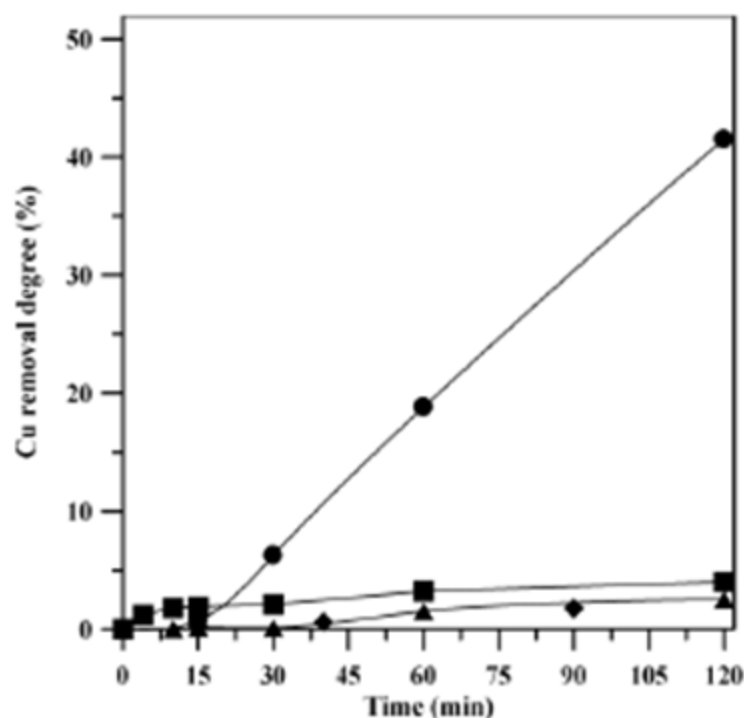
## Sacrificial photocatalysis

(de-aerated conditions)

Heterogenous photocatalytic process



For Copper .....

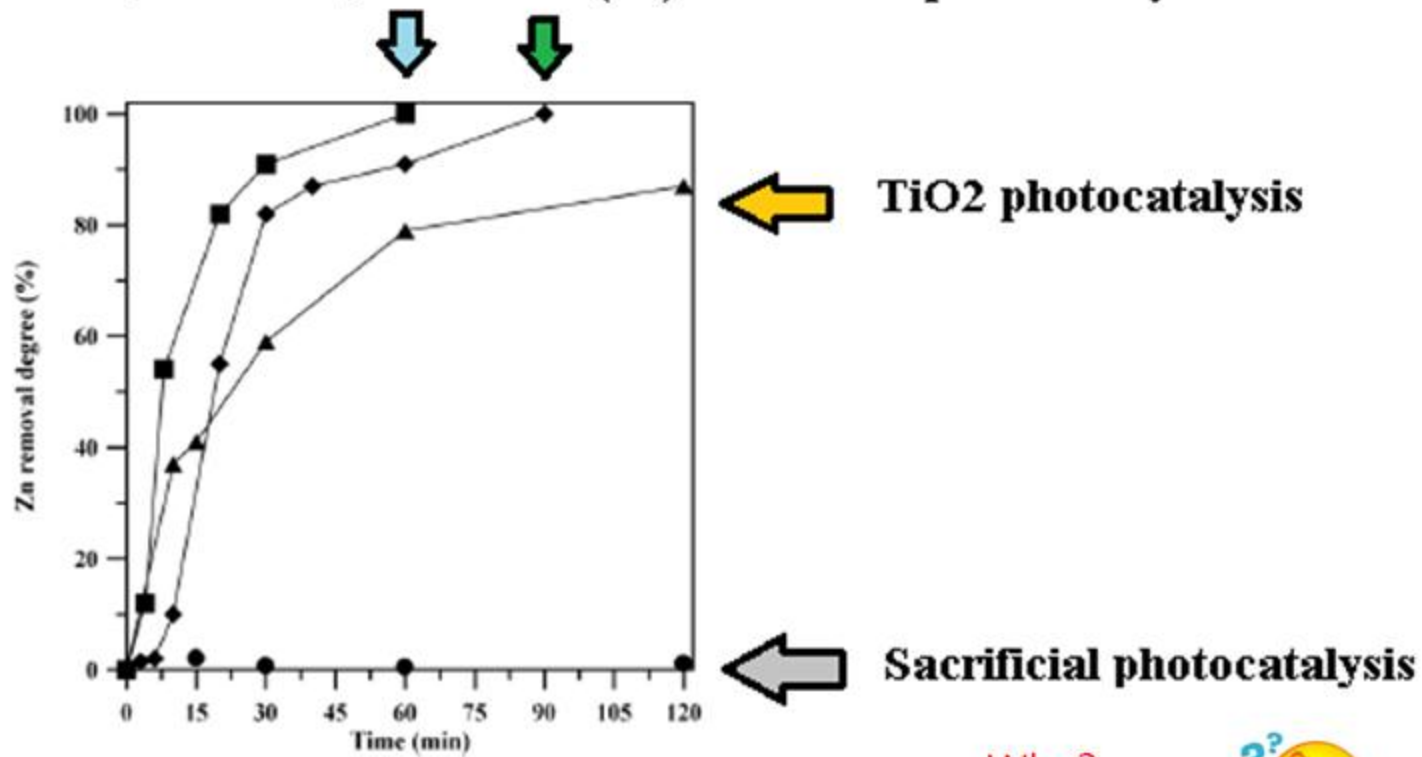


← **Sacrificial photocatalysis** OK!

← **TiO<sub>2</sub> photocatalysis**  
**Fe(III)-EDDS/Air photocatalysis**  
**Fe(III)-EDDS/H<sub>2</sub>O<sub>2</sub> photocatalysis**

In the case of Zinc.....

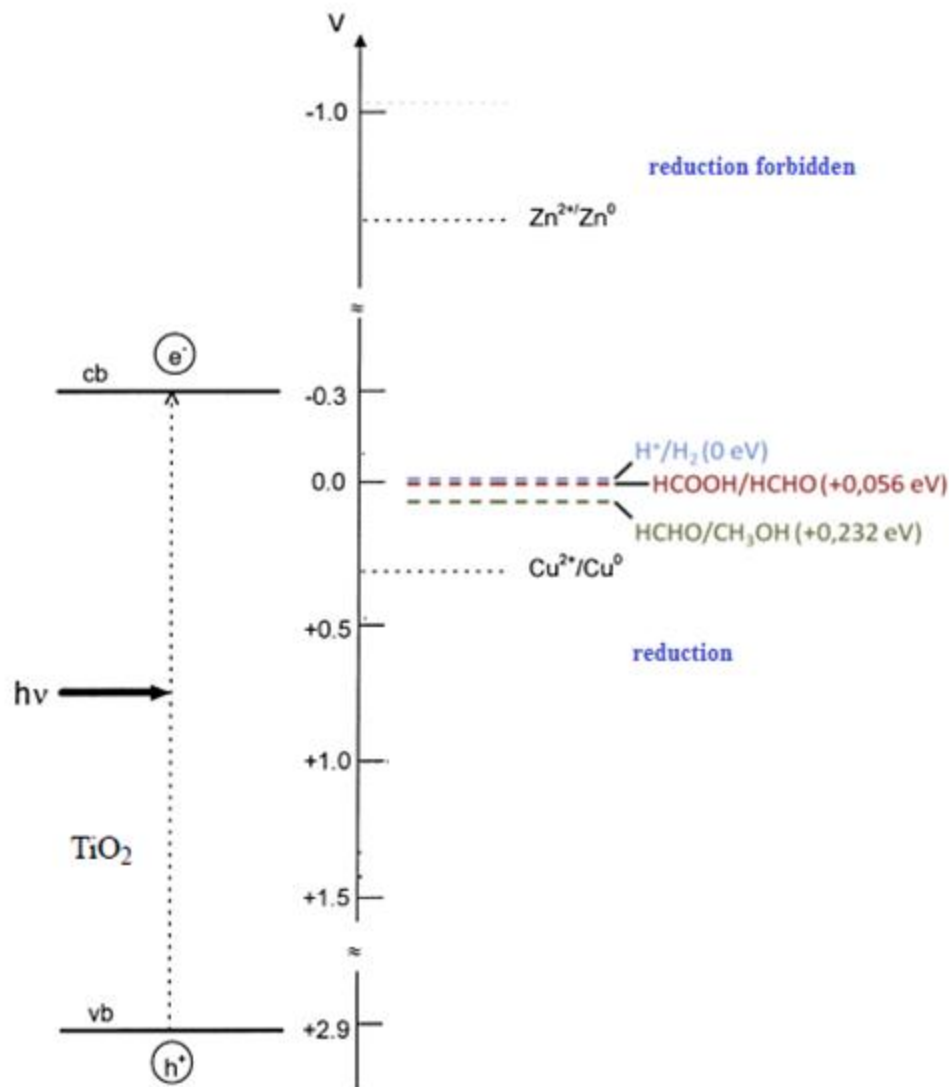
**Fe(III)-EDDS/H<sub>2</sub>O<sub>2</sub> photocatalysis**      **Fe(III)-EDDS/Air photocatalysis**



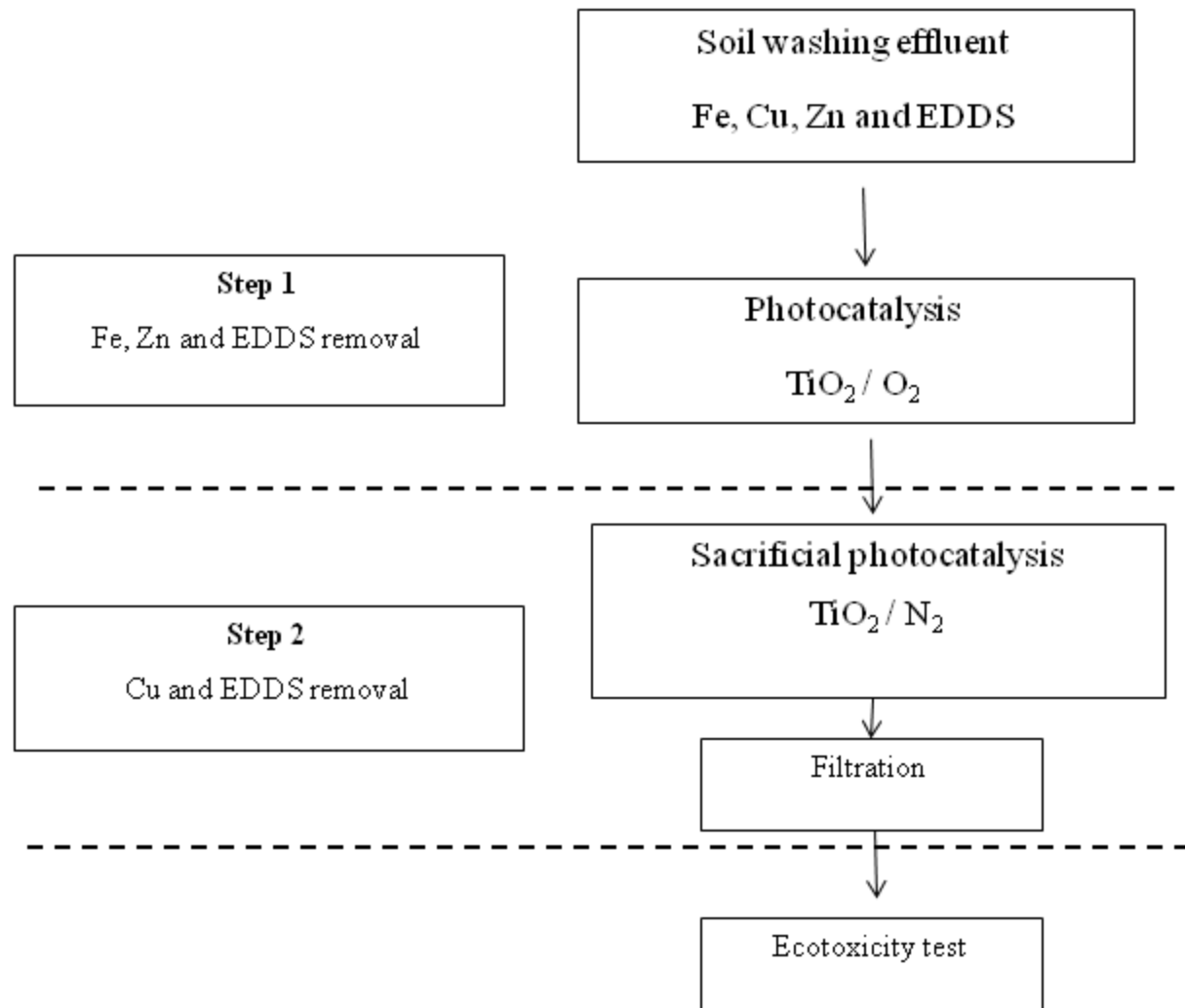
Why?



To achieve a redox reaction, the **conduction band** must be located at a **more negative potential** than the reduction potential of the chemical species that will be reduced, while the **valence band** must be positioned **more positively** than the oxidation potential of the chemical species that will be oxidized



One choice could be firstly the removal of iron, zinc and EDDS through a  $\text{TiO}_2$ -photocatalysis with oxygen, followed by a photocatalytic step (sacrificial  $\text{TiO}_2$ -photocatalysis) under inert atmosphere for the abatement of the residual metals, particularly copper, and residual organics.



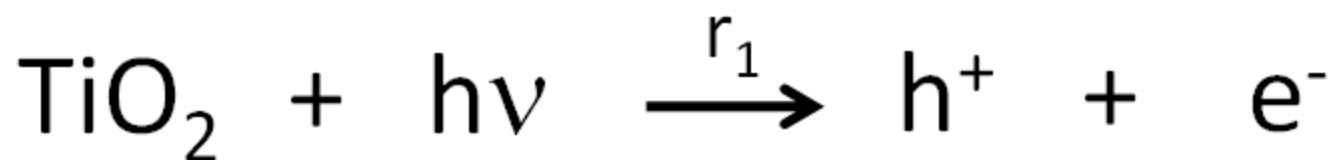
# Mechanism and Kinetics for sacrificial photocatalysis

**Different mechanisms may be proposed to account for the photocatalytic conversion of an organic substrate (S) depending on degree of adsorption of the latter on the  $\text{TiO}_2$  photocatalyst surface**

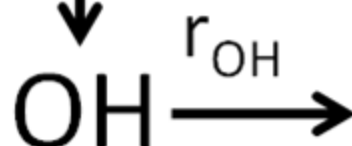
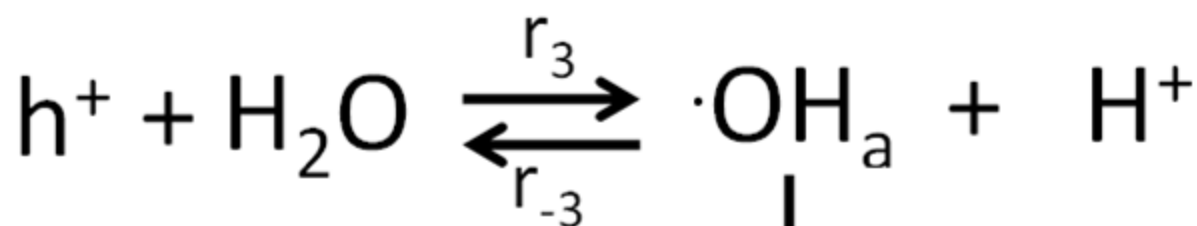
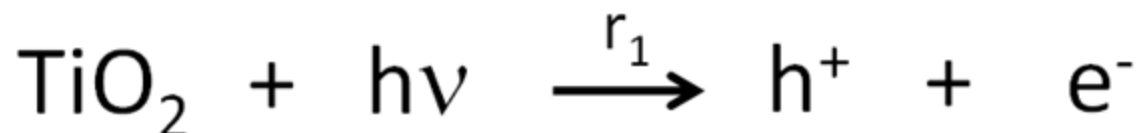
*Langmuir* 2000, 16, 8964-8972

*Environ. Sci. Technol.* 2005, 39, 1880-1886

For **strongly** adsorbed organics, the reaction proceeds directly between adsorbed substrate molecules and photogenerated surface holes



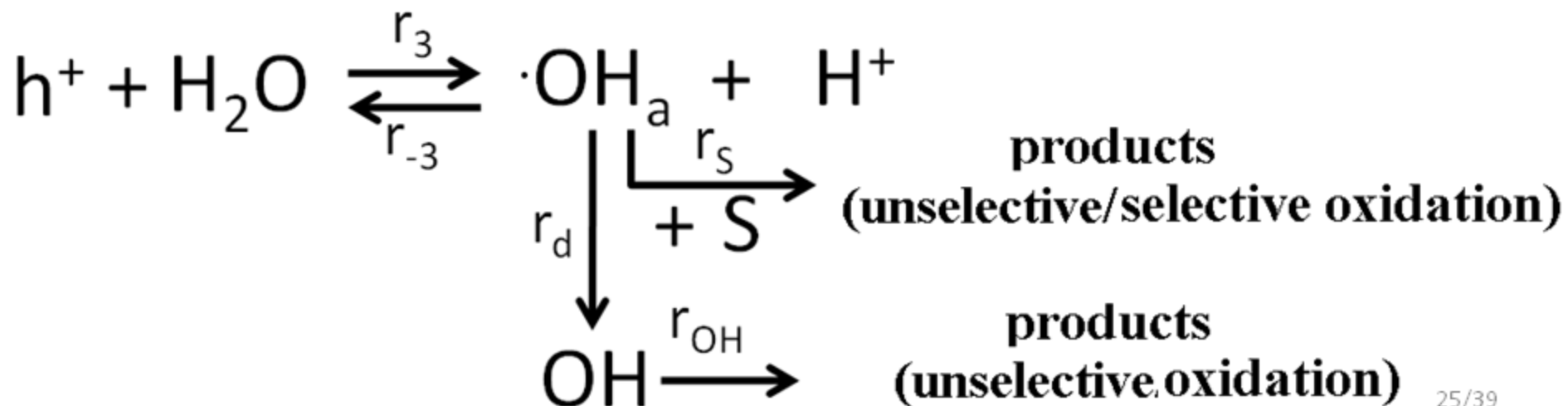
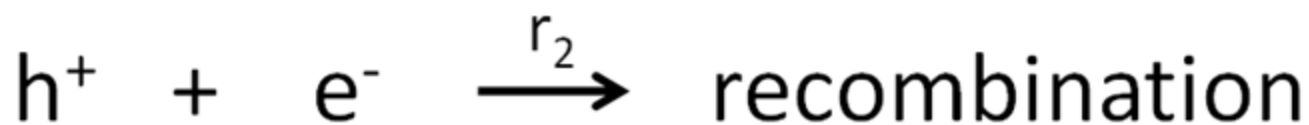
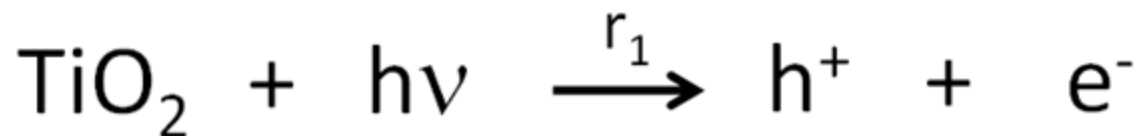
For **not** adsorbed substrates, the photo-oxidation reaction involves the dissolved organic species and free OH radicals (reaction  $r_{OH}$ )



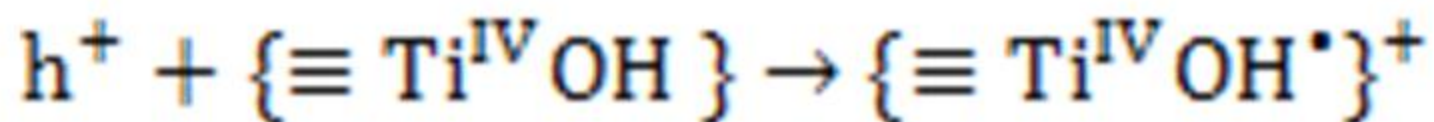
**products**  
**(unselective oxidation)**



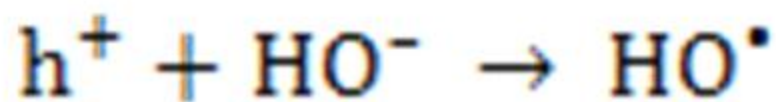
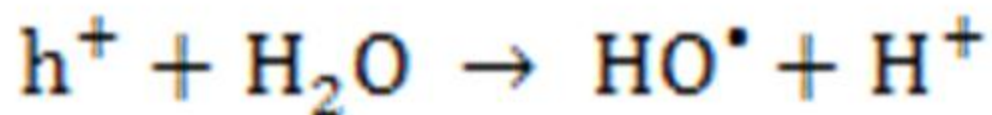
For **weakly** adsorbed substrates, the photo-oxidation reaction involves the dissolved organic species and surface-bound hydroxyl radicals (reaction  $r_s$ ) or free OH radicals (reaction  $r_{OH}$ )



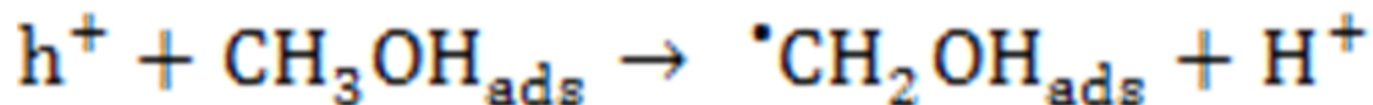
In particular, positive holes can migrate to the  $\text{TiO}_2$  surface, where they are trapped by surface titanol groups that generate superficial  $\text{HO}^\bullet$  radicals



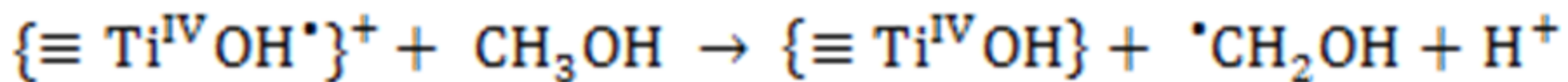
or they can react with adsorbed water molecules or  $\text{HO}^-$  anions, and thus generate free  $\text{HO}^\bullet$  radicals



For example, the  $\text{TiO}_2$  photo-oxidation of methanol (adsorbed species) can be promoted either by direct hole transfer:



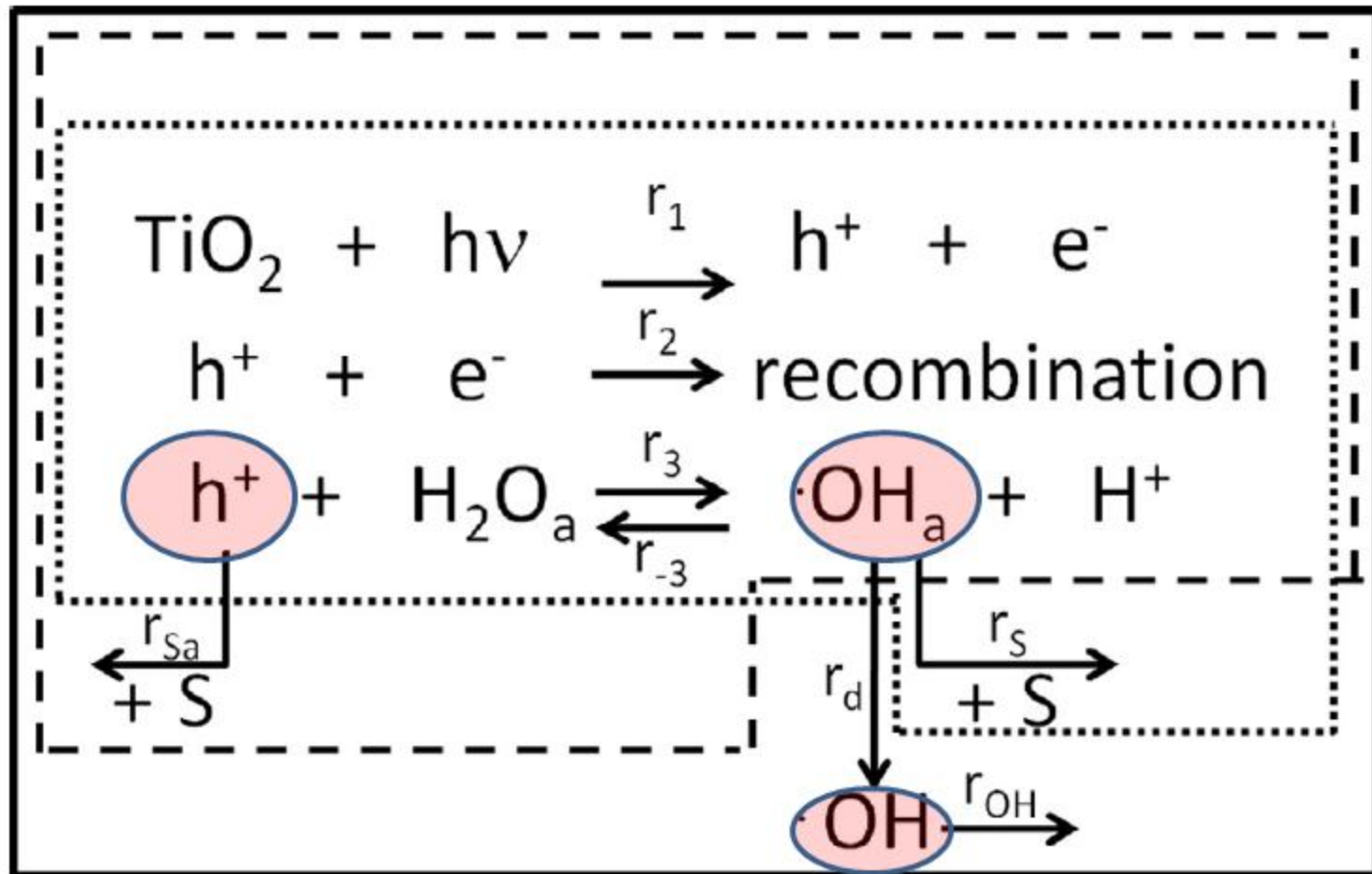
or by a reaction with surface radicals:



*Electrochimica Acta* 51 (2006) 2230–2236

unselective oxidation

For EDDS, as chelating agent, **three** different chemical models can be supposed



- Model 1- continuous line (—)
- Model 1.1- dashed line (- - -)
- Model 1.2.1- dotted line (.....)

Which is the correct mechanism?



## Verification of the Proposed Mechanism using Scavengers

*Effect of Iodide Ion.* Iodide ion is a scavenger and reacts with  $h_{\text{vb}}^+$  and  $\cdot\text{OH}_{\text{ads}}$ , reducing the number of oxidizing species available at the surface of the catalyst. The valence band hole is easily captured by  $\text{I}^-$  (the redox potential of the couple  $\text{I}^{\cdot}/\text{I}^-$  is 1.3 V) and pathways due to oxidation by surface hydroxyl radicals are also possible because the rate constant of reaction with  $\cdot\text{OH}_{\text{ads}}$  is  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$

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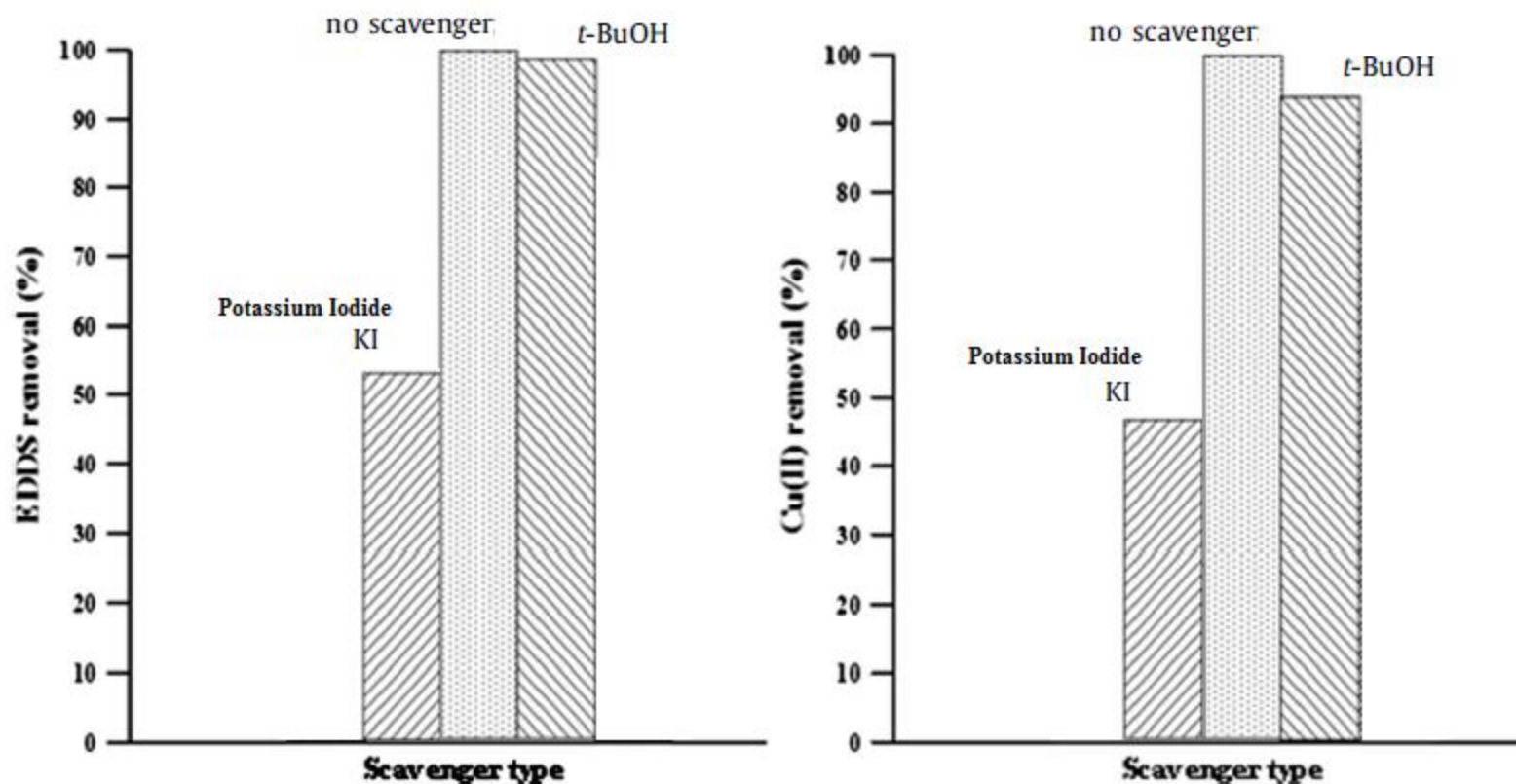
**Iodide can react with both free positive holes and surface-bound hydroxyl radicals**

*Effect of Tert-Butyl Alcohol.* *t*-BuOH can react quickly with  $\cdot\text{OH}$  with a rate constant of  $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

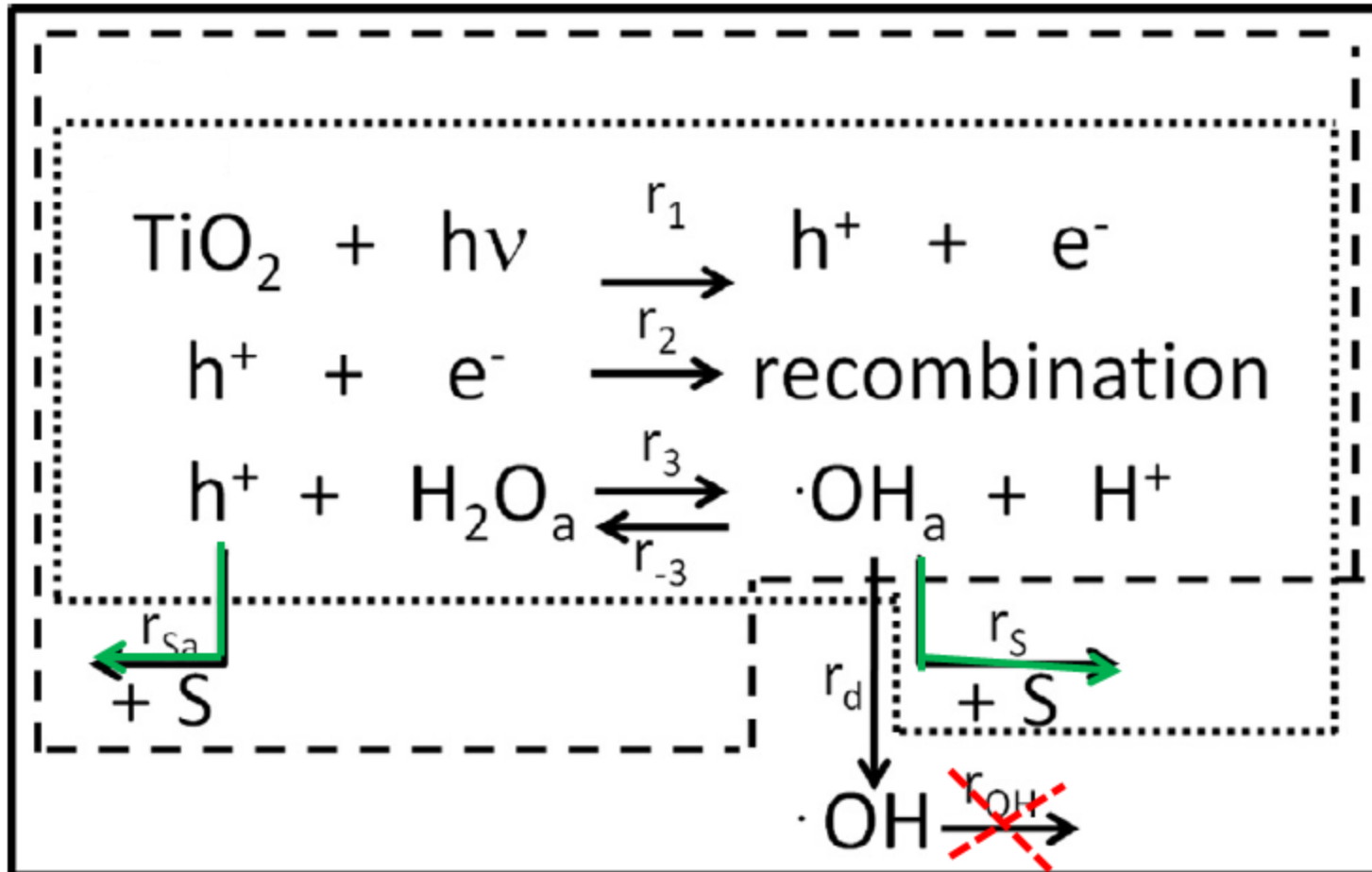
*Environ. Sci. Technol.* **2004**, 38 (24), 6875–6880.

**Ter-butanol is a hydroxyl radical scavenger**

In presence of **Tert-butyl alcohol**, only **negligible** effects have been observed on the consumption rates of EDDS and Cu(II), on the other hand, in case of **Iodide** addition, there is a **marked** reduction of the system reactivity



EDDS (left) and cupric species (right) photocatalytic removals at 60 min of treatment. ■ no scavenger; ▨ KI (3.0 mM); ▩ t-BuOH (3.0 mM); [EDDS]<sub>0</sub> 0.2 mM; [CuSO<sub>4</sub>]<sub>0</sub> 1.0 mM; [TiO<sub>2</sub>] 50 mg L<sup>-1</sup>, pH 2.0, purging gas: N<sub>2</sub>. T: 25 °C.



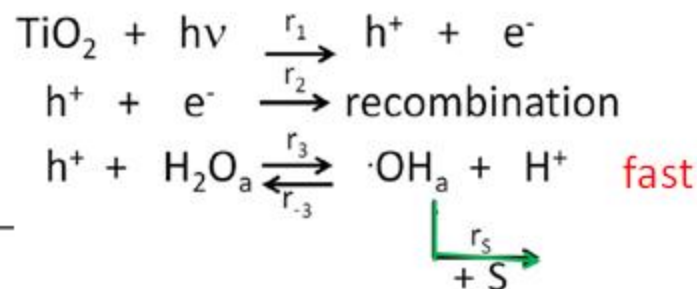
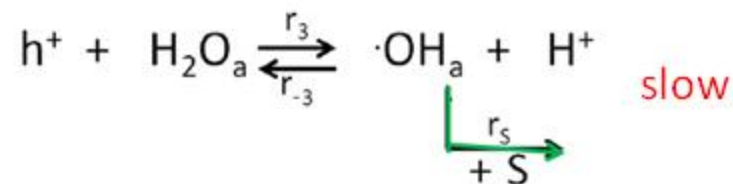
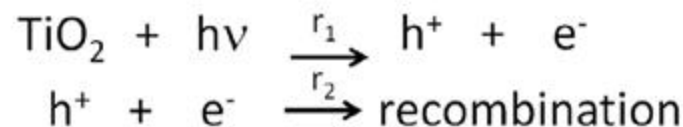
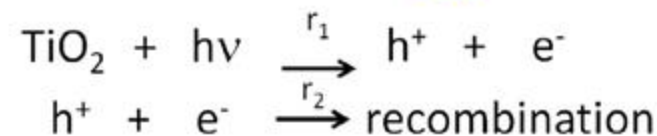
- ~~Model 1- continuous line~~ (——)
- Model 1.1- dashed line (---)
- Model 1.2.1- dotted line (.....)



Positive holes or surface-bound HO radicals?

**Models proposed and tested.**

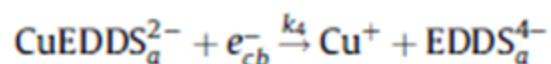
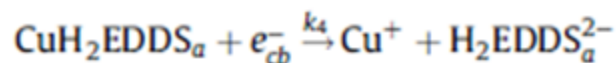
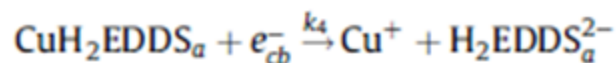
Model	Reactions considered for the organic species consumption	Equations adopted for the mass balances
1.1	Reaction between substrate adsorbed on the surface and positive holes- $r_{9t}$ , $r_{10t}$ , $r_{11}$	$\frac{d[HO_2]}{dt} = r_3 - r_{-3} = 0$ $\frac{d[h^+]}{dt} = r_1 - r_2 - 2 \cdot (r_{9t} + r_{10t} + r_{11}) - r_{12} - r_{13}$
1.2.1	Reaction between the dissolved substrate and the surface-bound hydroxyl radicals- $r_{6t}$ , $r_{7t}$ , $r_8$	$\frac{d[HO_2]}{dt} = r_3 - r_{-3} - 2 \cdot (r_{6t} + r_{7t} + r_8) = 0$ $[\cdot OH_a] = \frac{k_3[h^+][H_2O_a]}{k_{-3} + 2 \cdot (k_{6t}[S_{co}] + k_{7t}[S_p] + k_8[P])}$ $\frac{d[h^+]}{dt} = r_1 - r_2 - r_3 + r_{-3} - r_{12} - r_{13}$
1.2.2	Reaction between the dissolved substrate and the surface-bound hydroxyl radicals considering fast equilibration of surface-bound hydroxyl radicals with the positive holes- $r_{6t}$ , $r_{7t}$ , $r_8$	$[\cdot OH_a] = \frac{K_{eq}[h^+][H_2O_a]}{[H^+]}$ $\frac{d[h^+]}{dt} = \frac{[r_1 - r_2 - 2 \cdot h^+ \cdot (k_{6t}[S_{co}] + k_{7t}[S_p] + k_8[P]) - r_{12} - r_{13}]}{1 + K_{eq} \frac{[H_2O_a]}{[H^+]}}$



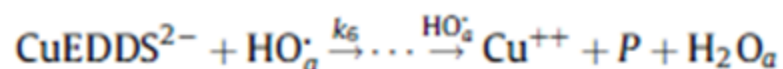
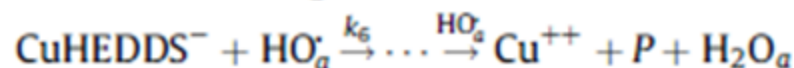
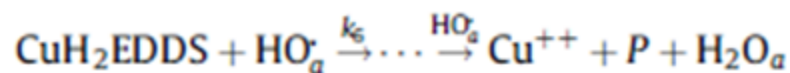


Due to the **complexity** of the reacting system, some simplifications have been made:

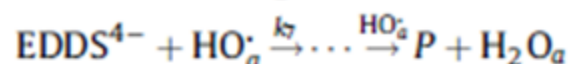
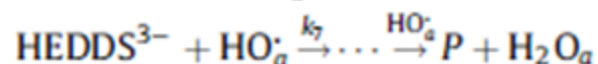
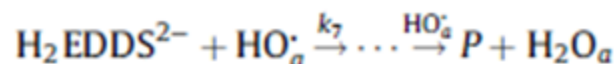
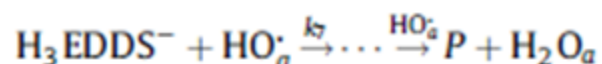
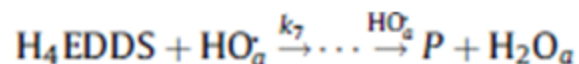
a single kinetic constant ( $k_4$ ) for reactions of different CuEDDS species with electrons



a single kinetic constant ( $k_6$ ) for reactions of different CuEDDS species with holes



a single kinetic constant ( $k_7$ ) for reactions of different EDDS species with holes



Equilibrium equations for substrate adsorption on the catalyst surface.

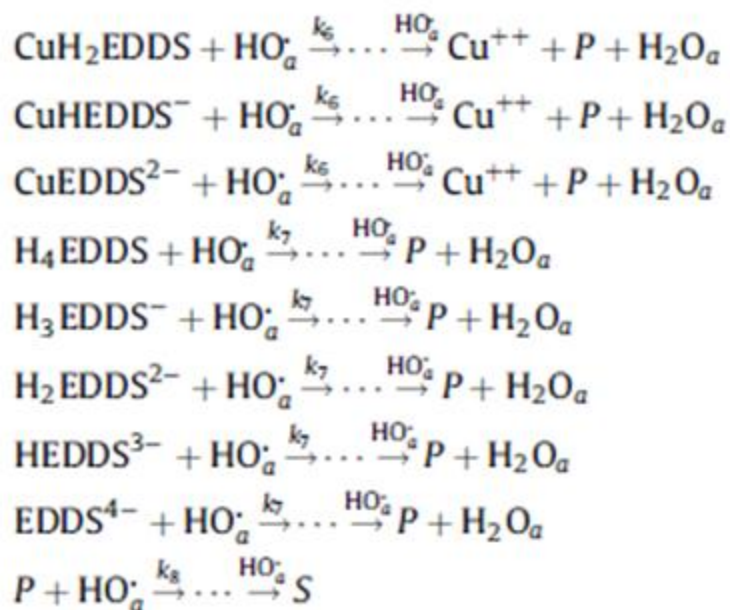
n°	Equilibrium adsorption
Eq.1	$[CuH_2EDDS_a] = K_{ad} \cdot [CuH_2EDDS] \cdot [C_f]$
Eq.2	$[CuHEDDS_a^-] = K_{ad} \cdot [CuHEDDS^-] \cdot [C_f]$
Eq.3	$[CuEDDS_a^{2-}] = K_{ad} \cdot [CuEDDS^{2-}] \cdot [C_f]$
Eq.4	$[H_4EDDS_a] = K_{ad} \cdot [H_4EDDS] \cdot [C_f]$
Eq.5	$[H_3EDDS_a^-] = K_{ad} \cdot [H_3EDDS^-] \cdot [C_f]$
Eq.6	$[H_2EDDS_a^{2-}] = K_{ad} \cdot [H_2EDDS^{2-}] \cdot [C_f]$
Eq.7	$[HEDDS_a^{3-}] = K_{ad} \cdot [HEDDS^{3-}] \cdot [C_f]$
Eq.8	$[EDDS_a^{4-}] = K_{ad} \cdot [EDDS^{4-}] \cdot [C_f]$

[C<sub>f</sub>] is the concentration of free active sites on the photocatalyst surface.

Due to the absence of experimental evidence of EDDS adsorption on the TiO<sub>2</sub> surface, is assumed

~~$$[C_{tot}] = [C_f] + [C_{sa}]$$~~

all by-products are considered as a single component



steady-state hypothesis for all radical species

$$\frac{d[\cdot\text{OH}_a]}{dt} = r_3 - r_{-3} - r_S = 0$$

**Table 1**

Reaction network proposed for the investigated chemical system. (1)  $\text{HSO}_4^-$  is in equilibrium with  $\text{SO}_4^-$  (see below the equilibrium of deprotonation of hydrogensulfate ion). The presence of these species is due to the fact that the cupric ions have been added to the solution as  $\text{CuSO}_4$  and the reacting solution pH has been adjusted at the desired value by using concentrated  $\text{H}_2\text{SO}_4$ .

$r^i$	Reaction	Rate equation
$r_1$	$\text{TiO}_2 + h\nu \xrightarrow{k_1} e_{\text{CB}}^- + h_{\text{VB}}^+$	$r_1 = k_1 \cdot [\text{TiO}_2] = \frac{\Phi_{\text{TiO}_2} \cdot I_0}{h\nu}$
$r_2$	$e_{\text{CB}}^- + h_{\text{VB}}^+ \xrightarrow{k_2} \text{heat}$	$r_2 = k_2 \cdot [e_{\text{CB}}^-] \cdot [h_{\text{VB}}^+]$
$r_3$	$h_{\text{VB}}^+ + \text{H}_2\text{O} \xrightarrow{k_3} \text{HO}_2^+ + \text{H}^+$	$r_3 = k_3 \cdot [h_{\text{VB}}^+] \cdot [\text{H}_2\text{O}]$
$r_{-3}$	$\text{HO}_2^+ + \text{H}^+ \xrightarrow{k_{-3}} h_{\text{VB}}^+ + \text{H}_2\text{O}$	$r_{-3} = k_{-3} \cdot [\text{HO}_2^+]$
<i>Reactions with photogenerated electrons</i>		
$r_{4a}$	$\text{CuH}_2\text{EDDS}_0 + e_{\text{CB}}^- \xrightarrow{k_4} \text{Cu}^+ + \text{H}_2\text{EDDS}_0^{2-}$	$r_{4a} = k_4 \cdot [e_{\text{CB}}^-] \cdot [\text{CuH}_2\text{EDDS}_0]$
$r_{4b}$	$\text{CuHEDDS}_0^- + e_{\text{CB}}^- \xrightarrow{k_4} \text{Cu}^+ + \text{H}_2\text{EDDS}_0^{2-}$	$r_{4b} = k_4 \cdot [e_{\text{CB}}^-] \cdot [\text{CuHEDDS}_0^-]$
$r_{4c}$	$\text{CuEDDS}_0^{2-} + e_{\text{CB}}^- \xrightarrow{k_4} \text{Cu}^+ + \text{EDDS}_0^{4-}$	$r_{4c} = k_4 \cdot [e_{\text{CB}}^-] \cdot [\text{CuEDDS}_0^{2-}]$
$r_5$	$\text{Cu}^+ + e_{\text{CB}}^- \xrightarrow{k_5} \text{Cu}^0$	$r_5 = k_5 \cdot [\text{Cu}^+] \cdot [e_{\text{CB}}^-]$
<i>Reactions with surface-bound hydroxyl radicals</i>		
$r_{6a}$	$\text{CuH}_2\text{EDDS} + \text{HO}_2^+ \xrightarrow{k_6} \dots \xrightarrow{\text{HO}_2^+} \text{Cu}^{++} + \text{P} + \text{H}_2\text{O}_2$	$r_{6a} = k_6 \cdot [\text{HO}_2^+] \cdot [\text{CuH}_2\text{EDDS}]$
$r_{6b}$	$\text{CuHEDDS}^- + \text{HO}_2^+ \xrightarrow{k_6} \dots \xrightarrow{\text{HO}_2^+} \text{Cu}^{++} + \text{P} + \text{H}_2\text{O}_2$	$r_{6b} = k_6 \cdot [\text{HO}_2^+] \cdot [\text{CuHEDDS}^-]$
$r_{6c}$	$\text{CuEDDS}^{2-} + \text{HO}_2^+ \xrightarrow{k_6} \dots \xrightarrow{\text{HO}_2^+} \text{Cu}^{++} + \text{P} + \text{H}_2\text{O}_2$	$r_{6c} = k_6 \cdot [\text{HO}_2^+] \cdot [\text{CuEDDS}^{2-}]$
$r_{7a}$	$\text{H}_4\text{EDDS} + \text{HO}_2^+ \xrightarrow{k_7} \dots \xrightarrow{\text{HO}_2^+} \text{P} + \text{H}_2\text{O}_2$	$r_{7a} = k_7 \cdot [\text{HO}_2^+] \cdot [\text{H}_4\text{EDDS}]$
$r_{7b}$	$\text{H}_3\text{EDDS}^- + \text{HO}_2^+ \xrightarrow{k_7} \dots \xrightarrow{\text{HO}_2^+} \text{P} + \text{H}_2\text{O}_2$	$r_{7b} = k_7 \cdot [\text{HO}_2^+] \cdot [\text{H}_3\text{EDDS}^-]$
$r_{7c}$	$\text{H}_2\text{EDDS}^{2-} + \text{HO}_2^+ \xrightarrow{k_7} \dots \xrightarrow{\text{HO}_2^+} \text{P} + \text{H}_2\text{O}_2$	$r_{7c} = k_7 \cdot [\text{HO}_2^+] \cdot [\text{H}_2\text{EDDS}^{2-}]$
$r_{7d}$	$\text{HEDDS}^{3-} + \text{HO}_2^+ \xrightarrow{k_7} \dots \xrightarrow{\text{HO}_2^+} \text{P} + \text{H}_2\text{O}_2$	$r_{7d} = k_7 \cdot [\text{HO}_2^+] \cdot [\text{HEDDS}^{3-}]$
$r_{7e}$	$\text{EDDS}^{4-} + \text{HO}_2^+ \xrightarrow{k_7} \dots \xrightarrow{\text{HO}_2^+} \text{P} + \text{H}_2\text{O}_2$	$r_{7e} = k_7 \cdot [\text{HO}_2^+] \cdot [\text{EDDS}^{4-}]$
$r_8$	$\text{P} + \text{HO}_2^+ \xrightarrow{k_8} \dots \xrightarrow{\text{HO}_2^+} \text{S}$	$r_8 = k_8 \cdot [\text{P}] \cdot [\text{HO}_2^+]$
<i>Reactions with photogenerated holes</i>		
$r_{9a}$	$\text{CuH}_2\text{EDDS}_0 + h_{\text{VB}}^+ \xrightarrow{k_9} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+ + \text{Cu}^{++}$	$r_{9a} = k_9 \cdot [h_{\text{VB}}^+] \cdot [\text{CuH}_2\text{EDDS}_0]$
$r_{9b}$	$\text{CuHEDDS}_0^- + h_{\text{VB}}^+ \xrightarrow{k_9} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+ + \text{Cu}^{++}$	$r_{9b} = k_9 \cdot [h_{\text{VB}}^+] \cdot [\text{CuHEDDS}_0^-]$
$r_{9c}$	$\text{CuEDDS}_0^{2-} + h_{\text{VB}}^+ \xrightarrow{k_9} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+ + \text{Cu}^{++}$	$r_{9c} = k_9 \cdot [h_{\text{VB}}^+] \cdot [\text{CuEDDS}_0^{2-}]$
$r_{10a}$	$\text{H}_4\text{EDDS}_0 + h_{\text{VB}}^+ \xrightarrow{k_{10}} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+$	$r_{10a} = k_{10} \cdot [h_{\text{VB}}^+] \cdot [\text{H}_4\text{EDDS}_0]$
$r_{10b}$	$\text{H}_3\text{EDDS}_0^- + h_{\text{VB}}^+ \xrightarrow{k_{10}} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+$	$r_{10b} = k_{10} \cdot [h_{\text{VB}}^+] \cdot [\text{H}_3\text{EDDS}_0^-]$
$r_{10c}$	$\text{H}_2\text{EDDS}_0^{2-} + h_{\text{VB}}^+ \xrightarrow{k_{10}} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+$	$r_{10c} = k_{10} \cdot [h_{\text{VB}}^+] \cdot [\text{H}_2\text{EDDS}_0^{2-}]$
$r_{10d}$	$\text{HEDDS}_0^{3-} + h_{\text{VB}}^+ \xrightarrow{k_{10}} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+$	$r_{10d} = k_{10} \cdot [h_{\text{VB}}^+] \cdot [\text{HEDDS}_0^{3-}]$
$r_{10e}$	$\text{EDDS}_0^{4-} + h_{\text{VB}}^+ \xrightarrow{k_{10}} \dots \xrightarrow{h_{\text{VB}}^+} \text{P} + \text{H}^+$	$r_{10e} = k_{10} \cdot [h_{\text{VB}}^+] \cdot [\text{H}_4\text{EDDS}_0] \cdot [\text{EDDS}_0^{4-}]$
$r_{11}$	$\text{P} + h_{\text{VB}}^+ \xrightarrow{k_{11}} \dots \xrightarrow{h_{\text{VB}}^+} \text{S}$	$r_{11} = k_{11} \cdot [\text{P}] \cdot [h_{\text{VB}}^+]$
$r_{12}$	$\text{Cu}^+ + h_{\text{VB}}^+ \xrightarrow{k_{12}} \text{Cu}^{++}$	$r_{12} = k_{12} \cdot [\text{Cu}^+] \cdot [h_{\text{VB}}^+]$
$r_{13}$	$\text{HSO}_4^- + h_{\text{VB}}^+ \xrightarrow{k_{13}} \text{HSO}_4^{(1)}$	$r_{13} = k_{13} \cdot [\text{HSO}_4^-] \cdot [h_{\text{VB}}^+]$

Mass balance equations for the species included in the reaction network reported in the Model 1.  $r_{nt} = (r_{na} + r_{nb} + \dots)$  with  $n = 6, 7, 9, 10$ .

n.	Balance	Species
Bal.1	$\frac{d[e^-]}{dt} = r_1 - r_2 - r_{4a} - r_{4b} - r_{4c} - r_5$	Electrons
Bal.2	$\frac{d[h^+]}{dt} = r_1 - r_2 - r_3 + r_{-3} - 2 \cdot (r_{9t} + r_{10t} + r_{11}) - r_{12} - r_{13}$	Holes
Bal.3	$\frac{d[H_2O_a]}{dt} = constant$	Water
Bal.4	$\frac{d[HO_a]}{dt} = r_3 - r_{-3} - 2 \cdot (r_{6t} + r_{7t} + r_8)$	$HO_a$
Bal.5	$\frac{d[Cu^0]}{dt} = r_5$	$Cu^0$
Bal.6	$\frac{d[Cu^+]}{dt} = r_{4a} + r_{4b} + r_{4c} - r_5 - r_{12}$	$Cu^+$
Bal.7	$\frac{d[P]}{dt} = r_{6t} + r_{7t} - r_8 + r_{9t} + r_{10t} - r_{11}$	P
Bal.8	$\frac{d[S]}{dt} = r_8 + r_{11}$	S
Bal.9	$[SO_4^{2-}]_0 = [SO_4^{2-}] + [HSO_4^-] + [HSO_{4a}^-]$	$HSO_4^-$
Bal.10	$[Cu^{2+}] = \frac{[CuSO_4]_0 - [Cu_0] - [Cu^+]}{1 + [H_4EDDS] \cdot Den_2 \cdot (1 + K_{ad} \cdot [C_f])}$	$Cu^{2+}$
Bal.11	$[H_4EDDS] = \frac{[EDDS_0] - [P] - [S]}{(1 + K_{ad} \cdot [C_f]) \cdot (1 + Den_1 + Den_2 \cdot [Cu^{2+}])}$	$H_4Edds$

where:

$$[Cu_1] = [CuEDDS^{2-}] + [CuHEDDS^-] + [CuH_2EDDS].$$

$$[Cu_a] = K_{ad} \cdot [C_f] \cdot [Cu_1].$$

$$[EDDS_f] = [EDDS^{4-}] + [HEDDS^{3-}] + [H_2EDDS^{2-}] + [H_3EDDS^-] + [Cu_1].$$

$$[EDDS_a] = K_{ad} \cdot [C_f] \cdot [EDDS_f] + [H_4EDDS_a].$$



## Unknown parameters

Kinetic parameters	$[M^{-1} s^{-1}]$
$k_4$	$(4.27 \pm 0.45) \cdot 10^9$
$k_6$	$(1.42 \pm 0.15) \cdot 10^7$
$k_7$	$(5.88 \pm 0.28) \cdot 10^6$
$k_8$	$(6.26 \pm 0.85) \cdot 10^6$
Equilibrium constant	[expression dependent]
$K_{ad}$	$(1.36 \pm 0.12) \cdot 10^1 [M^{-1}]$
$K_{eq} \cdot [H_2O_a]$	$\forall K_{eq} \cdot [H_2O_a] \in [10^{-4} \ 10^4] [M]$

## Simulation examples

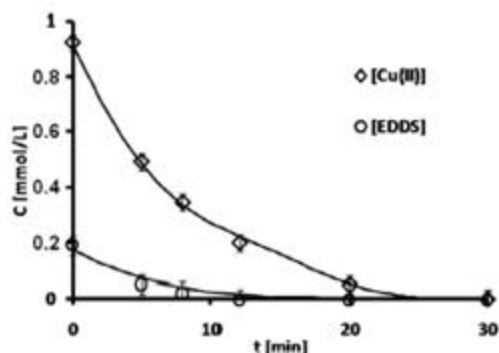


Fig. 3. Comparison between experimental (symbol) and evaluated (continuous lines) data:  $[EDDS]_0 = 0.19 \text{ mM}$ ,  $[CuSO_4]_0 = 0.92 \text{ mM}$ ,  $TiO_2$  (pure anatase) =  $500 \text{ mg L}^{-1}$ , purging gas =  $N_2$ , Hg vapor lamp,  $pH = 2.0$ ,  $T = 25 \text{ }^\circ\text{C}$ .

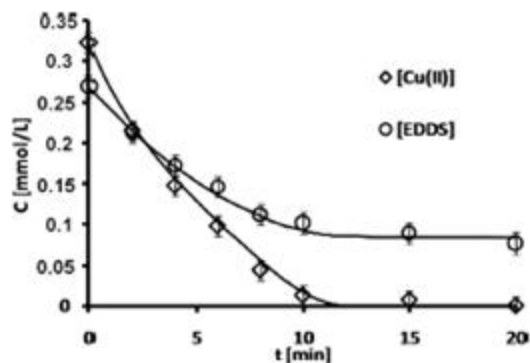


Fig. 6. Comparison between experimental (symbol) and simulated (continuous lines) data:  $[EDDS]_0 = 0.27 \text{ mM}$ ,  $[CuSO_4]_0 = 0.32 \text{ mM}$ ,  $TiO_2$  (pure anatase) =  $50 \text{ mg L}^{-1}$ , purging gas =  $N_2$ , Hg vapor lamp,  $pH = 2.0$ ,  $T = 25 \text{ }^\circ\text{C}$ .

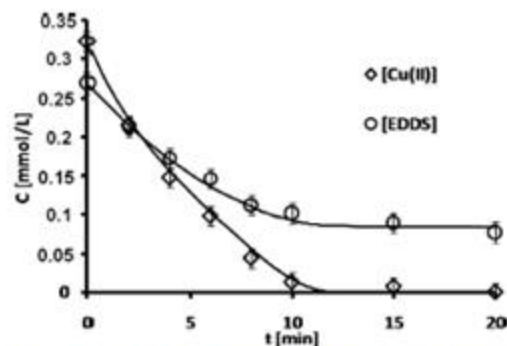


Fig. 6. Comparison between experimental (symbol) and simulated (continuous lines) data:  $[EDDS]_0 = 0.27 \text{ mM}$ ,  $[CuSO_4]_0 = 0.32 \text{ mM}$ ,  $TiO_2$  (pure anatase) =  $50 \text{ mg L}^{-1}$ , purging gas =  $N_2$ , Hg vapor lamp,  $pH = 2.0$ ,  $T = 25 \text{ }^\circ\text{C}$ .

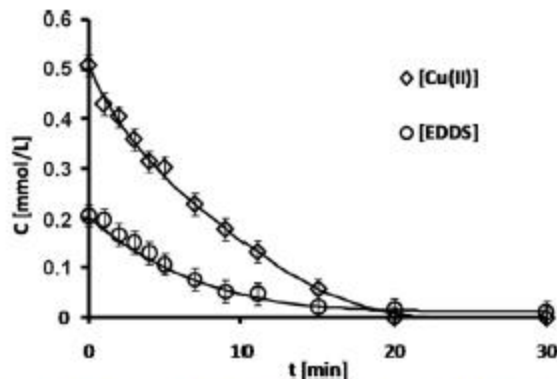


Fig. 5. Comparison between experimental (symbol) and evaluated (continuous lines) data:  $[EDDS]_0 = 0.21 \text{ mM}$ ,  $[CuSO_4]_0 = 0.51 \text{ mM}$ ,  $TiO_2$  (pure anatase) =  $50 \text{ mg L}^{-1}$ , purging gas =  $N_2$ , Hg vapor lamp,  $pH = 2.0$ ,  $T = 25 \text{ }^\circ\text{C}$ .

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## LIFE11/ENV/IT/275 - ECOREMED

**IMPLEMENTATION OF ECO-COMPATIBLE PROTOCOLS FOR AGRICULTURAL SOIL  
REMEDiation IN LITORALE DOMIZIO-AGRO AVERSANO**