Influence of TiO_2 Physico-Chemical Characteristics on Photocatalytic *E. coli* Inactivation

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Contents

Context – Objectives

1) TiO_2 characterization

2) *E. coli* inactivation with suspended TiO_2

3) *E. coli* inactivation with supported TiO_2

Conclusion

Influence of TiO_2 characteristics

The **rate of formation of the oxidative surface species** and the **interaction between TiO_2 and organics and/or bacteria** are function of :

- particle size
- aggregated size
- BET specific surface area
- Crystalline phase
- Isoelectric point (IEP)
- other parameters

Objectives

- To characterize 13 commercial TiO_2 powders
- To relate these characteristics with *E. coli* inactivation

TiO_2 characterization methods

- **Crystalline phase** (Anatase, Rutile)

  X-ray diffraction measurements (XRD)

- **BET** (Specific Surface Area)

  Gas adsorption measurements

- **TiO_2 particle size**

  Transmission electron microscopy (TEM)

- **TiO_2 aggregate size**

  Electroacoustic spectroscopy

- **Isoelectric Point (IEP) - Zeta potential**

  Electroacoustic spectroscopy

C. Morais, P. Bowen, *LTP, STI*

Electroacoustic spectroscopy

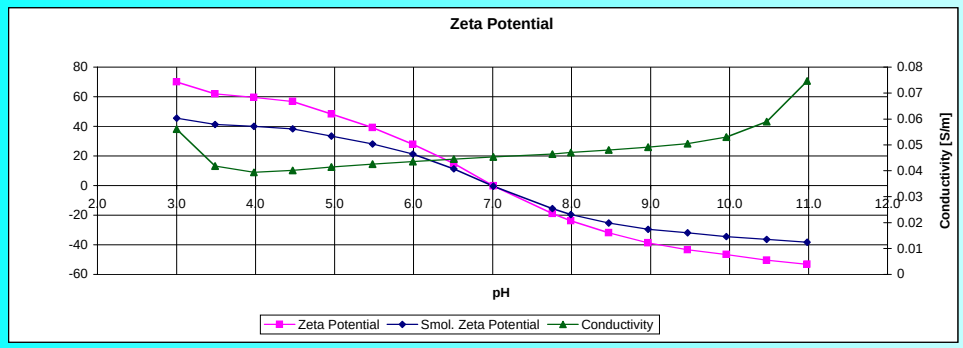
The electroacoustic procedure measures the dynamic (or electrophoretic) mobility μ_d

(O'Brien et al., *Colloid. Interface. Sci*, 1995, *173*, 406-418.)

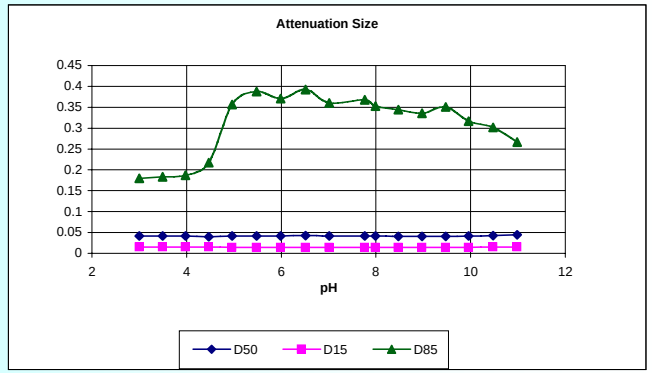
μ_d → 1) Zeta potential & IEP

acoustic attenuation spectroscopy → 2) Aggregate size distribution

(O'Brien, R. W. J. *Fluid mech*., 1988, *190*, 71-85.)



P25



pH < IEP → TiO_2 surface : positively charged ($TiOH_2^+$)

pH = IEP → TiO_2 surface : neutral

pH > IEP → TiO_2 surface: negatively charged (TiO^-)

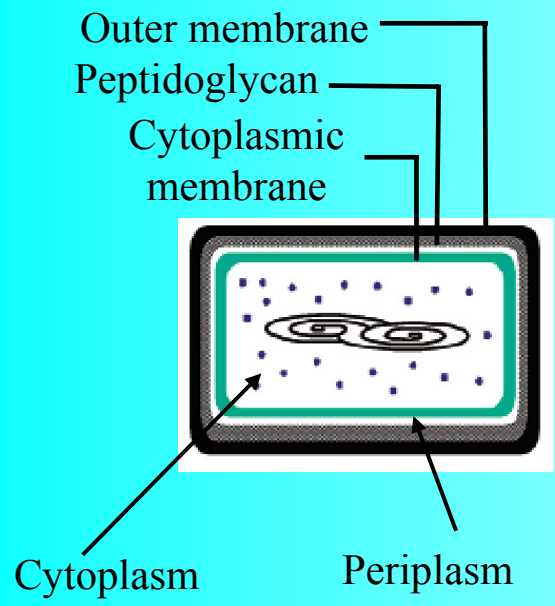
TiO_2 characteristics

Type of TiO_2	Crystalline phase	BET (m^2/g)	Particule size (nm)	Aggregate radius (nm)	IEP
Degussa P25	Ana.-Rutile	56	25-35	370	7.0
Degussa P25 TN90	Ana.-Rutile	90	<100	14000	7.0
Mil. PC10	Anatase	10	70	1000	5.7
Mil. PC50	Anatase	50	20-30	8200	6.8
Mil. PC500	Anatase	335	5-10	1400	6.2
Mil. S5-300A	Anatase	280	30-60	1500	7.0
Huntsmann AHR	Anatase	11	150	6000	<3
Fluka	Anatase	9	700	40000	3.5
Tayca JA1	Anatase	9	180	9200	<3
Tayca TKS201	Anatase	214	6	130	7.5
Tayca TKS203	Anatase	241	6	200	<3
Tayca TKP101	Anatase	300	6	1850	4.7
Tayca TKP103	Anatase	280	6	350	<3

E. coli (1)

- 1-2 μm diameter (~ same as TiO_2 aggregate size)

- Outer membrane is negatively charged between pH 3 and 9



GRAM –

Outer membrane (6 -18 nm)

50% lipopolysaccharides, 35% phospholipids, 15% lipoproteins

Mechanical protection, influence permeability of moderate and large size molecules, etc.

Cytoplasmic membrane (7.5 nm) phospholipids bi-layer

Selective permeability, maintaining osmotic equilibrium, electron-transport machinery, etc.

E. coli (2)

1. **Natural generation** in the cell of $O_2^{\bullet-}$ and H_2O_2 during respiration

Protective mechanism for all aerobic life form:

- Superoxyde dismutase (SOD) enzyme (to dismutate $O_2^{\bullet-}$ to H_2O_2 and O_2)
- Catalase enzyme (to convert H_2O_2 to H_2O and O_2)

2. H_2O_2 can react with Fe in the cell and generated intern $OH^{\bullet}$ by the Fenton reaction

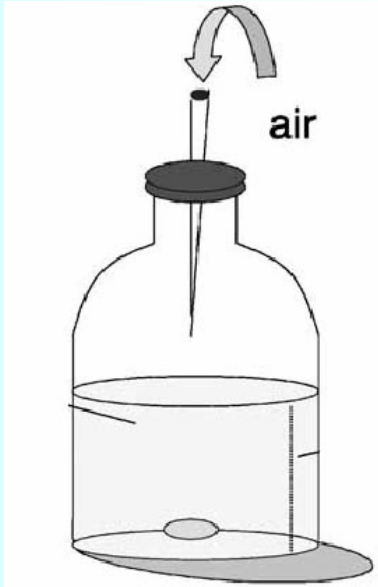
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

3. Different mechanisms of reparation (DNA/RNA, etc.)

4. No mechanism to protect bacteria against external $OH^{\bullet}$ attack

5. There are several evidences of membrane and cell wall destruction and of internal materials leaching
   No evidence of oxygen reactive species diffusion inside the cell
   (Sunada et *al.*, *J. Photochem. Photobiol.*, 156 (2003) - Manness et *al. J. Appl. Environ. Microbiol.*, 65 (1999))

Photocatalytic Experiments

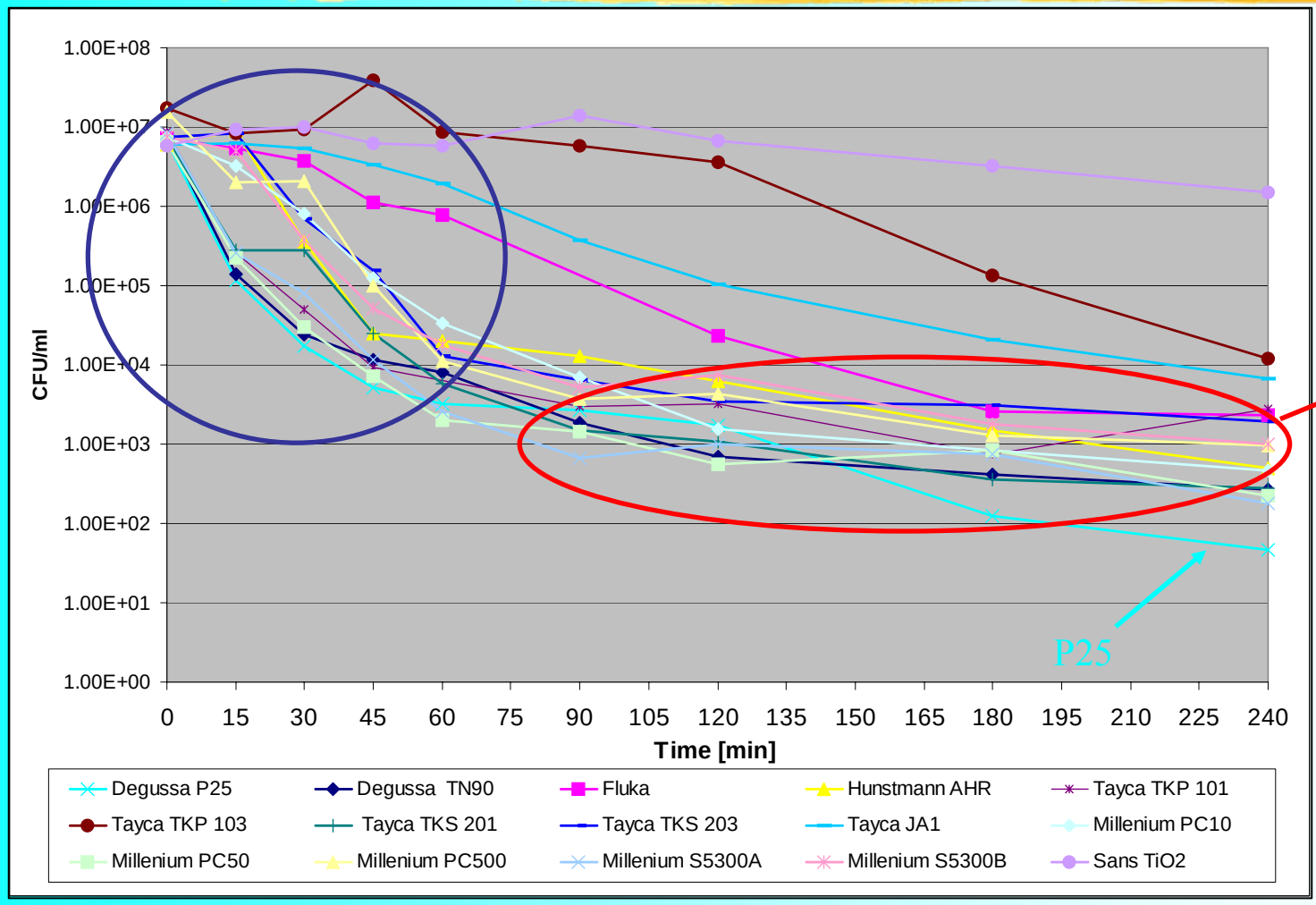


- **Suntest Lamp** with UV B_C filter (<290 nm)
- I = **70**, 100 & 140 mW/cm^2
- 4h illumination
- 4 reactors in parallel

- 50 ml Pyrex Glass Reactor
- [*E. coli*] = ~7 10^6 CFU/ml

  Stationary growth phase (15 h, 37°C, LB)
- Saline solution: NaCl 8 g/l , KCl 0.2 g/l
- pH adjusted to 4.5, **6** and 8.5
- **3** or **4** x repetition

E. coli abatement



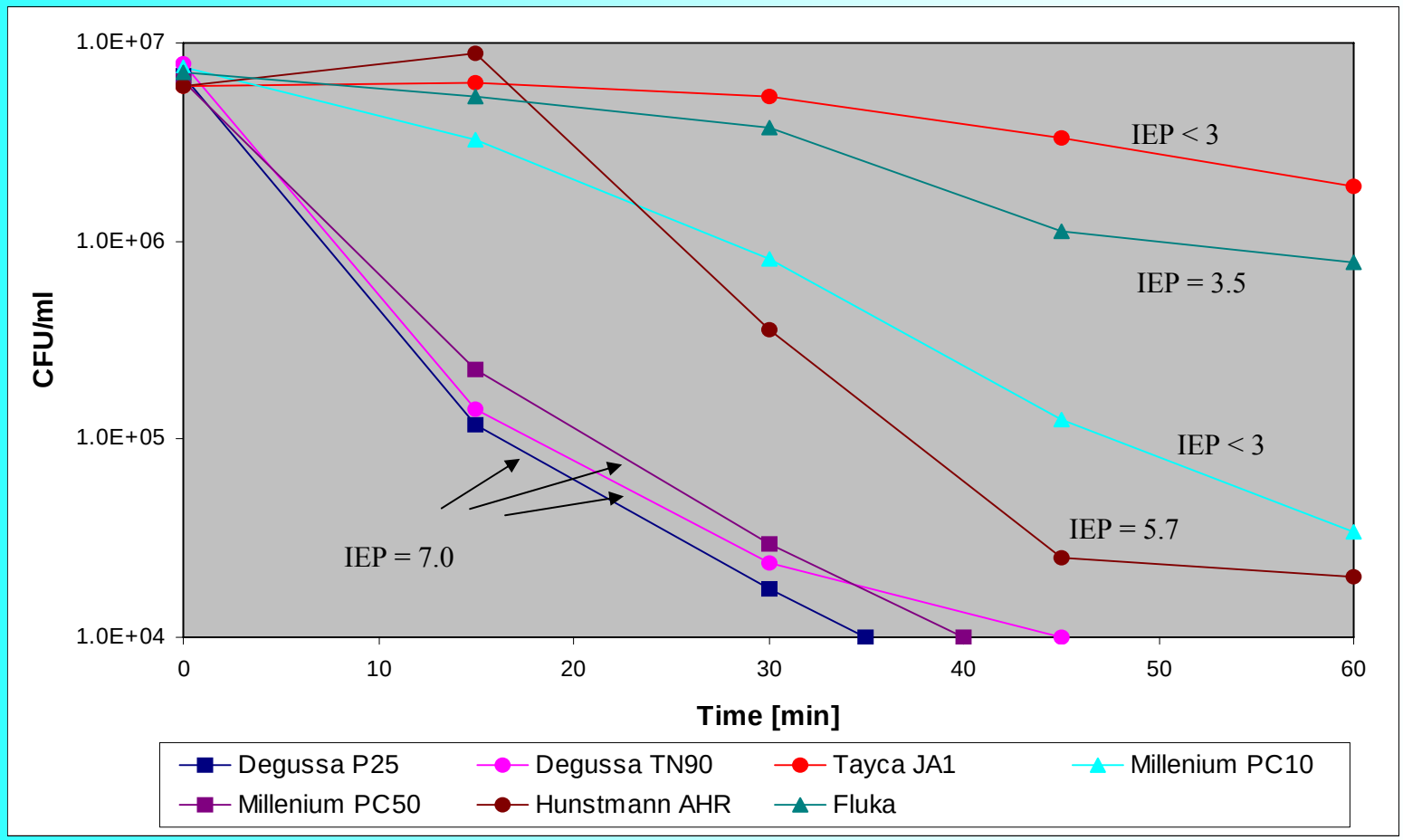
Probably because of the accumulation of organic material in the bulk

→

Competition with alive bacteria

$[E.\ coli]_{ini} = 7\ 10^6$ CFU/ml ; $V_{ill} = 50$ ml , $TiO_2 = 0.2$ g/l ; $I = 70$ mW/cm^2 ; pH 6

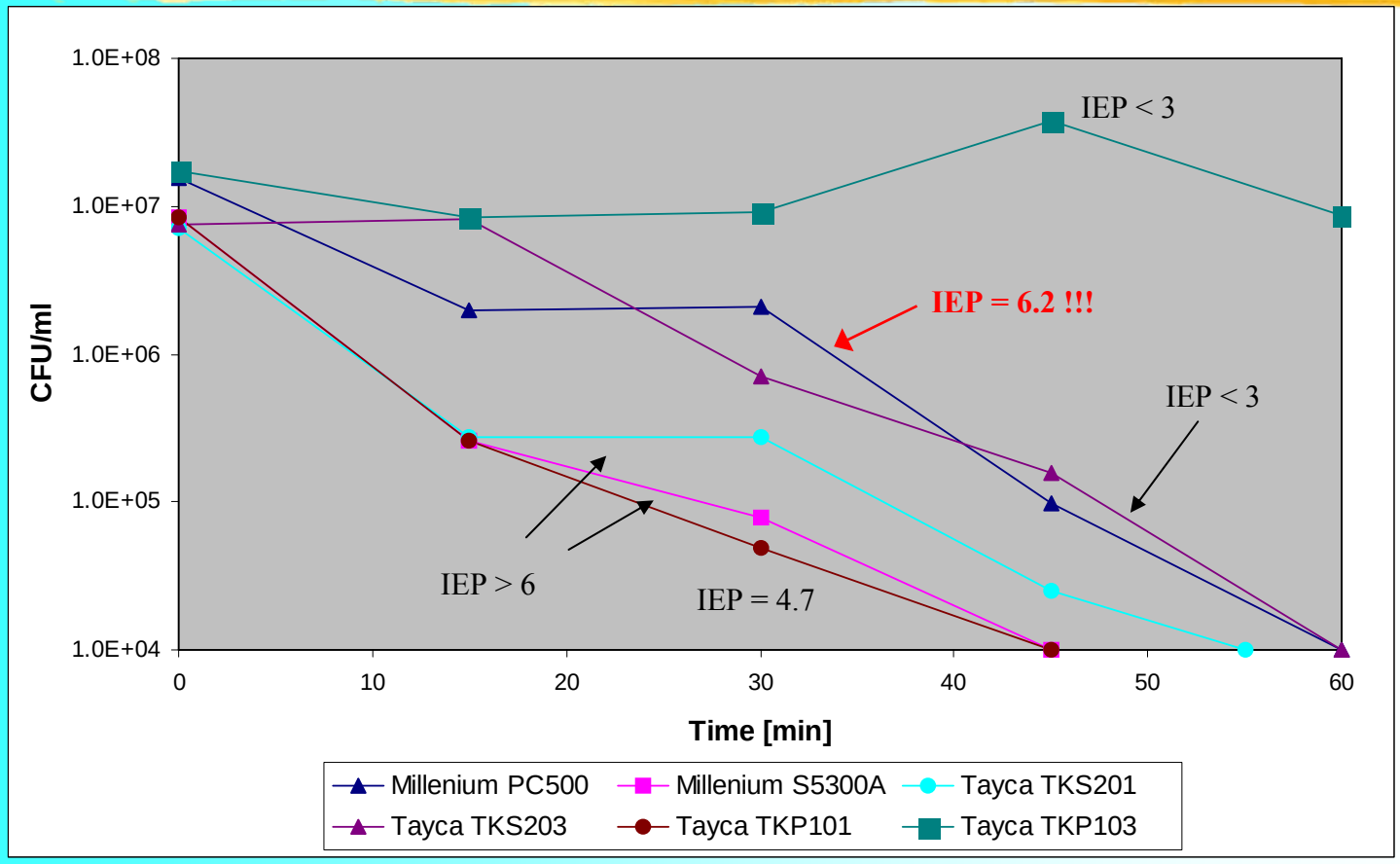
BET < 200 m^2/g
(except P25, aggregate size > 1 µm)



- Lag period for TiO_2 with acidic IEP, probably due to an electrostatic repulsive effect
- No correlation between BET (or particle size) and *E. coli* inactivation

BET > 200 m^2/g

small aggregate size



- Apparently: repulsive effect for TiO_2 with acidic IEP
- No correlation between BET (or particle size) and *E. coli* inactivation

pH and IEP

Study of the electrostatic attraction between *E. coli* and TiO_2

***E. coli*:** Negatively charged between pH 3 & 9
(carboxylic and phosphate groups)

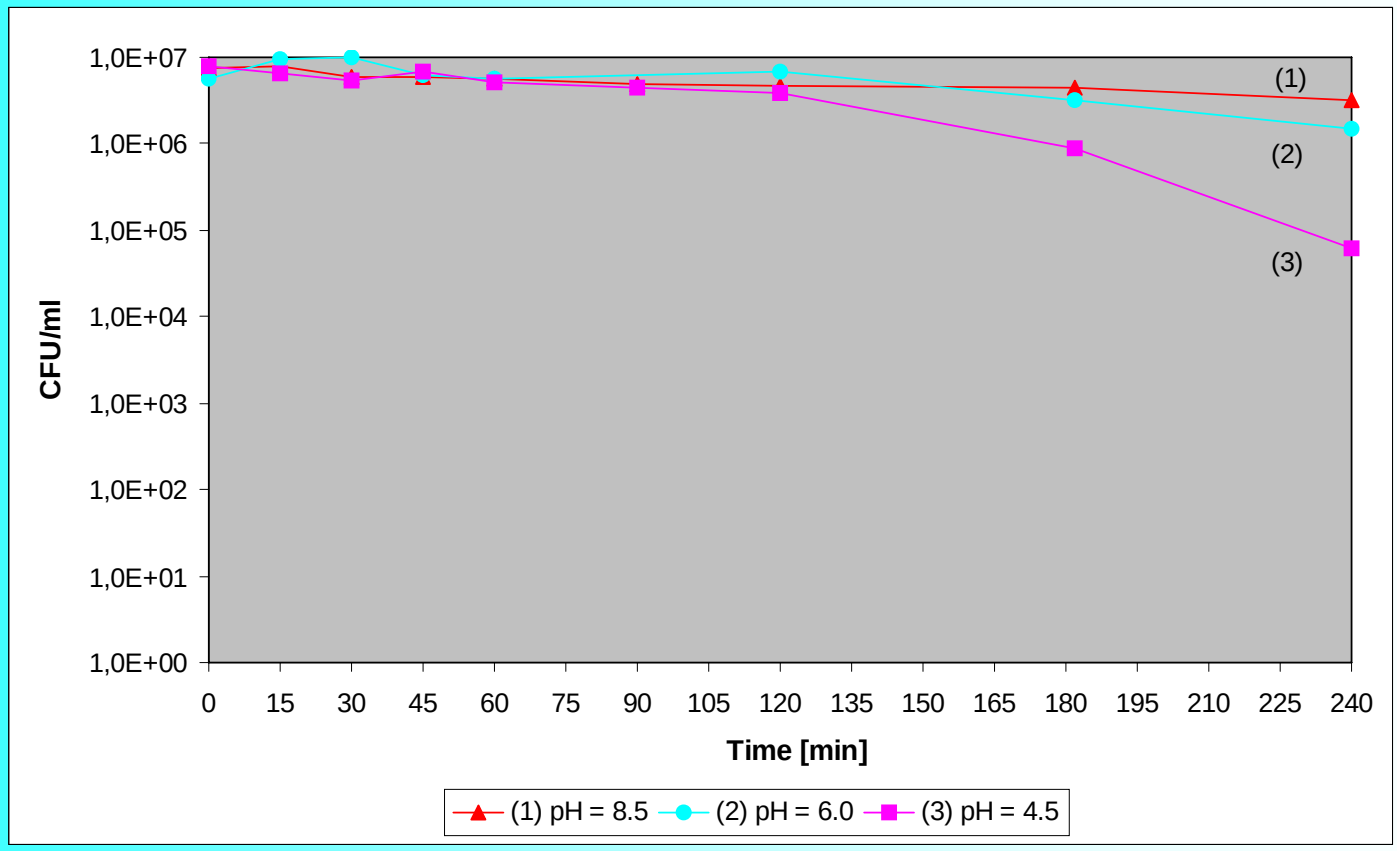
pH < IEP → TiO_2 surface : positively charged ($TiOH_2^+$)

TiO_2: pH = IEP → TiO_2 surface : neutral

pH > IEP → TiO_2 surface: negatively charged (TiO^-)

→ Experiments at different pH

Photo-inactivation at different pH



- **No abatement under light irradiation at pH 6 & 8.5**
- **Small abatement at pH 4.5**

$[E.\ coli]_{ini}$ = 7 10^6 CFU/ml ; V_{ill} = 50 ml , TiO_2 = **0.0** g/l ; I = 70 mW/cm^2

pH and IEP

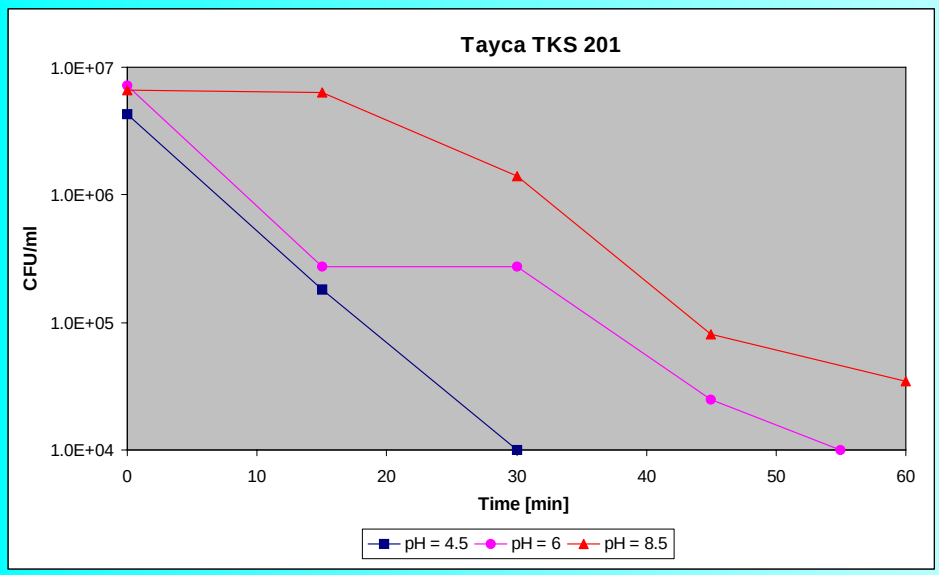
Type of TiO_2	Crystalline phase	BET (m^2/g)	Particule size (nm)	Aggregate radius (nm)	IEP
Tayca TKS201	Anatase	214	6	130	**7.5**
Tayca TKS203	Anatase	241	6	200	**<3**

Pairs of TiO_2 with different surface charge but similar surface properties

Tayca TKS

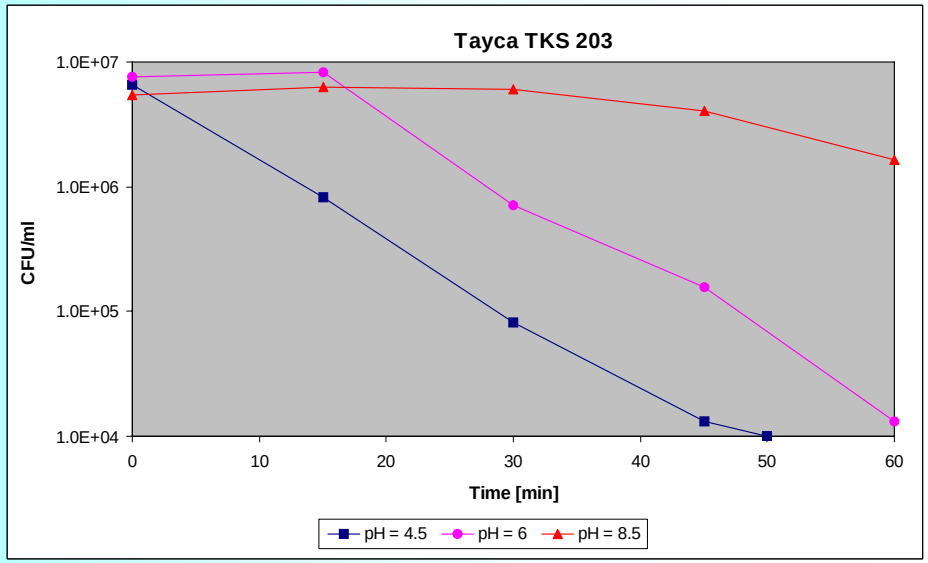
IEP = 7.5

Surface negatively charged for pH 8.5 and positively charged for pH 4.5 & 6.0



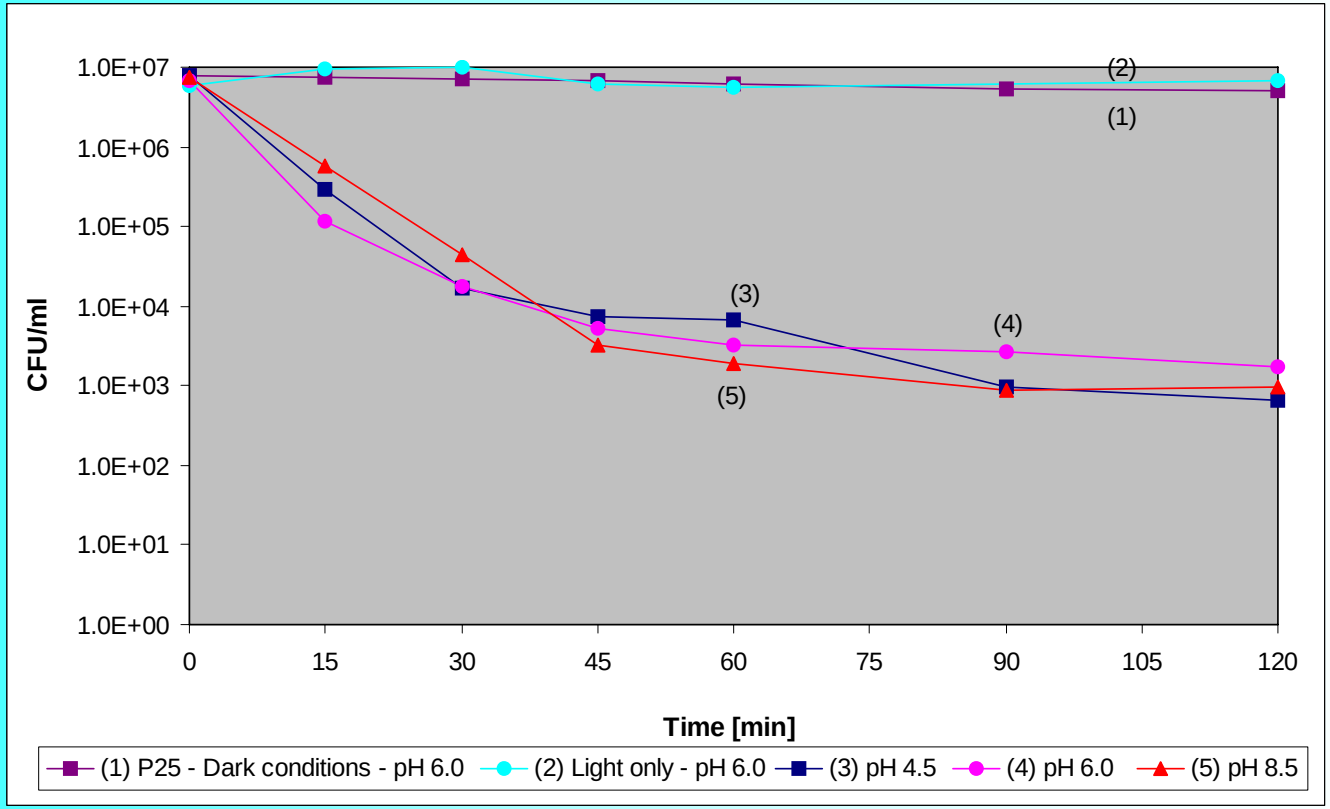
IEP <3

Surface negatively charged for the 3 pH



→ **Electrostatic attraction seems to be a determinant factor for Tayca TKS**

Degussa P25

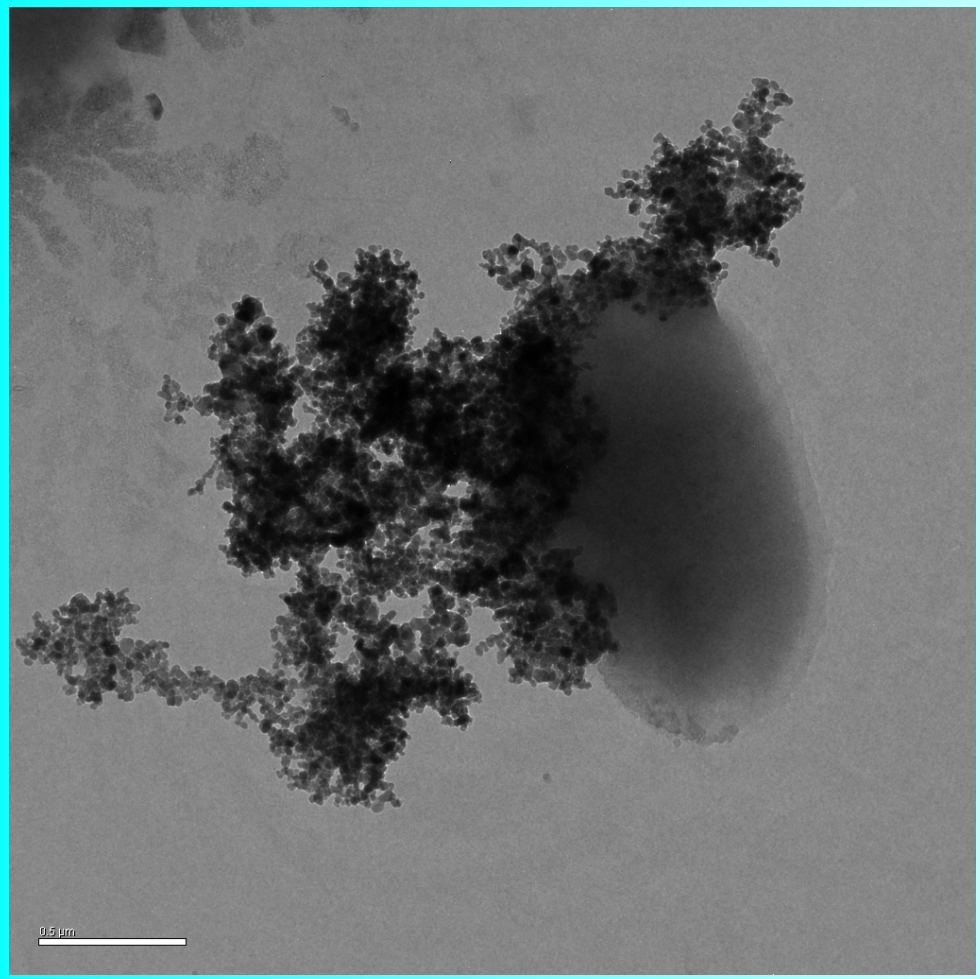


***E. coli* abatement : pH 8.5 ~ pH 6 ~ pH 4**

→ **Electrostatic attraction seems not to be a determinant factor with P25 ???**

→ **Direct observation with microscopic methods (optical, TEM, AFM)**

TEM



1. Determination of particles and clusters size up to the nanometer range (450'000x)

2. Interaction between P25 and *E. coli*

At pH 6:

TiO_2: $TiOH_2^+$ on surface (P25: IEP = 7)

300-400 nm

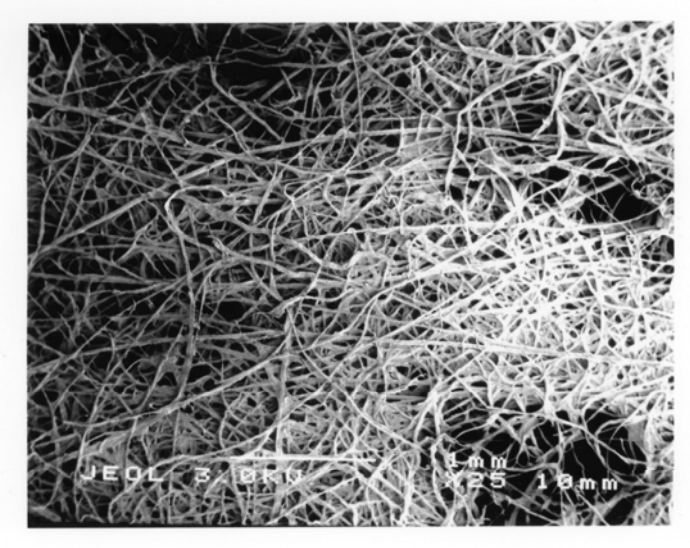
***E. coli*:** – charged (between pH 3 & 9) (carboxylic and phosphate groups)

~ 1 µm

→ **Partial contact**, a significant part of the TiO_2 particle remain in the solution outside the electrostatic field of *E. coli*

TiO_2 Supported

Ahlstrom paper **NW 10**



- SEM picture of NW10 (25x)

- Thin film reactor (5mm) with coated TiO_2

- Non-woven web (natural and synthetic fibers, 0.2 mm thick)
- TiO_2 P-25 and PC500 coated using an inorganic binder - **SiO_2 - IEP < 2**
- TiO_2 loading: 5.5, 10.0 and 13 g/m^2
- High photoactivity for phenolic compounds degradation with the same experimental conditions

(Gumy et al., *Sol. Energy*, 2005, in press)

Reactor - Suntest

- Continuously recirculated:
  Flow = 150 ml/min

- I = 140 [mW/cm^2] (~6% UV)

Volume **without** support:

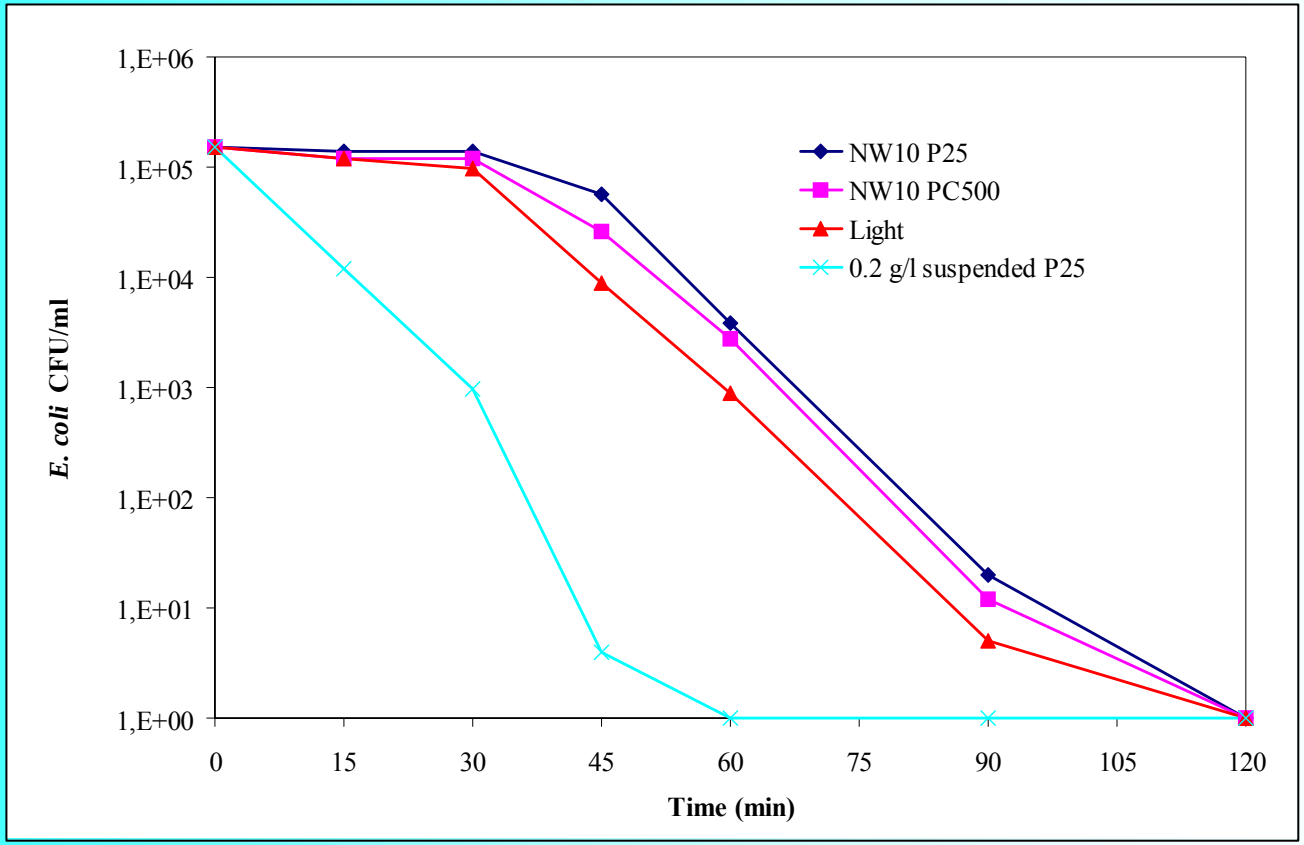
- V_{total} = 200 ml ; $V_{ill.}$ = 100 ml

Volume **with** support:

- V_{total} = 100 ml ; V_{ill} = 25 ml

- $Ø_{int.}$ = 40 mm ; $Ø_{support}$ = 30 mm

Paper NW10 – *E. coli*



Bacterial inactivation is not enhanced by fixed TiO_2 probably because there is not enough "contact" between bacteria and TiO_2

This could be due to the electrostatic repulsion between SiO_2-TiO_2 and the bacteria

Continuously recirculated reactor, V_{total} = 100 ml ; V_{ill} = 25 ml, S_{NW10} = 65 cm^2

Conclusion & perspective

- Correlation between IEP (therefore electrostatic attraction) and inactivation kinetics was observed
- No correlation between BET (and/or particle size) and inactivation kinetics was observed
- Mixed anatase/rutile P25 was the more active catalysts for bacterial inactivation
- TiO_2 coated on "paper" with silica binder do not enhanced the photoinactivation of *E. coli* (probably because of the presence of silica binder)
- Direct observation by microscopic technique to understand better the interaction between bacteria and TiO_2

Acknowledgments

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and You!