

Materiales para Fotocatálisis: TiO₂ con W(VI) superficial

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Objectives

The goal of this work is to help to answer several questions

Can we prepared photocatalysts tuned to degrade a specific contaminant?

Can we modify the adsorption properties of TiO_2 ?

Is it enough to improve the adsorption capacity of a photocatalyst to enhance its activity?

Strategy

As photocatalysts we used W-TiO₂

It is known that W(VI)-TiO₂ display photocatalytic activity.

W(VI) is acid and can change the point of zero charge (pzc) to lower values than pure TiO₂

As photolite we used Crystal Violet (CV)

CV is a cationic dye that can be adsorbed on negatively charge surfaces

Plan of work

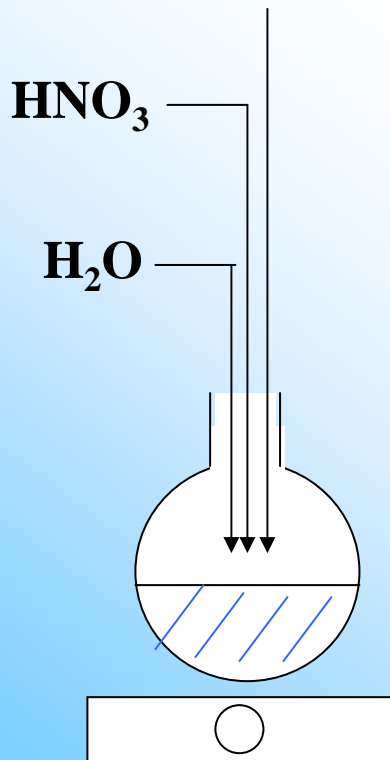
Catalysts, synthesis and characterization

Adsorption Isotherms (crystal violet)

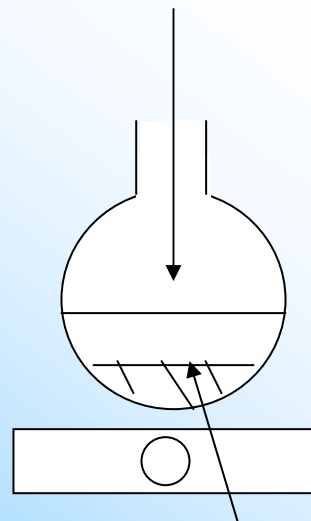
Photocatalytic degradation of Crystal Violet

Synthesis: Sol-gel process

$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\cdot 7\text{H}_2\text{O}$
(ammonium metatungstate)

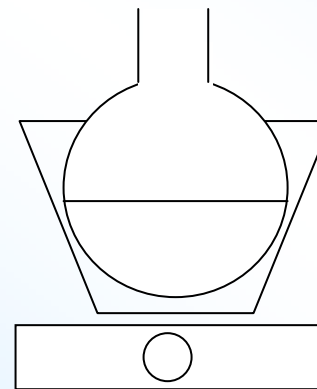


$\text{Ti}(\text{n-BuT})_4$
Titanium n-butoxide

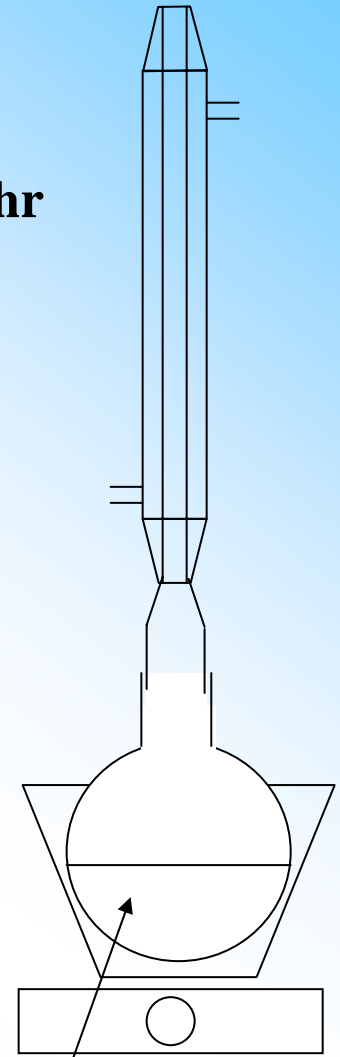


W-TiO₂ precipitate

80 °C, 1 hr



**80 °C, 3 hr
reflux**



W-TiO₂ sol

Catalysts preparation:

- 1) Dry the sols at 40 °C (xerogel)*
- 2) Grind the xerogels in an agate mortar*
- 3) Fire the powder at 500 °C or 700 °C (3 hr, 5°C/min)*
- 4) Grind the powder*
- 5) Sift the powder through a Pt mesh*

Characterization

X-Ray Diffraction (XRD)

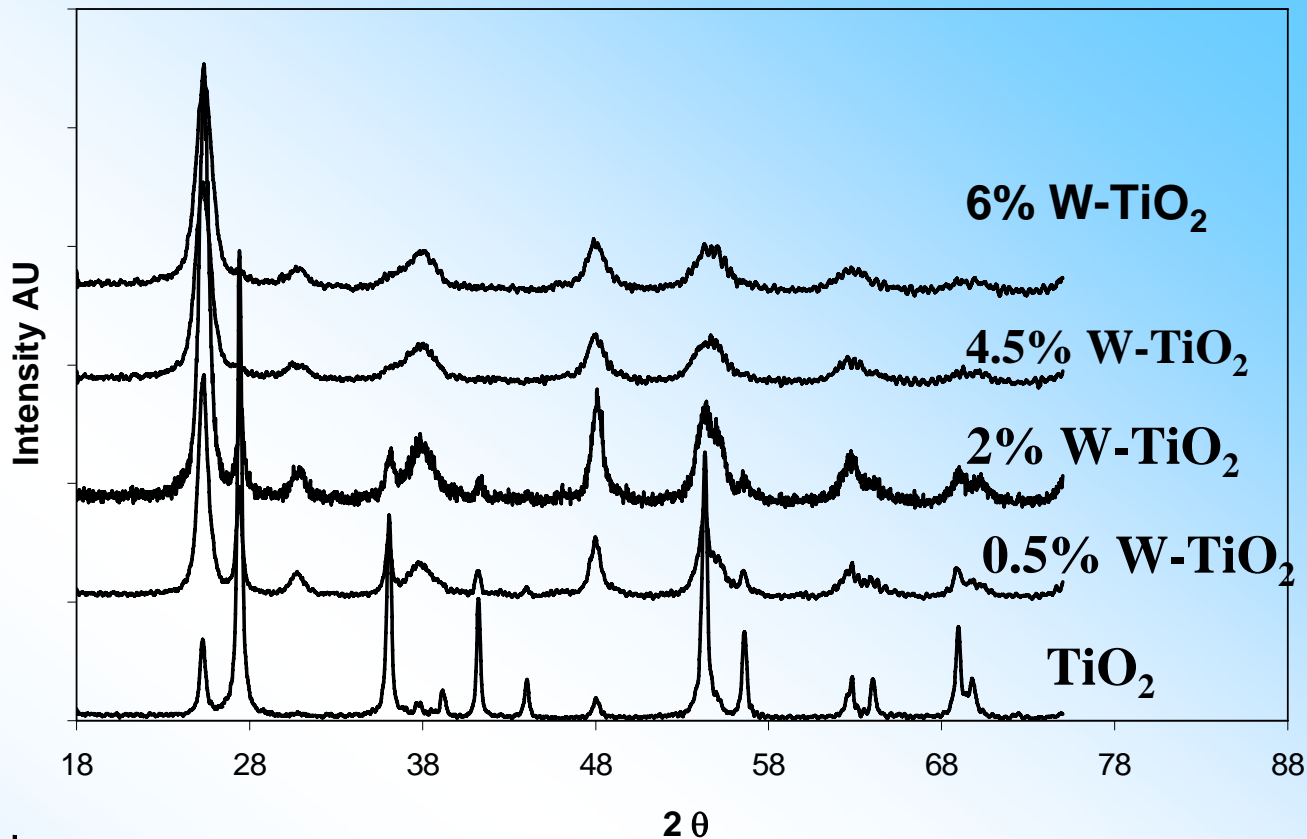
Electrophoretic mobility

Surface area (BET approach)

Scanning electron microscopy (SEM)

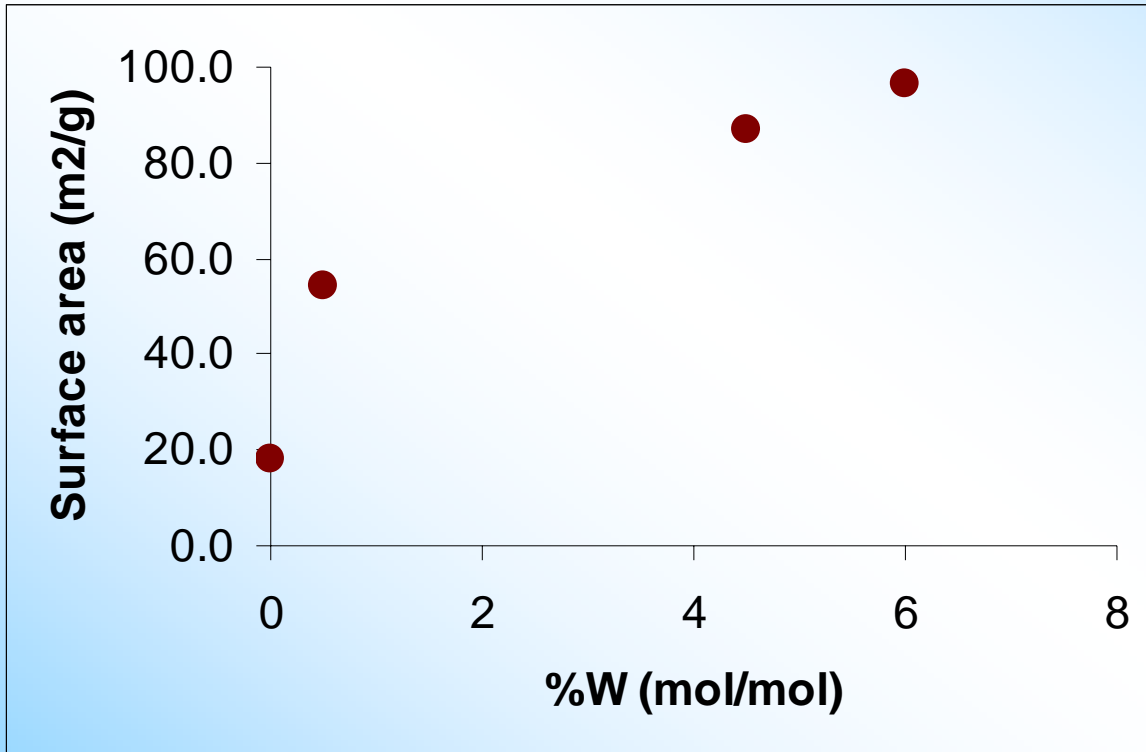
X Ray disperse energy analysis (EDX)

XRD



Sample	Anatase percentage	Crystalline domine (nm)
TiO_2	12	35
0.5% W- TiO_2	60	13
2% W- TiO_2	73	10
4.5% W- TiO_2	>90	8
6% W- TiO_2	100	<8

Surface area (BET)



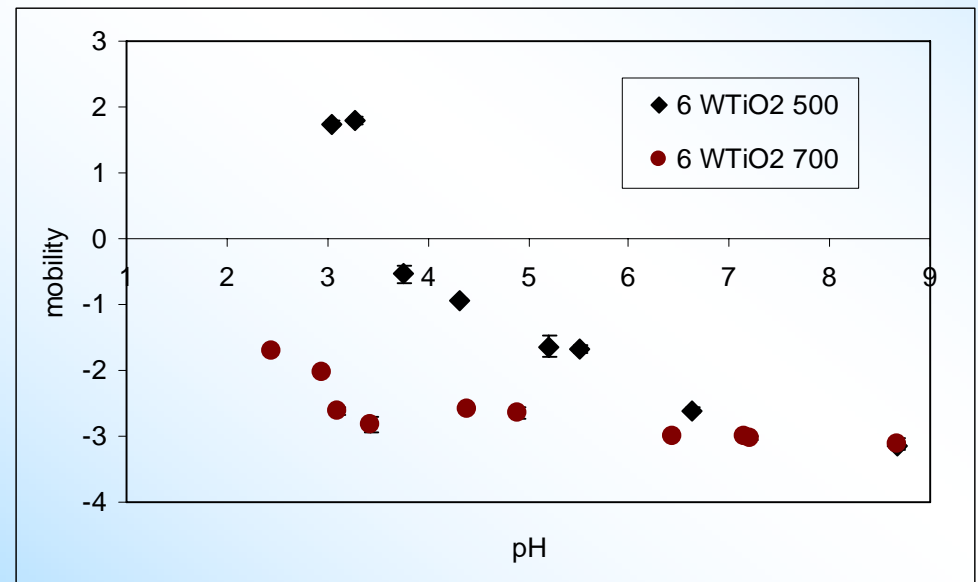
W (mol/mol) percentage	Firing Temperature (°C)	BET m ² /g
0	500	18,3
0.5	500	54,4
2	500	40,5
4.5	500	86,9
6	500	96,6
0	700	<10
6	700	40,5

Electrophoretic mobility

W percentage mol/mol	Firing Temperature (°C)	pzc
0.0	500	4.7
2.0	500	4.4
4.5	500	3.9
6.0	500	3.5
0.0	700	4.1
6.0	700	1.9

*Shift to lower pzc as the
content of tungsten
increases*

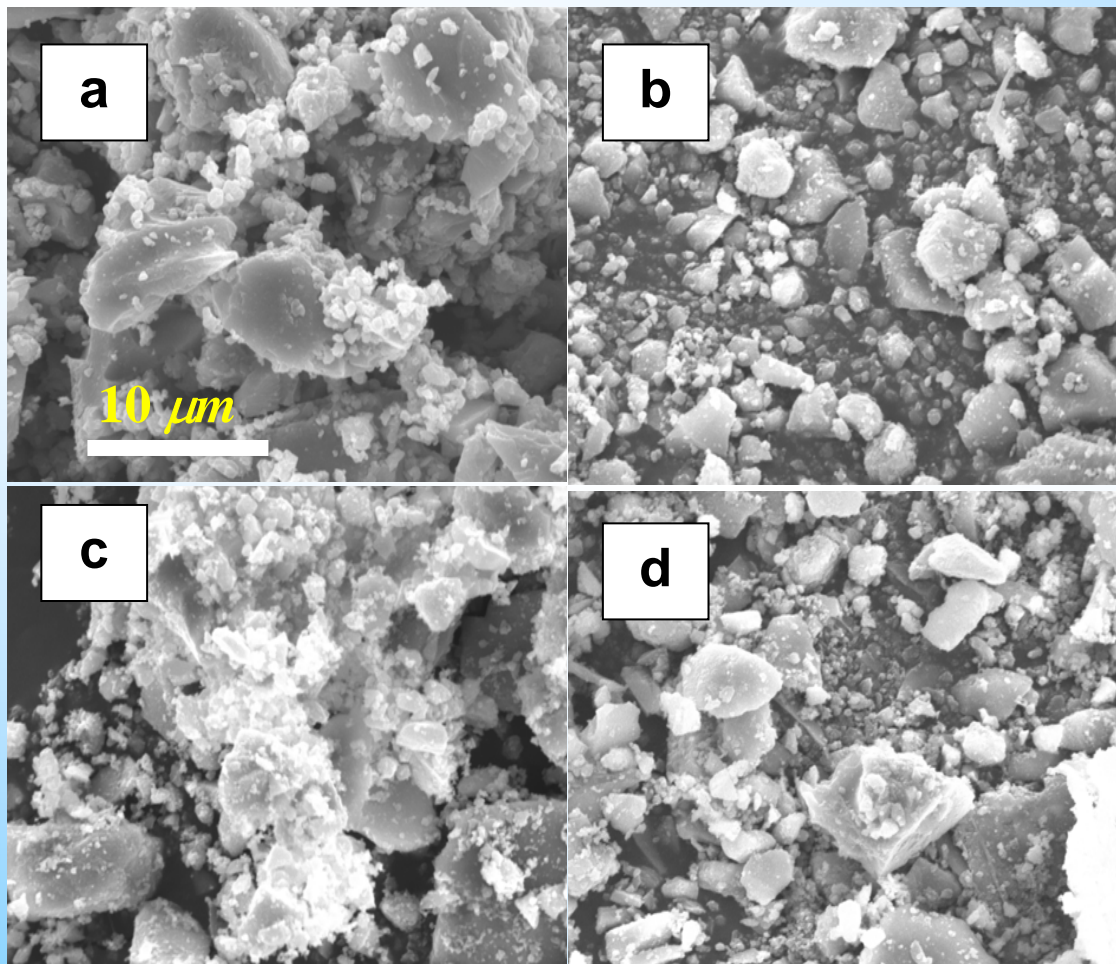
*Segregation of W to the surface
was shown by other authors
(Palmisano, Faraday Trans.,
1996; Alcober, J. Mat. Sci. Lett,
2002*



Scanning electron microscopy

a) 4.5 % W(VI) before photocatalysis; b) 4.5% W(VI) after photocatalysis

c) 2% W(VI) before photocatalysis; d) 2% W(VI) after photocatalysis



Particles de-aggregate after photocatalytic process

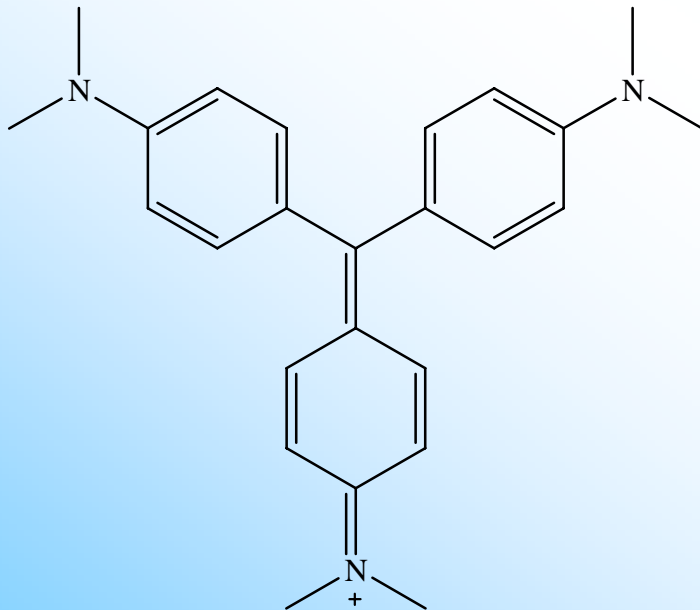
W/Ti ratio determined by EDX in W-TiO₂ samples before and after the photocatalytic treatment

	Nominal W(VI) %	W/Ti determined by EDX			
		before		after	
		Average	Std. Dev.	Average	Std. Dev.
pH: 4.5	2	2,5	0,2	3,14	0,3
	4,5	5,5	0,4	5,6	0,7
pH: 2.3	4,5	5,5	0,4	5,2	0,9
	6	7,1	0,5	7,2	0,5

Tungsten is not release to the solution

Adsorption Isotherms

Adsorbate: Crystal violet



Cationic dye

Stable in the pH range 3 - 10

Experiments:

Suspensions of 1g/L of catalysts were adjusted to the desire pH

Enough concentrate CV solution at the pH of work was added to the suspension to get the final desired total CV concentration

Systems were equilibrated in the dark for four hours

The catalyst was separated form the solution by centrifugation

The concentration of the supernatant solution was determined by UV-visible spectroscopy

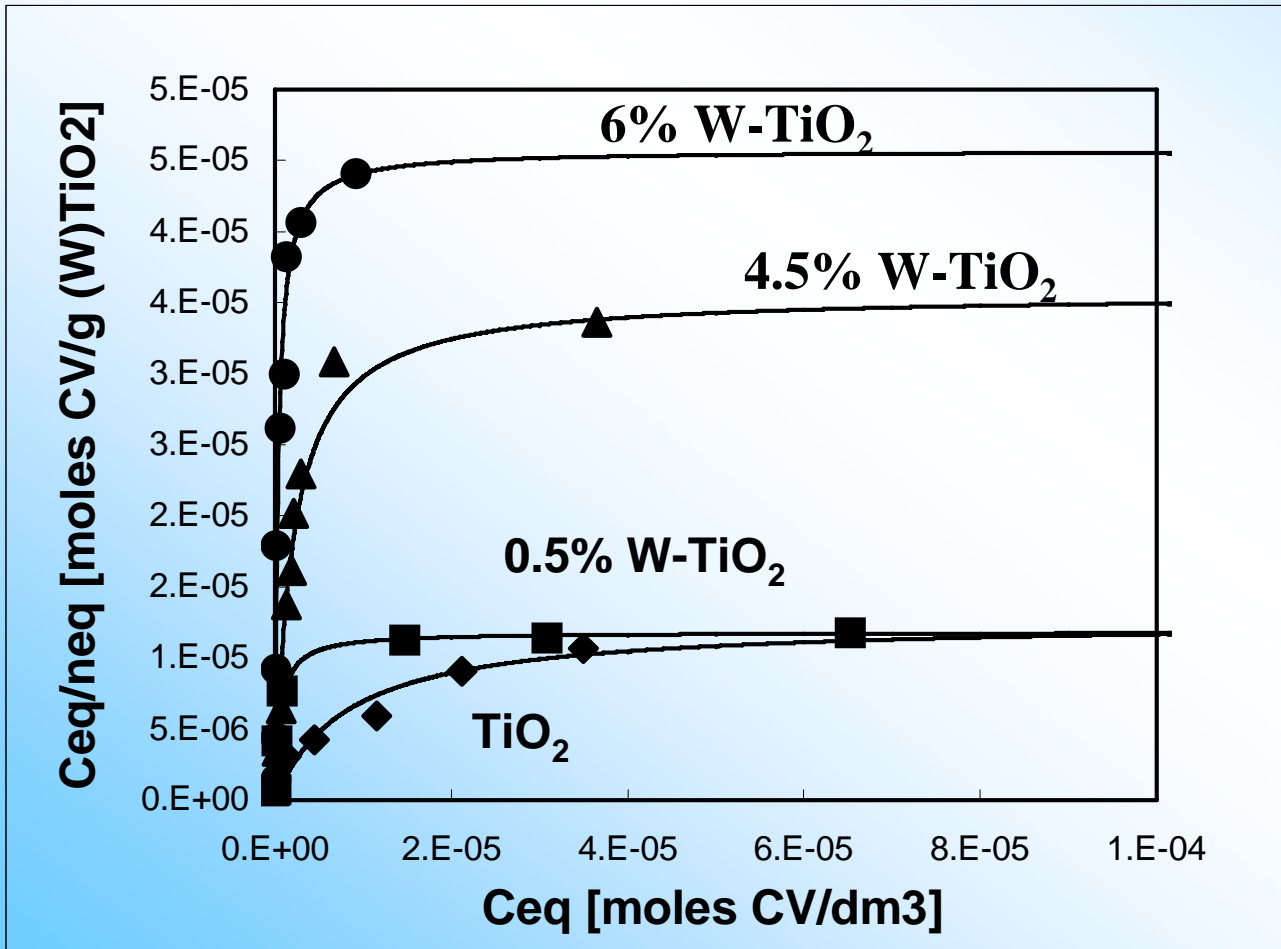
CV Adsorption Isotherms

Effect of W load

Firing temperature: 500 °C

pH: 4.5-5.2 (“natural pH”)

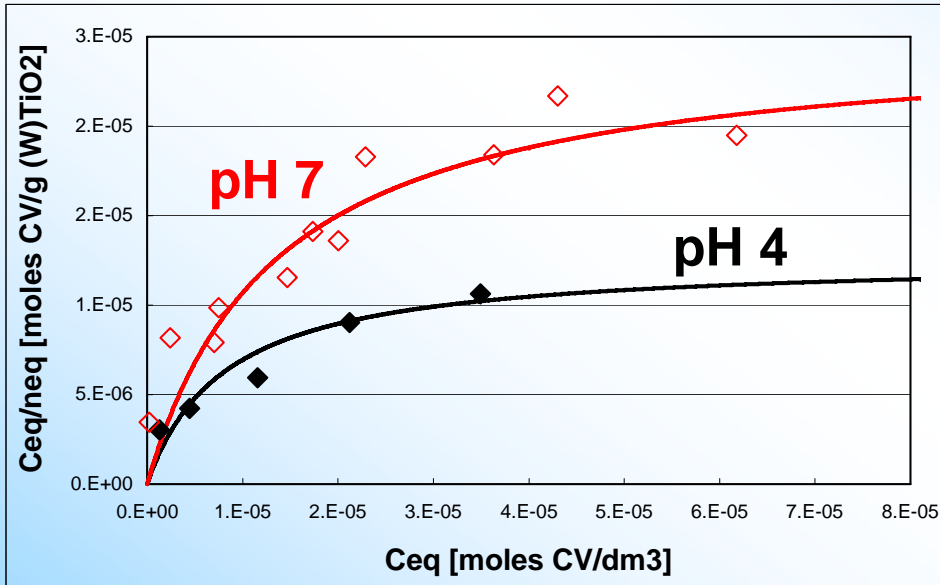
Measured in the dark



**Tungsten
enhance the
adsorption of
CV on the TiO₂
catalyst**

CV Adsorption Isotherms

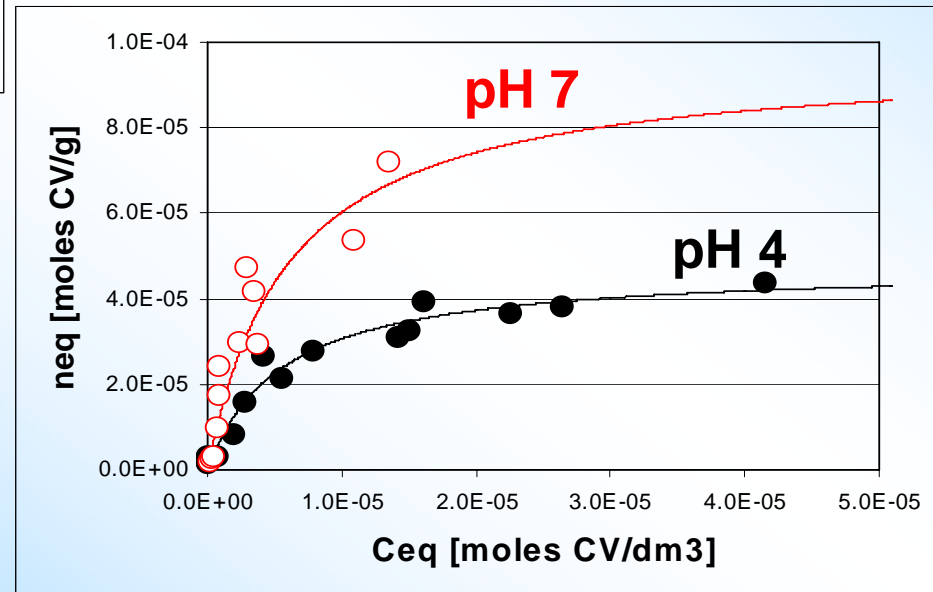
Effect of pH



TiO_2 Fired 500°C

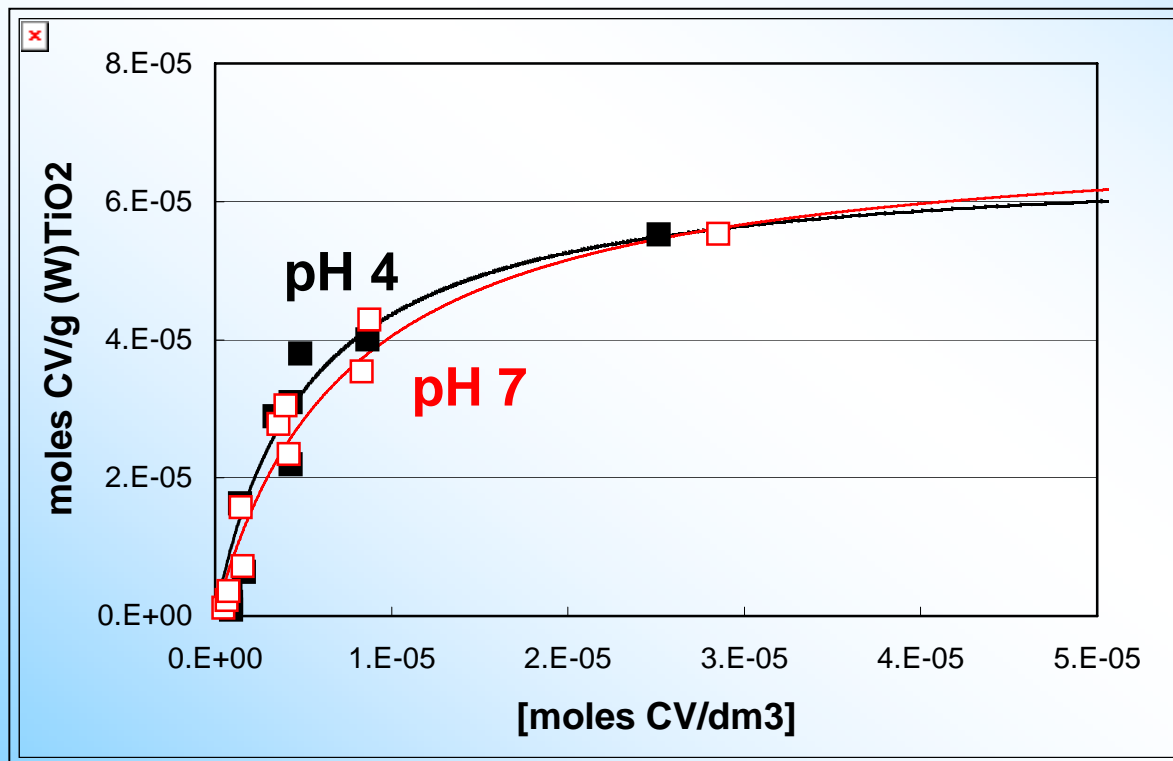
Increasing the pH enhance CV adsorption

6% W- TiO_2 Fired 500°C



CV Adsorption Isotherms

Effect of firing temperature



**Pzc of 6% W-TiO₂
700°C is so low
that adsorption
is similar at pH 4
and pH 7**

6% W-TiO₂

Firing temperature 700°C

Adsorption can be modeled by Langmuir equation

$$n_{eq} = \frac{n_s K C_{eq}}{(1 + K C_{eq})}$$

%W	T (°C)	pH4		pH 7		Surface area (g/m ²)
		n _s (mol/g)	K (dm ³ /mol)	n _s (mol/g)	K (dm ³ /mol)	
0	500	1.3 x 10 ⁻⁵	1.2 x 10 ⁵	2.5 x 10 ⁻⁵	7.4 x 10 ⁵	18,3
6.0	500	4.7 x 10 ⁻⁵	1.8 x 10 ⁵	9.6 x 10 ⁻⁵	1.7 x 10 ⁵	96,6
6.0	700	7.0 x 10 ⁻⁵	1.3 x 10 ⁵	6.7 x 10 ⁻⁵	1.9 x 10 ⁵	40,5

Conclusions of this part

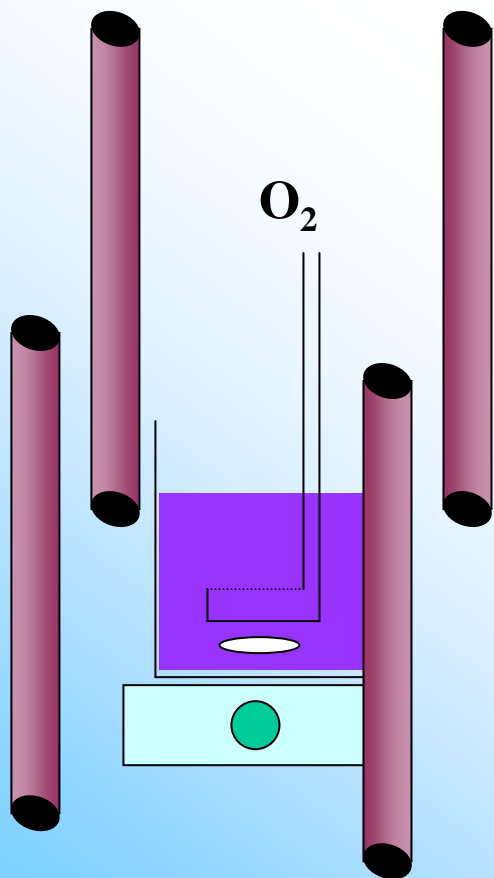
Tungsten enhance the adsorption of CV on the TiO₂ catalyst

Increasing the pH enhance CV adsorption

pzc and adsorption are related: the lowest the pzc the highest the adsorption at a given pH

Photocatalytic degradation of Crystal Violet

Experiments



1g/L catalyst

[CV] 38 ppm

pH adjusted to 4.0 or 7.0

O₂ bubbling

1 hr. pre-equilibrated in the dark

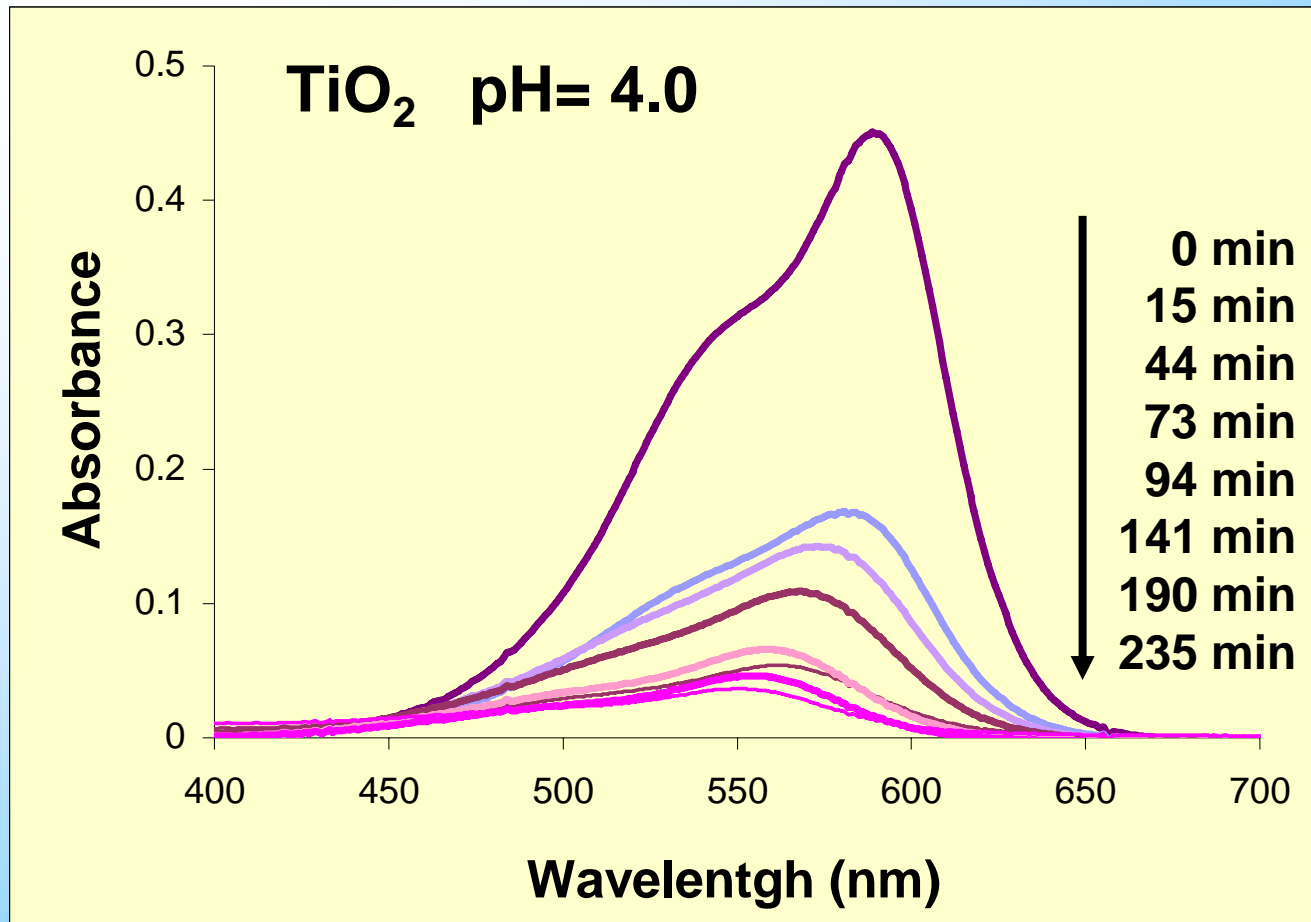
Temperature : 30 °C

Black light, 8W (total 2 mW/cm²)

**Catalyst was removed by
centrifugation**

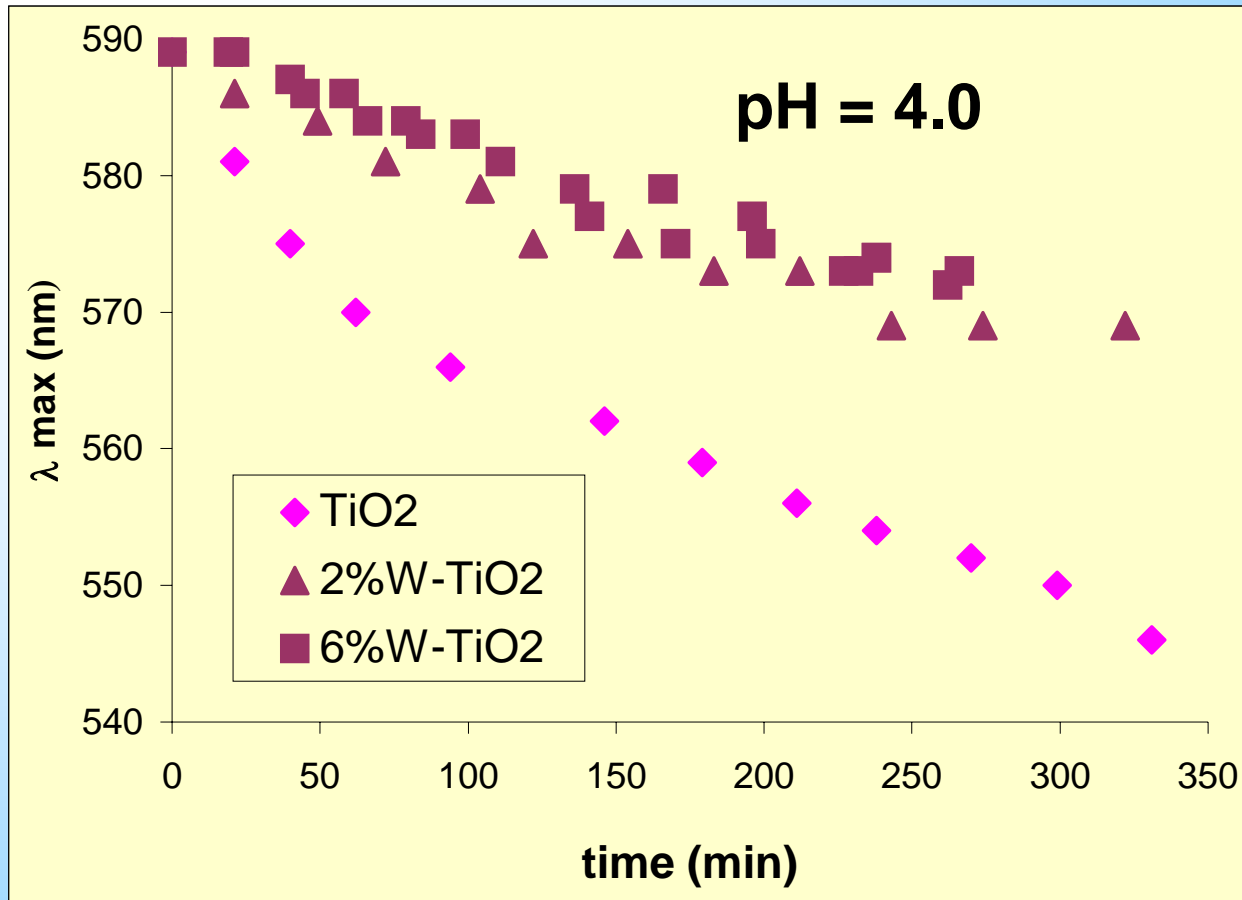
**[CV] determined by UV-visible
spectroscopy**

Effect of TiO₂-photocatalysis on the visible spectrum of CV



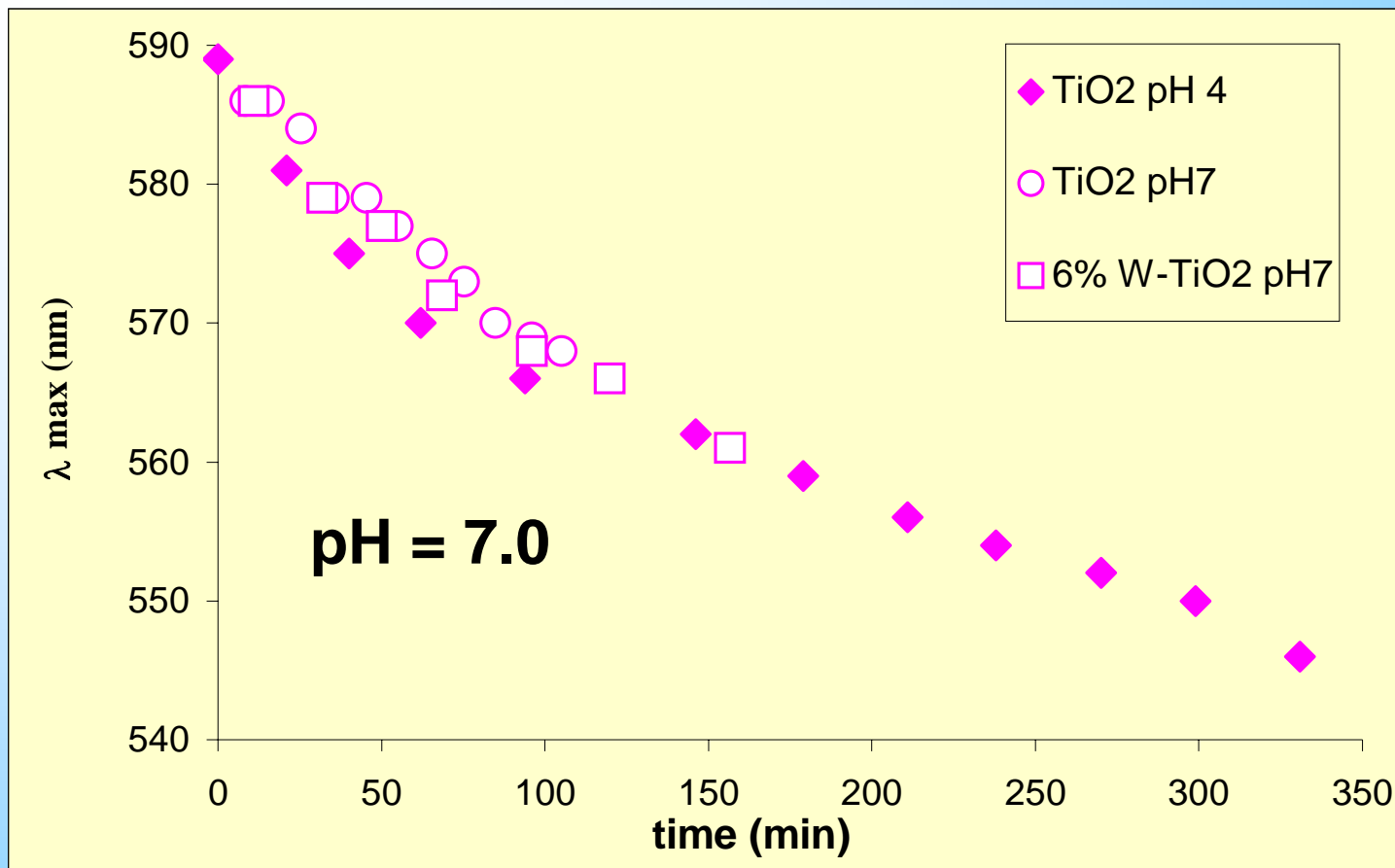
Hypsochromic shift to 540 nm

If TiO_2 is loaded with W(VI) , the effect is different



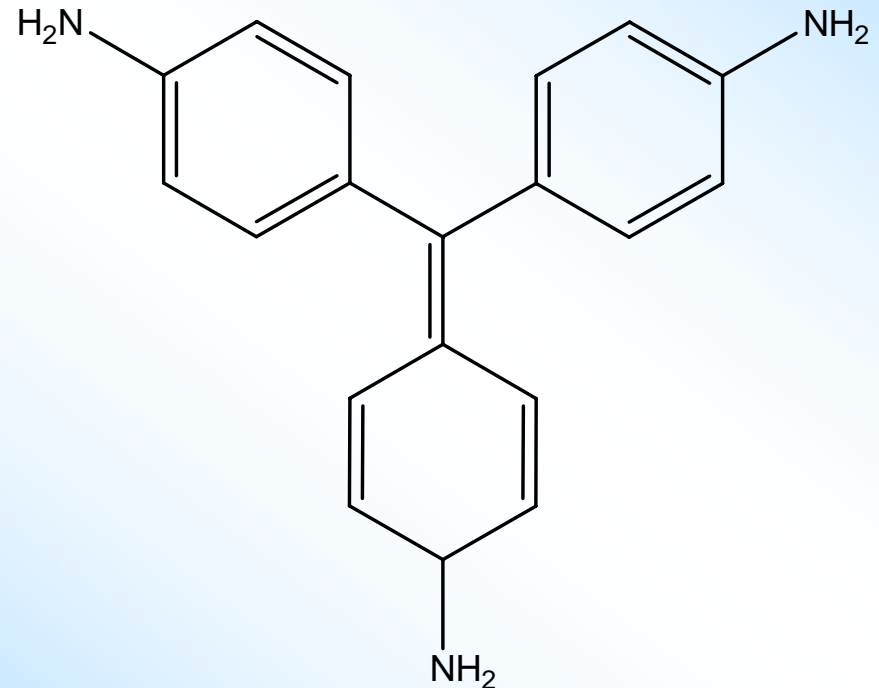
When W(VI) is present the shift to 540 nm is less important

At pH 7 the hypsochromic shift was noticeable in all the cases



The results indicate that s different mechanisms occurs when W(VI) is present in the TiO₂-catalyst at pH 4

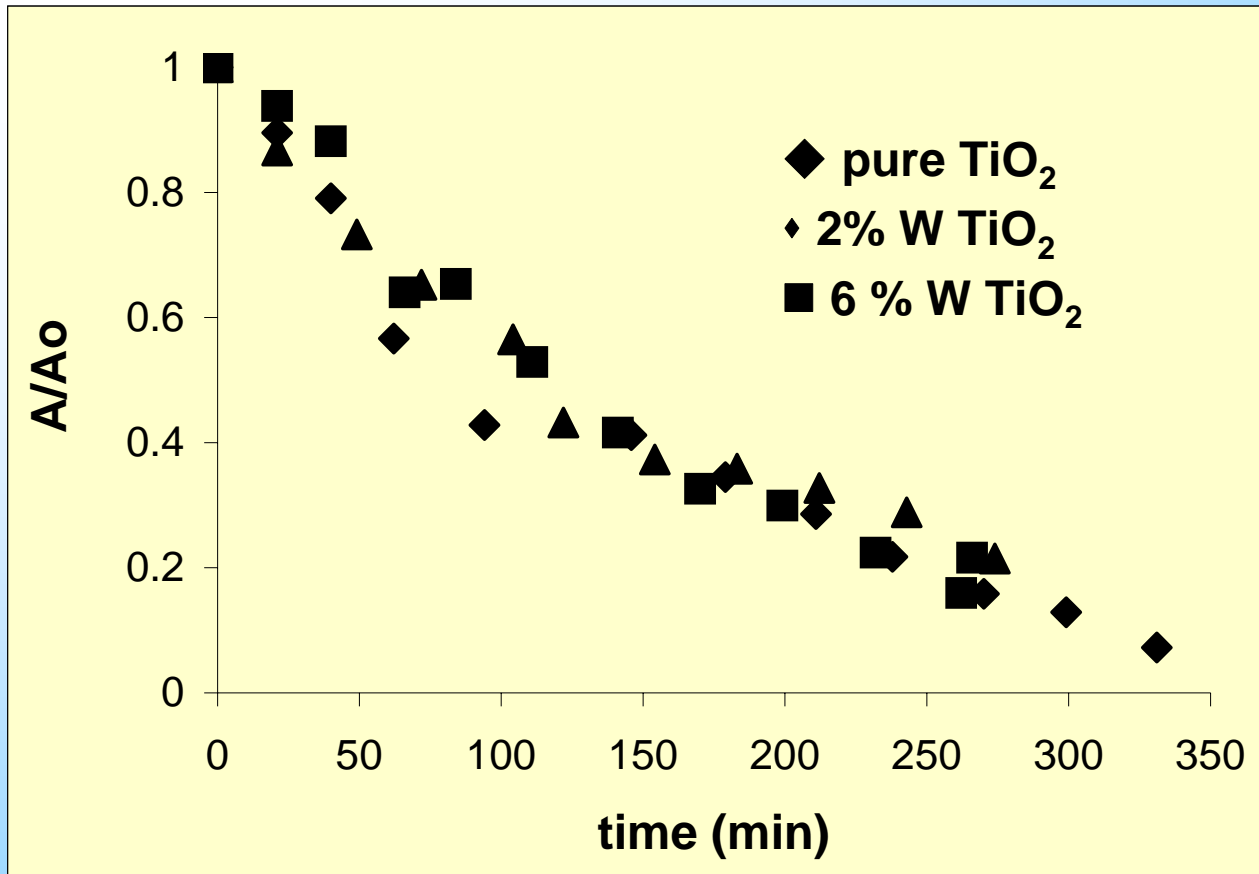
Zhao et al reported that in the degradation of CV by TiO₂ visible light fuchsin basic (*fucsina*) is produced as intermediate



Zhao, NJC, 23 (1999), 1193-96

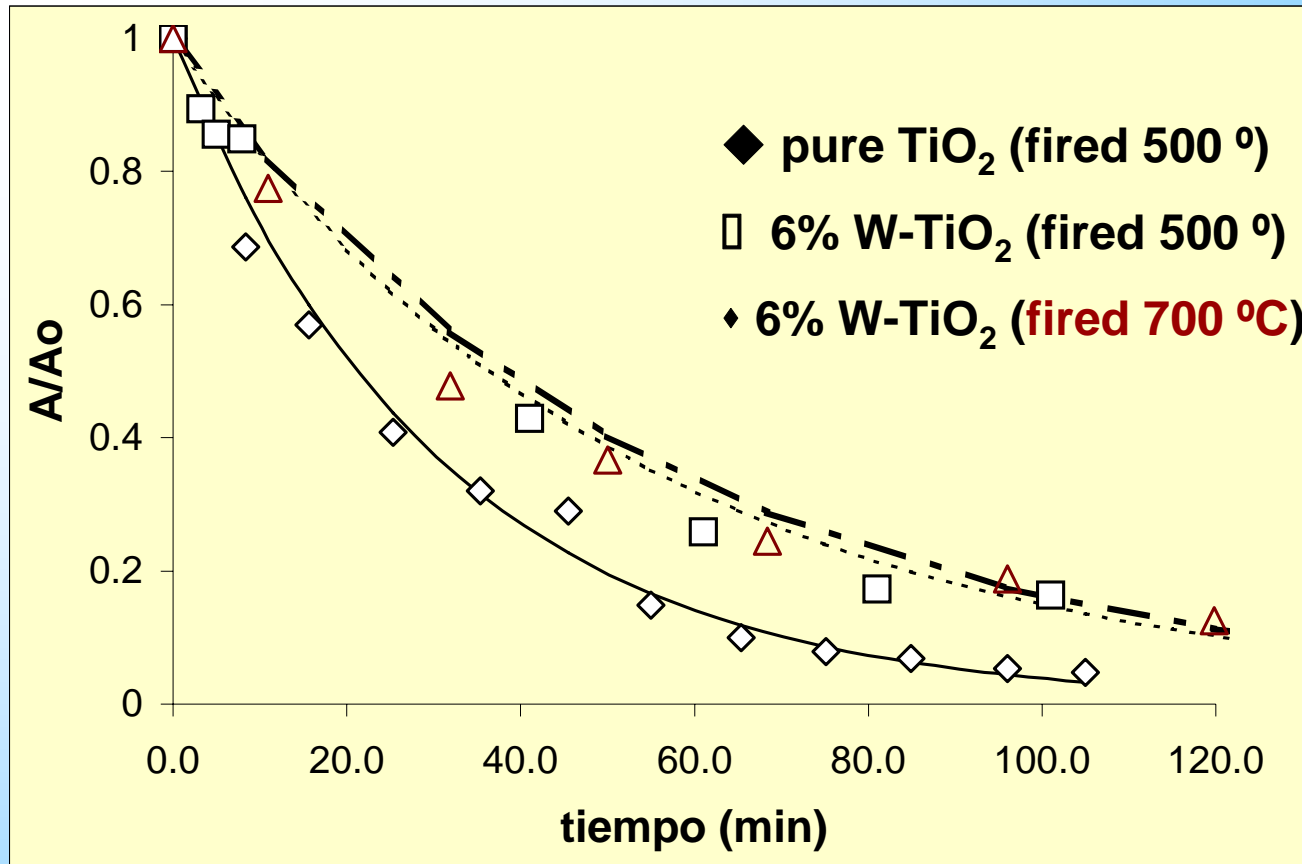
Effect of W(VI) load on CV degradation

Catalysts fired at 500 °C, pH 4



At pH = 4.0 the discoloration rate do not depends on W(VI) load

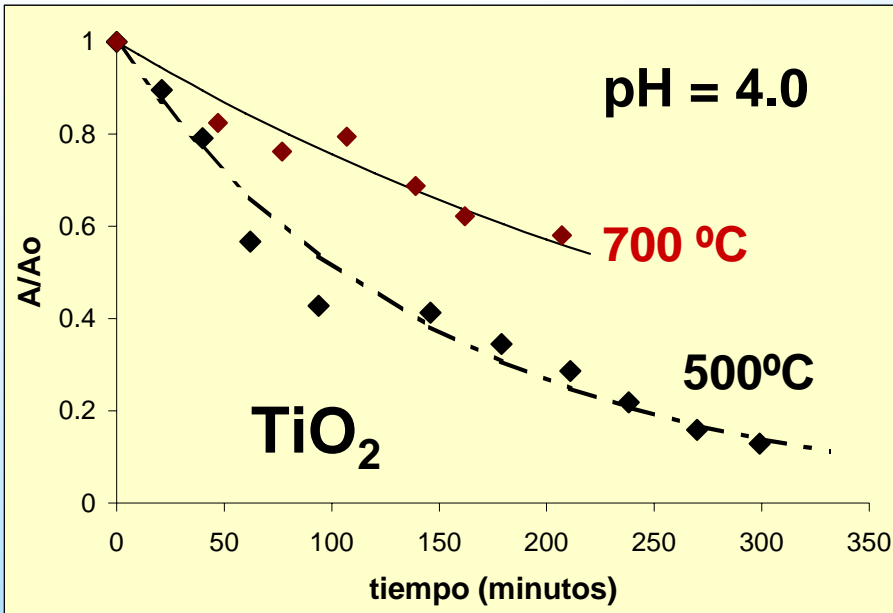
Catalysts fired at 500 °C, pH 7.0



Discoloration rate is much higher at pH 7.0 than 4.0

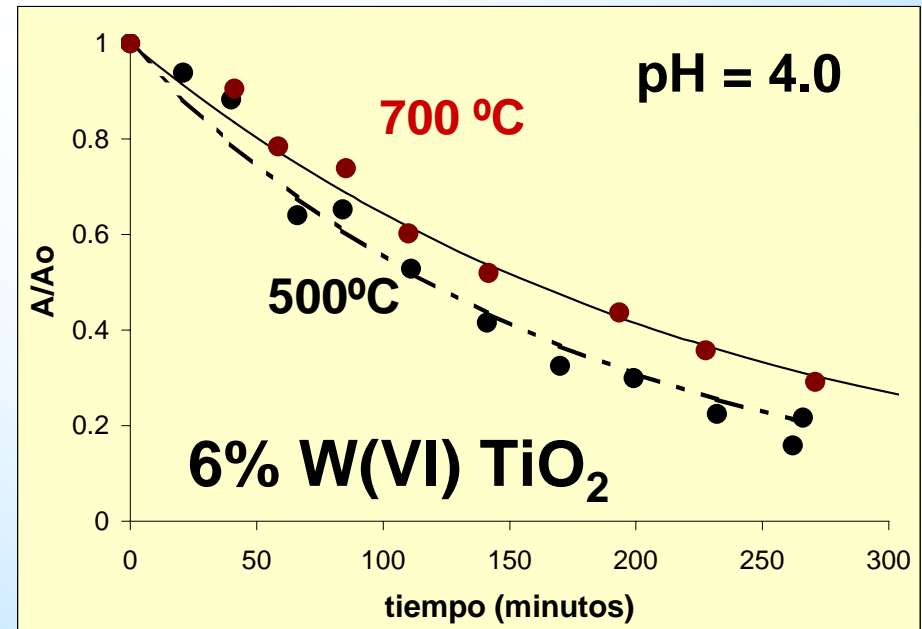
W(VI) reduce discoloration rate

Effect of firing temperature

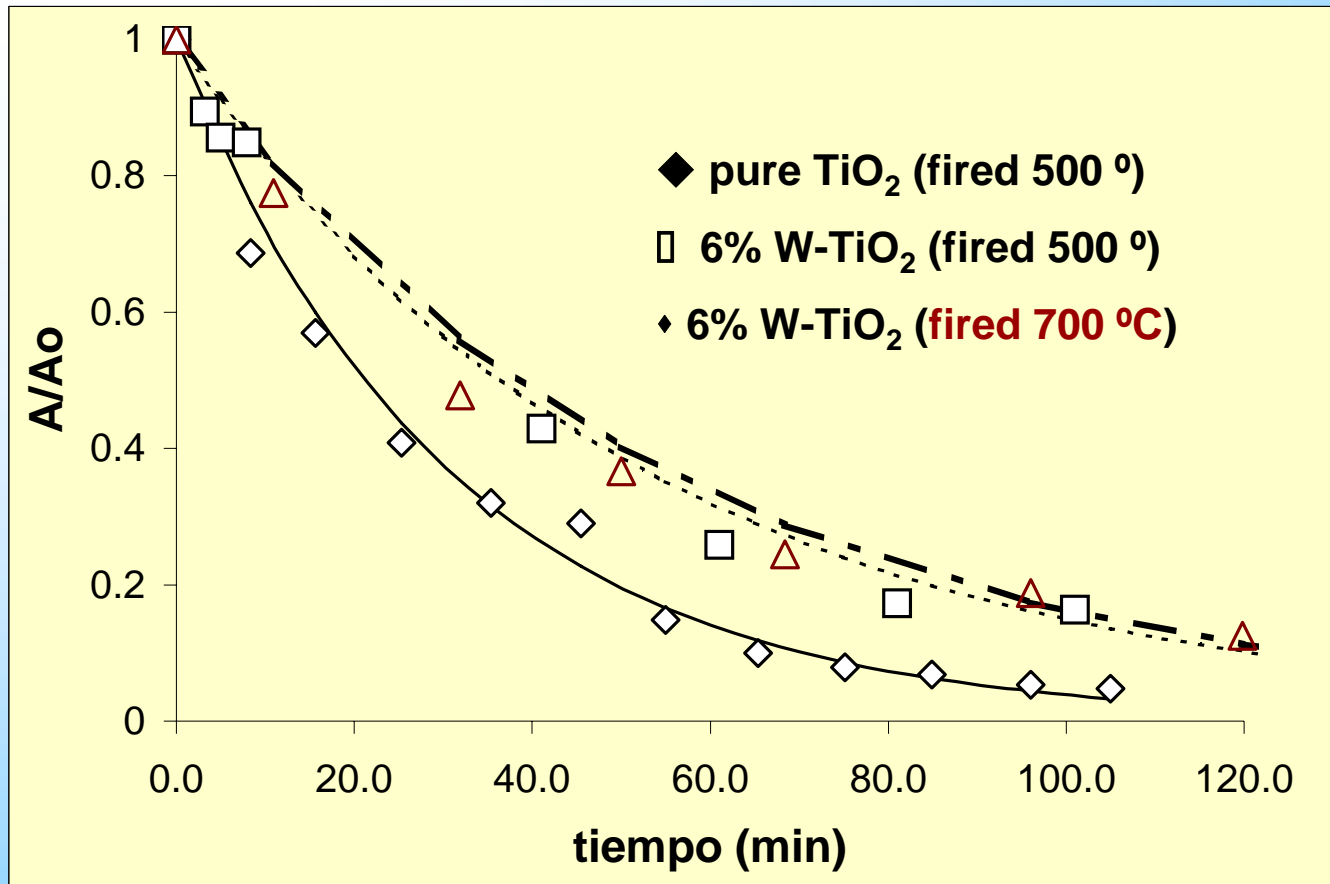


High firing temperatures reduce discoloration rate

Photocatalyst with W(V) show higher surface area



At pH 7.0 the discoloration rate is the same in photocatalysts fired at 700 °C, irrespective of fired temperature



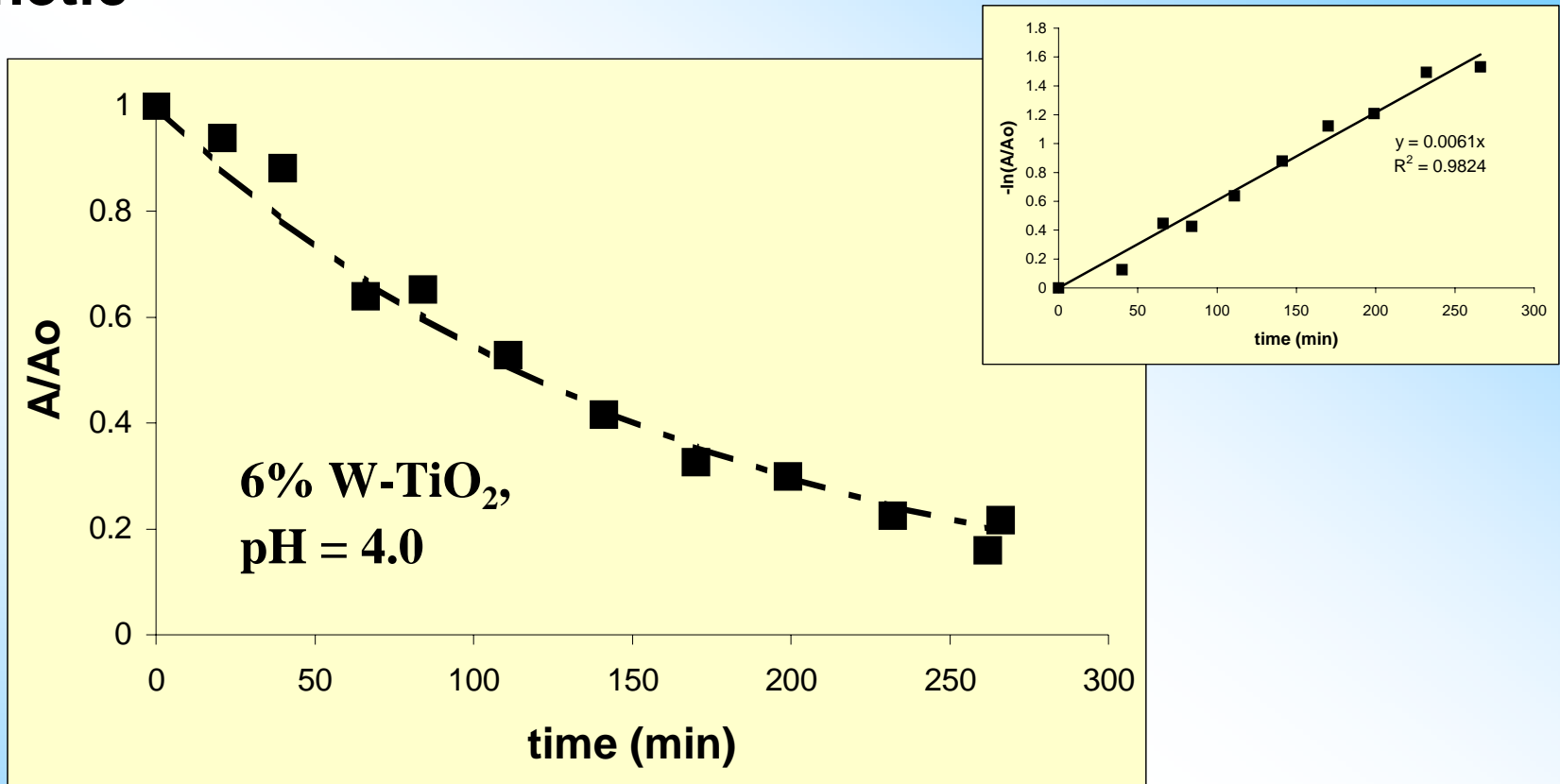
Discoloration rate at pH 4.0 do not depends on W(VI) load

At pH 7.0 the discoloration rate is higher than at pH 4.0 and is higher for pure TiO₂

Higher firing temperatures reduce photocatalytic activity

At pH 7.0 firing temperature do not have appreciable effect on photocatalytic activity of W(VI) load TiO₂

In all the cases discoloration follows a first order kinetic



$$\frac{dC}{dt} = \frac{k_r KC}{1 + KC}$$

$$KC \ll 1$$

$$\ln\left(\frac{C_0}{C}\right) = k_r KC$$

The Langmuir-Hinshelwood model helps to rationalize the degradation kinetics

$$- \frac{dC}{dt} = \frac{k_r KC}{1 + KC}$$

In our case the C_{eq} is lower than the absorption saturation concentration

$$KC < 1$$

$$k_{obs} = k_r K$$

Langmuir Hinshelwood applied even though the system is not in adsorption equilibrium during the photocatalytic process

In steady states conditions a L-H type rate law can be obtained for mechanisms that involve intermediates or oxidation for OH radicals

Kinetics and dark adsorption parameters

%W mol/mol	Firing Temperature (°C)	k_{obs} (1/min)		K (dark) dm^3/mol		n_s mol/g	
		pH 4.0	pH 7.0	pH 4.0	pH 7.0	pH 4.0	pH 7.0
0	500	0.0066	0.033	1.2×10^5	7.4×10^5	1.3×10^{-5}	2.5×10^{-5}
0	700	0.0028					
2	500	0.0054					
6	500	0.0061	0.019	1.8×10^5	1.7×10^5	4.7×10^{-5}	9.6×10^{-5}
6	700	0.0044	0.018	1.3×10^5	1.9×10^5	$7. \times 10^{-5}0$	6.7×10^{-5}

For 6% W-TiO₂ fired at 700°C K and n_s are similar at pH 4.0 and 7.0 but k_{obs} is much lower at pH 4.0

The effect of pH on degradation is not only related to electrostatic adsorption

How to compare the behavior of the different photocatalysts?

Intrinsic degradation rate: $v^* = (k_{obs} \times n_s)/A_s$ (mol/min m²)

is the degradation rate obtained if:

i) the surface is saturated with CV

ii) n_s/A_s is considered as a surface concentration

iii) the reaction is first order relative to the surface concentration

It works like an operational parameter that help to compare the different catalysts

Intrinsic degradation rate

%W mol/mol	Firing Temperature (°C)	k_{obs} (1/min)		v^* (mol/min m ²)		v^* (pH 7)/ v^* (pH 4)
		pH 4.0	pH 7.0	pH 4.0	pH 7.0	
0	500	0.0066	0.0326	4.54x10 ⁻⁹	4.49x10 ⁻⁸	9.9
6	500	0.0061	0.0190	3.00x10 ⁻⁹	1.90x10 ⁻⁸	6.3
6	700	0.0044	0.0182	7.70x10 ⁻⁹	2.97x10 ⁻⁸	3.8

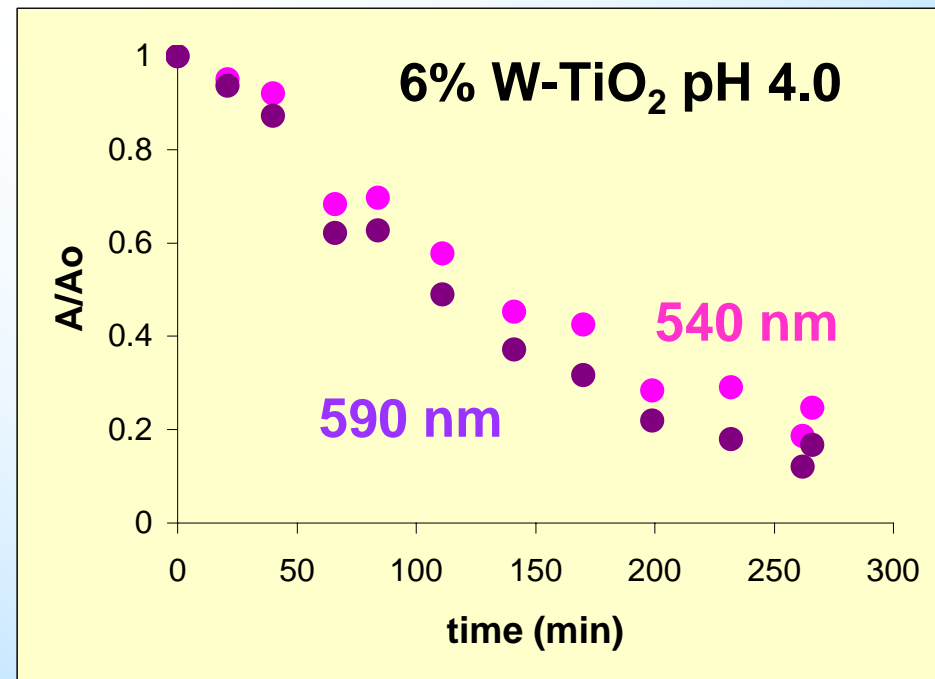
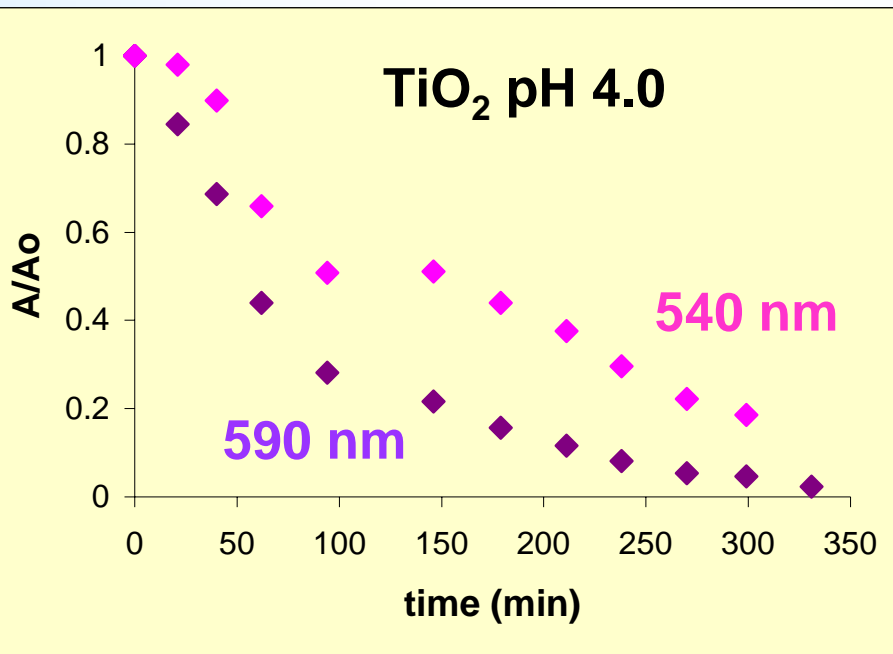
At pH 4.0 6% W-TiO₂ (700 °C) displays the highest efficiency. This is because its low pzc at pH 4.0

TiO₂ displays the higher efficiency is spite that adsorb less CV than W-TiO₂. Adsorption is not the only important condition

6% W-TiO₂ (700 °C) activity is less sensitive to changes in pH

How can be explained the effect of pH and W(VI) on degradation rate?

The reaction mechanism depends on pH and the presence of tungsten on the TiO₂-photocatalyst surface



Fuchsim is produce by *N-demethylation* of CV (Zhao et al, 1999)

The propose mechanism in visible light photocatalysis is by OH[•] attack to adsorbed CV

In our case this mechanism can be responsible for the enhancement of degradation rate as pH increases

Tungsten on TiO₂ leads the reaction for different steps (*may be direct hole injection to adsorbe CV?*)

Conclusions

Incorporation of W(VI) to TiO₂ hinder crystal growth and enhance anatase thermal stability. The pzc shift to lower pH values

Adsorption of CV increases with the amount of tungsten and with solution pH

Photocatalytic degradation of CV can be accomplished on pure and W(VI) doped TiO₂ with a pseudo-first order rate law

Higher amounts of surface tungsten lead to higher *intrinsic degradation rates*, but not to higher observed rate constants

At high pH the mechanism involve an step with production of fuchsim. Probably by OH[•] N-demethylation of CV

Tungsten improve the adsorption of CV on TiO₂, but do not improve the degradation rate. The mechanism change at pH 4.0 when tungsten is present. Important for photocatalytic synthesis

Acknowledgements

Solar Safe Water Symposium Organizers

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