I NOVANT'ANNI DEL PROF. BELLOBONO

Ultra Purificazione dell'aria, sia da micro inquinanti chimici che microbiologici, ed implementazione di sistemi ultra efficienti di condizionamento, mediante reattori a membrana fotocatalitica

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Indice

INTRODUZIONE

Contesto

Questo progetto (finanziato dalla Fondazione di Comunità Milano–Fondo Solidale Ignazio Renato Bellobono) si colloca all'interno del mio percorso di dottorato ed è durato da ottobre 2020 fino a settembre 2021.

L'obiettivo è studiare dei sistemi fotocatalitici da attivare tramite lampade per la purificazione dell'aria.

Ci siamo concentrati sull'abbattimento dei composti organici volatili. Composto target: propano (C_3H_8).

I risultati ottenuti sono stati pubblicati negli articoli

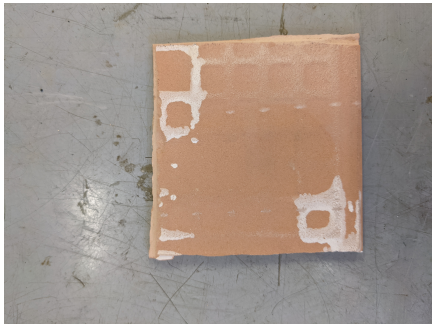
- Piferi, C., Brescia, A., Riccardi, C., 2021. Intensity comparison between UV lamps and plasma emission for air purification studies. AIP Advances 11, 085209.
- Piferi, C., Riccardi, C., 2021. High concentration propane depletion with photocatalysis. AIP Advances 11, 125008.

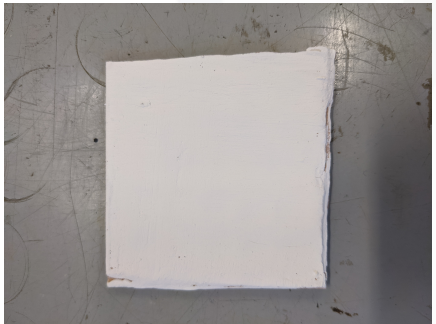
Catalizzatori

I catalizzatori che abbiamo utilizzato sono miscele di TiO_2 e WO_3 come cofotocatalizzatori immobilizzati secondo grafting chimico (brevetto italiano) su $CaCO_3$.

Il processo di deposizione utilizzato prevede la stesura del catalizzatore su un supporto rigido utilizzando un pennello; l'evaporazione della maggior parte dell'acqua all'aria, a temperatura ambiente, in un contenitore parzialmente chiuso per circa 2 ore introducendo ogni 10 minuti della CO_2 nel contenitore; e l'asciugatura a 55°C per circa tre ore.

Come supporto per la deposizione abbiamo scelto la parte porosa di una piastrella in ceramica di circa 7.5x7.5 cm^2. Abbiamo depositato circa 35 mg/cm^2 di fotocatalizzatore.





- **A**: 100% TiO_2
- **B**: 50% TiO_2 50% WO_3
- **C**: 100% WO_3

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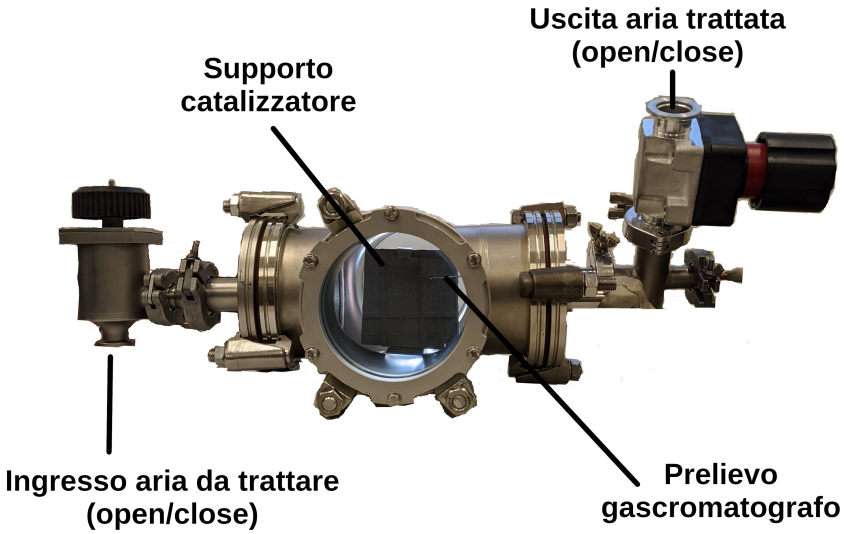
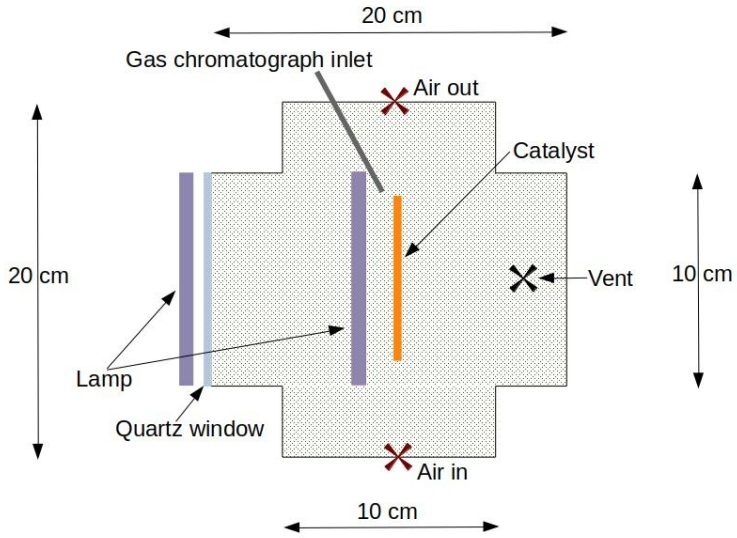
Lampade

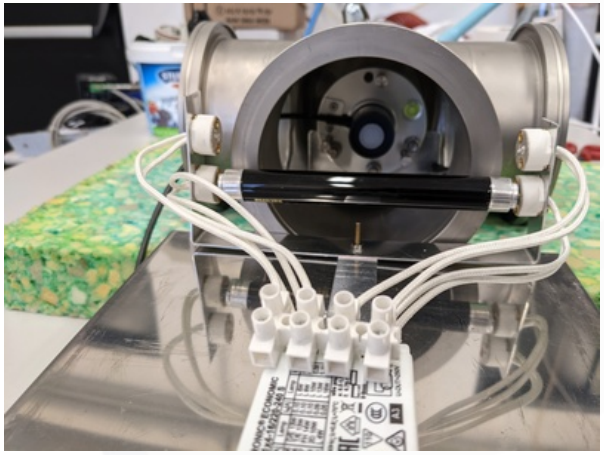
Come sorgenti luminose abbiamo utilizzato delle lampade da 4 W con diversi spettri

- UV-C: lampada UV Lawtronics con picco a 253.7 nm;
- UV-A: lampada UV Philips Lighting con picco a 370 nm;
- Visibile: led GLS Osram bianco freddo da 4000 K.

Reattore







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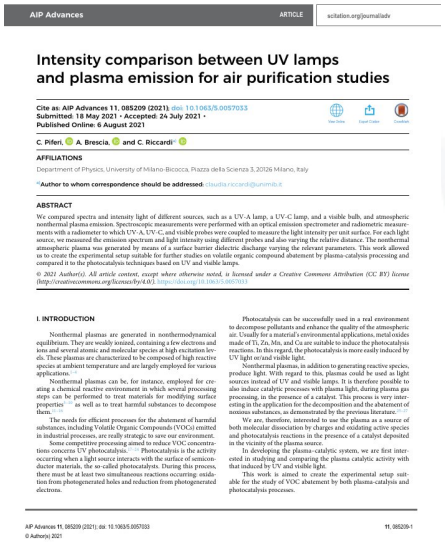
Piferi, C., Brescia, A., Riccardi, C., 2021. Intensity comparison between UV lamps and plasma emission for air purification studies. AIP Advances 11, 085209.



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Intensity comparison between UV lamps and plasma emission for air purification studies

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ABSTRACT

We compared spectra and intensity light of different sources, such as a UV-A lamp, a UV-C lamp, and a visible bulb, and atmospheric nonthermal plasma emission. Spectroscopic measurements were performed with an optical emission spectrometer and radiometric measurements with a radiometer to which UV-A, UV-C, and visible probes were coupled to measure the light intensity per unit surface. For each light source, we measured the emission spectrum and light intensity using different probes and also varying the relative distance. The nonthermal atmospheric plasma was generated by means of a surface barrier dielectric discharge varying the relevant parameters. This work allowed us to create the experimental setup suitable for further studies on volatile organic compound abatement by plasma-catalysis processing and compared it to the photocatalysis techniques based on UV and visible lamps.

I. INTRODUCTION

Nonthermal plasmas are generated in nonthermodynamical equilibrium. They are weakly ionized, containing a few electrons and ions and several atomic and molecular species at high excitation levels. These plasmas are characterized to be composed of high reactive species at ambient temperature and are largely employed for various applications.[1,2]

Nonthermal plasmas can be, for instance, employed for creating a chemical reactive environment in which several processing steps can be performed to treat materials for modifying surface properties[3,4] as well as to treat harmful substances to decompose them.[5,6]

The needs for efficient processes for the abatement of harmful substances, including Volatile Organic Compounds (VOCs) emitted in industrial processes, are really strategic to save our environment.

Some competitive processing aimed to reduce VOC concentrations concerns UV photocatalysis.[7–10] Photocatalysis is the activity occurring when a light source interacts with the surface of semiconductor materials, the so-called photocatalysts. During this process, there must be at least two simultaneous reactions occurring: oxidation from photogenerated holes and reduction from photogenerated electrons.

Photocatalysis can be successfully used in a real environment to decompose pollutants and enhance the quality of the atmospheric air. Usually for a material's environmental applications, metal oxides made of Ti, Zn, Mn, and Cu are suitable to induce the photocatalysis reactions. In this regard, the photocatalysis is more easily induced by UV light or/and visible light.

Nonthermal plasmas, in addition to generating reactive species, produce light. With regard to this, plasmas could be used as light sources instead of UV and visible lamps. It is therefore possible to also induce catalytic processes with plasma light, during plasma gas processing, in the presence of a catalyst. This process is very interesting in the application for the decomposition and the abatement of noxious substances, as demonstrated by the previous literature.[11–13]

We are, therefore, interested to use the plasma as a source of both molecular dissociation by charges and oxidating active species and photocatalysis reactions in the presence of a catalyst deposited in the vicinity of the plasma source.

In developing the plasma-catalytic system, we are first interested in studying and comparing the plasma catalytic activity with that induced by UV and visible light.

This work is aimed to create the experimental setup suitable for the study of VOC abatement by both plasma-catalysis and photocatalysis processes.

CARATTERIZZAZIONE LAMPADE

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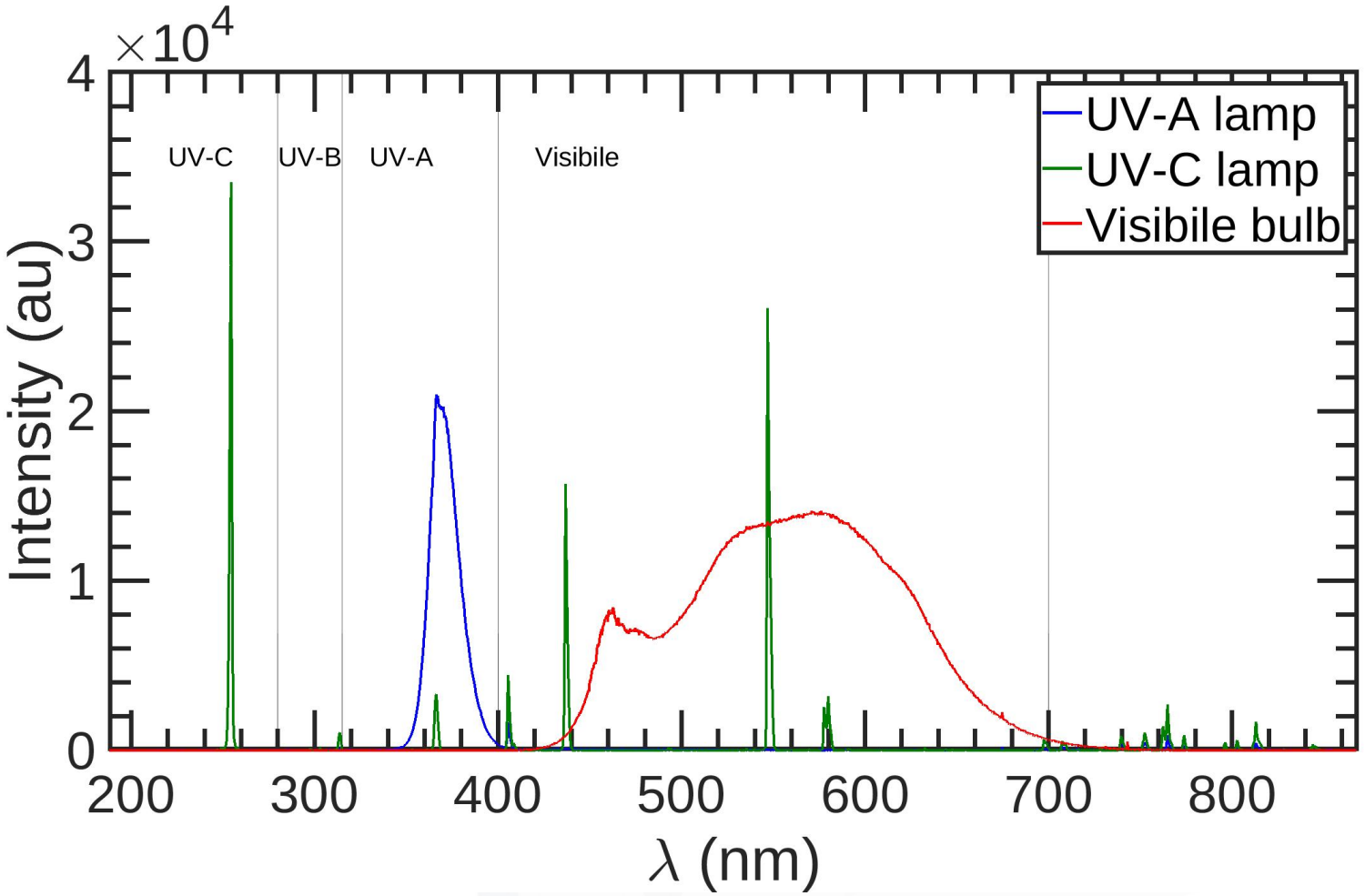
Spettro di emissione



Emissione delle lampade e trasmissione attraverso il quarzo

Source \ Probe	UV-C	UV-A	Visible	Transmission factor
UV-C lamp	1	0.02	0.14	55%
UV-A lamp	0	1	0.08	80%
Visible bulb	0	0	1	80%

Piferi, C., Riccardi, C., 2021. High concentration propane depletion with photocatalysis. AIP Advances 11, 125008.

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High concentration propane depletion with photocatalysis

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ABSTRACT

Our work is aimed at studying the abatement of volatile organic compounds produced by photocatalysts working in different light spectra, investigating the best catalyst able to treat propane in air mixtures at high concentrations of the order of thousands of ppm. The experimental data were analyzed in order to extract the relevant parameters and to compare the catalytic activities of these different photocatalysts, TiO_2, WO_3, and their mixtures. In a reactor box of 1.5 L photocatalysis processing with TiO_2 catalysts gave the best propane depletion of the order of 10% for initial propane concentrations of up to 5000 ppm after 22 min and UV-A lamps with an intensity of 0.4 mW/cm^2 while the TiO_2 and WO_3 catalysts produced an abatement of about 5% after 22 min using UV-C light at an intensity of 5×10^3 mW/cm^2.

I. INTRODUCTION

Several methods have been proposed for depletion of VOCs, including adsorption,[1] absorption,[2] thermal decomposition,[3] catalytic oxidation,[4] bio-filtration,[5] and membrane separation.[6]

Photocatalytic oxidation (PCO) of VOCs is a very attractive and promising alternative technology for air purification.[7]

It has been demonstrated that organics can be oxidized to carbon dioxide, water, and simple mineral acids at low temperatures on metal oxides catalysts using, for example, the TiO_2 catalyst. Several parameters affect the VOC conversion processes: the specific surface area of the catalyst and the VOC concentration. However, the time conversion takes hours and is effective for low VOC concentrations of the order of tens of ppm. In addition, it is critical that the choice of the substrate should be degraded as well as its concentration and its significance in actual use and the type of irradiation source and its irradiance at the sample surface.[8]

For VOC degradation at relatively higher concentrations of the order of hundreds and thousands of ppm, new studies have oriented to thermal plasmas, such as spark discharge[9–11] and non-thermal plasma (NTP).[12–15] While thermal plasmas are too expensive, non-thermal plasma (NTP) has recently attracted more attention as a convenient and clean alternative.

In the non-thermal plasma, chemical reaction charged species and radicals are produced under steady-state conditions. The primary electrons collide with background molecules producing secondary electrons, photons, ions, and radicals.[12] This process is highly non-selective and creates a chemical reactive environment able to treat materials as well as gases at room temperature.[16] Previous studies on NTP demonstrated they are very effective in material applications by employing different gas precursors because of their ability to highly dissociate molecules in the gas phase, producing very reactive chemical groups at room temperature: materials are not damaged and can be easily functionalized.[17–19] When generated at atmospheric pressure, plasma produces chemical species able to also dissociate VOC molecules at higher concentrations up to thousand ppm,[20–22] but the processes are non-selective.

Despite the success of NTP in VOC dissociation, the production of by-products such as ozone, aerosol particles, and incompletely oxidized compounds requires further research, including chemical simulations, in order to understand the process phenomenology.[23–25] A combination of NTP and catalysis was attempted in order to increase the depletion efficiency. The addition of a catalyst bed near the plasma zone seems to enhance the decomposition rate of pollutants, reducing the undesirable by-products due to the increase in retention time.[26]

In fact, NTPs can contain a diverse mix of highly reactive species, and they are difficult to operate in such a way as to produce single products in high yield and at high selectivity.[27,28] Integration of plasma and catalysts together promises to combine the advantages of the two to effect transformations that are currently difficult or impossible to achieve.[29,30]

ABBATTIMENTO PROPANO

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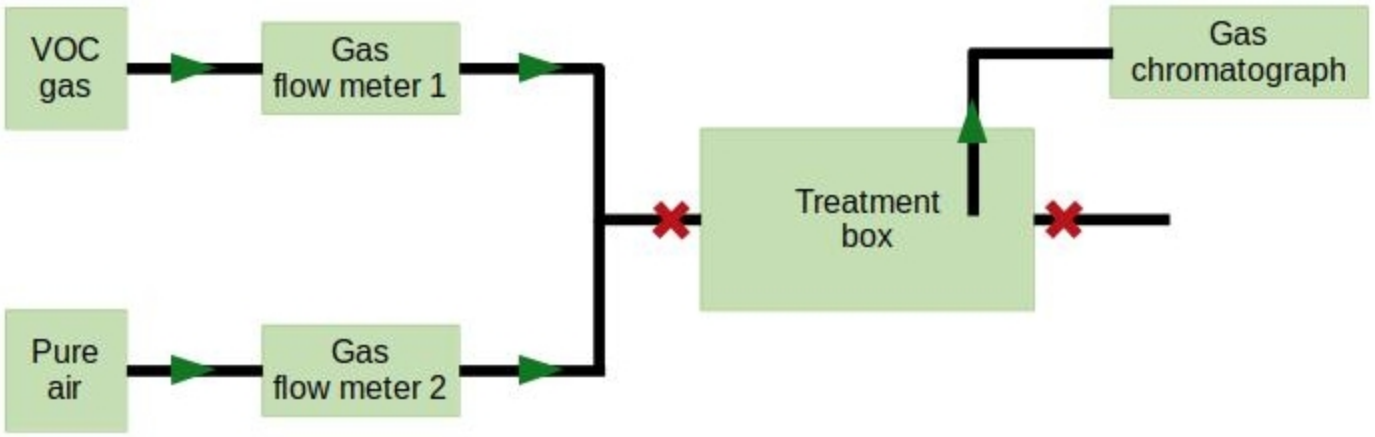
Sistema inserimento del gas

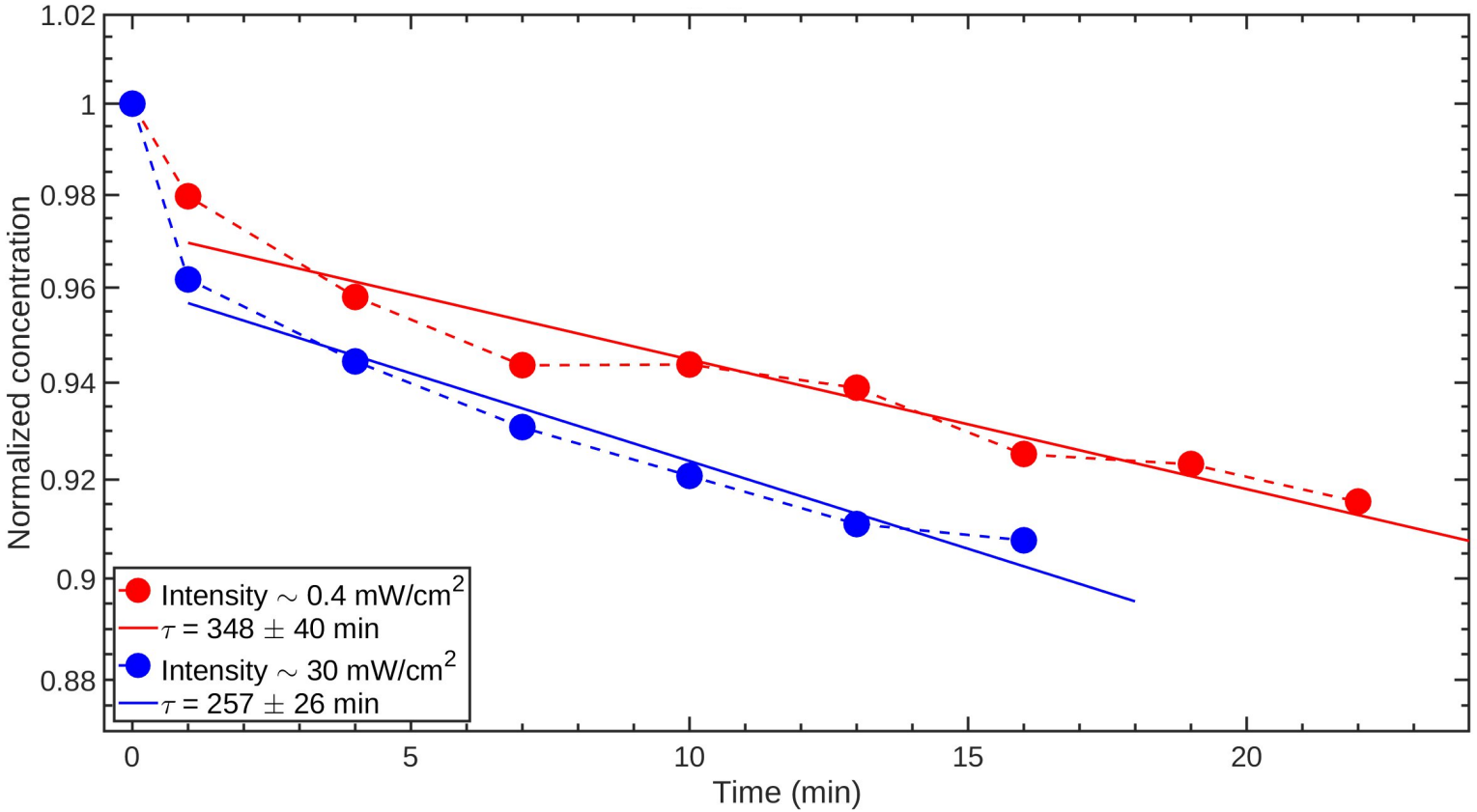


Concentrazione iniziali:

- 5000 ppm
- 2500 ppm
- 1200 ppm

Catalizzatore A - Lampada UV-A

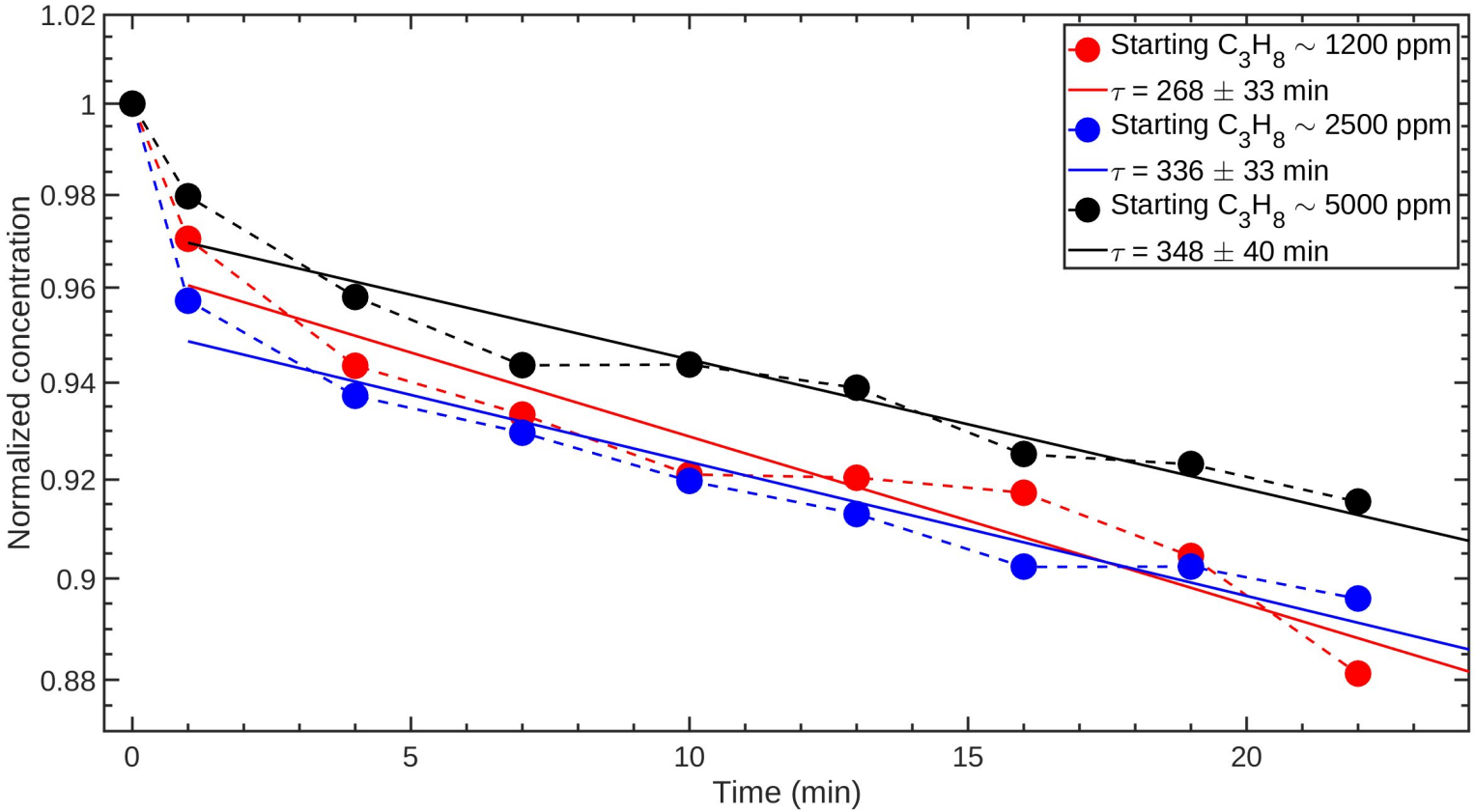
Diversa distanza della lampada
Concentrazione iniziale 5000 ppm



$$\frac{\rho_3(t)}{\rho_3(0)} = e^{-\frac{t}{\tau}}$$

Catalizzatore A - Lampada UV-A

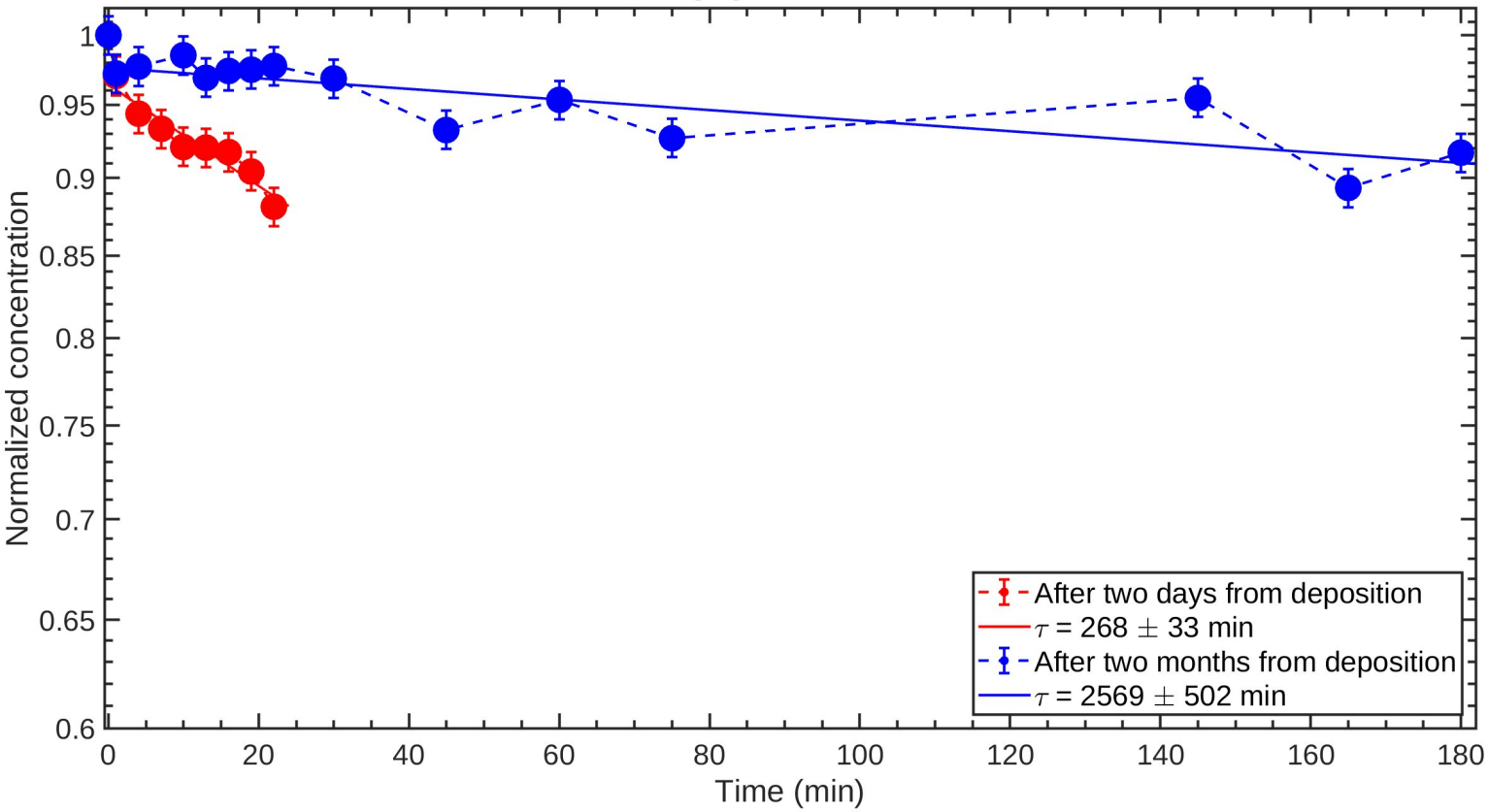
Diversa concentrazione iniziale



$$\frac{\rho_3(t)}{\rho_3(0)} = e^{-\frac{t}{\tau}}$$

Catalizzatore A - Lampada UV-A

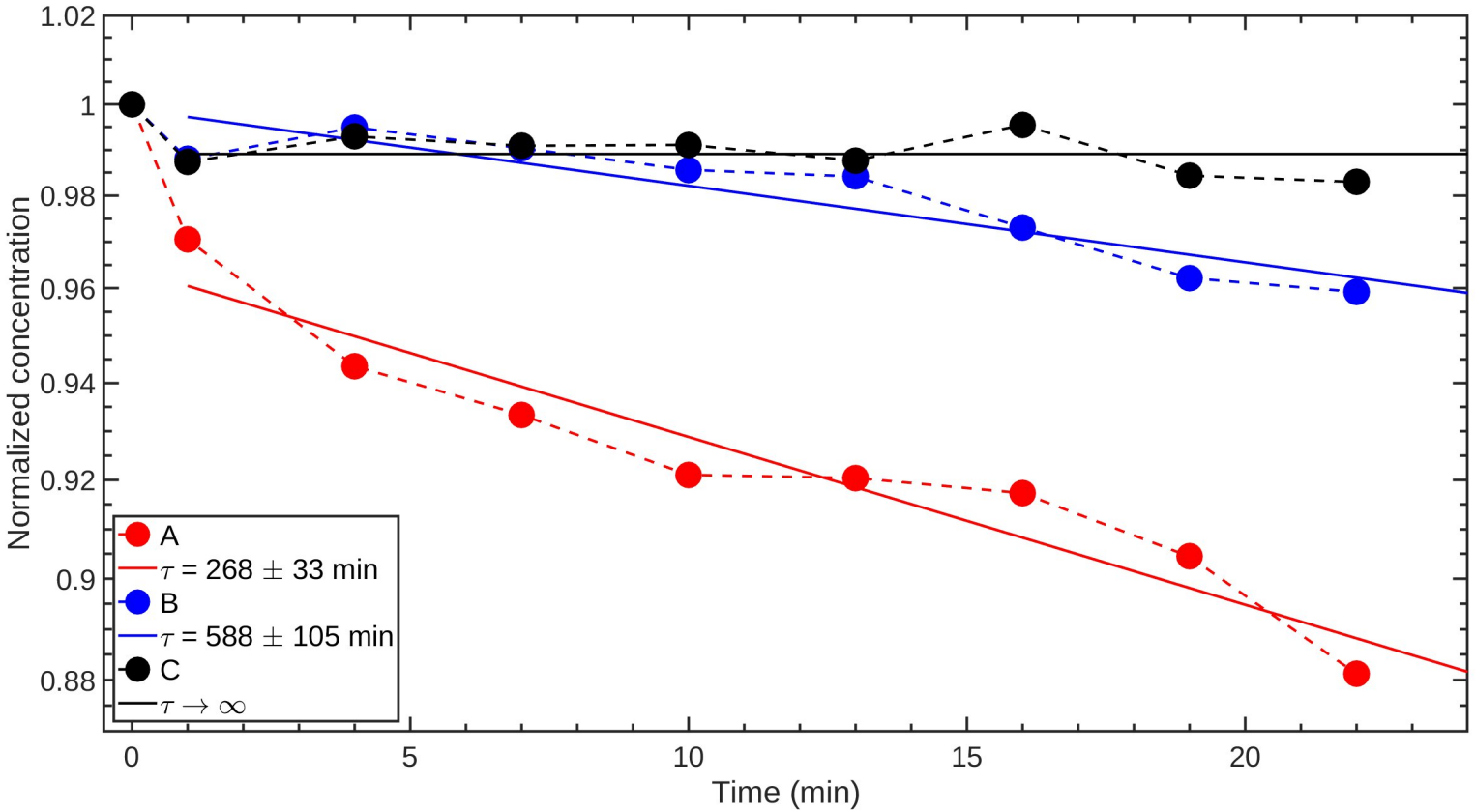
Diverso tempo dalla deposizione
Concentrazione iniziale 1200 ppm



$$\frac{\rho_3(t)}{\rho_3(0)} = e^{-\frac{t}{\tau}}$$

Differenti catalizzatori - Lampada UV-A

Concentrazione iniziale 1200 ppm



- **A**: 100% TiO_2
- **B**: 50% TiO_2 50% WO_3
- **C**: 100% WO_3

$$\frac{\rho_3(t)}{\rho_3(0)} = e^{-\frac{t}{\tau}}$$

CONCLUSIONI

Conclusioni

- Abbiamo caratterizzato diversi tipi di lampade.
- Abbattimento di alte concentrazioni di propano con il catalizzatore A indipendentemente dalla concentrazione iniziale.
- Tempi scala di abbattimento dell'ordine delle ore.
- Problema dell'aging.
- Punto di partenza per studi di abbattimento di VOC con questi fotocatalizzatori.

GRAZIE PER L'ATTENZIONE

Composti Organici Volatili

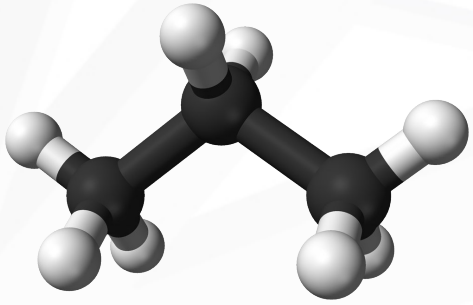
Art.268 del DLgs152/2006
VOC: qualsiasi composto organico che a 293.15 K ha una pressione di vapore di 0.01 kPa o superiore.

Dannosi per l'ambiente e per le persone.
Alcuni sono classificati come cancerogeni o possibili cancerogeni.

Usati in numerosi processi industriali.
Presenti nei materiali per l'edilizia.
Componenti dei gas di scarico.

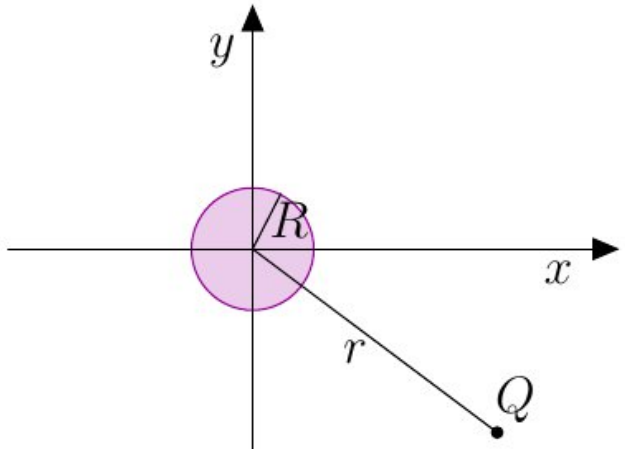
Diffondono molto rapidamente nell'ambiente.
Non sono sostituibili con altri composti.
Necessario studiare metodi per la loro rimozione dopo la diffusione nell'ambiente.

Come composto target abbiamo usato il propano (C_3H_8)

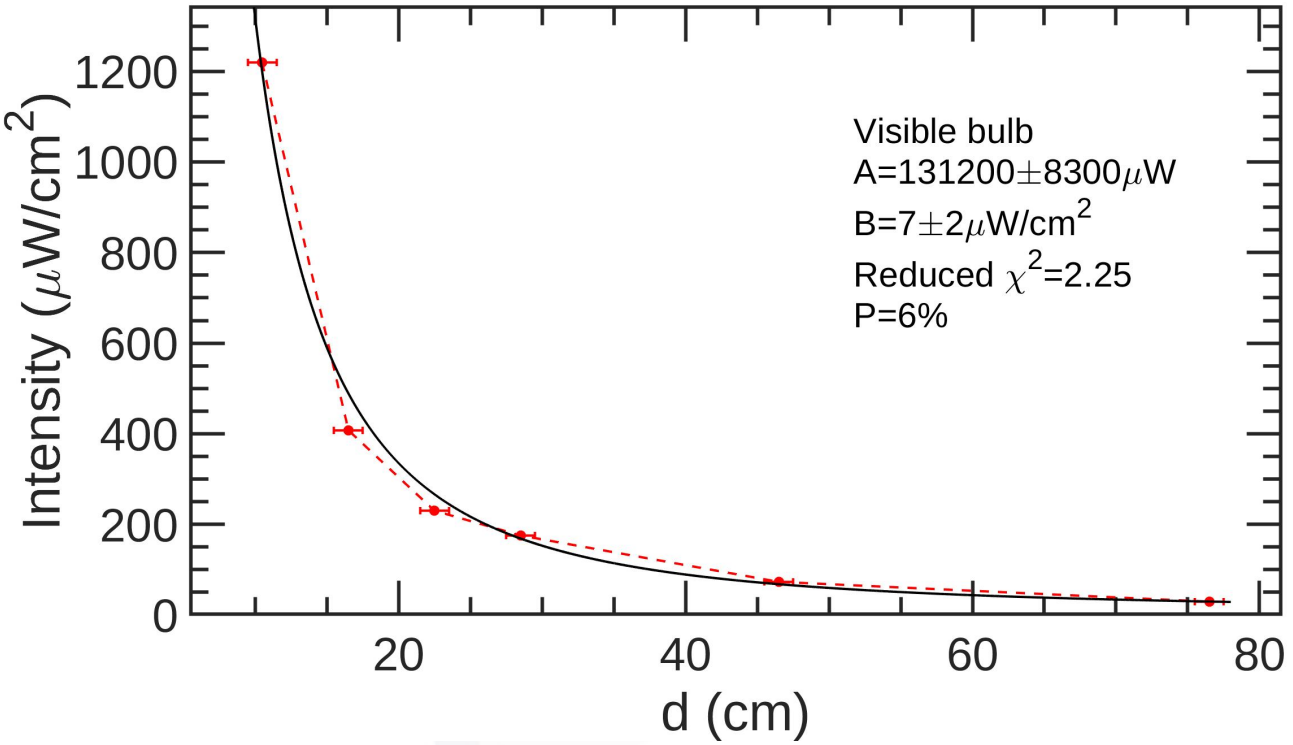


Di Ben Mills - Opera propria, Pubblico dominio, https://commons.wikimedia.org/w/index.php?curid=4415799

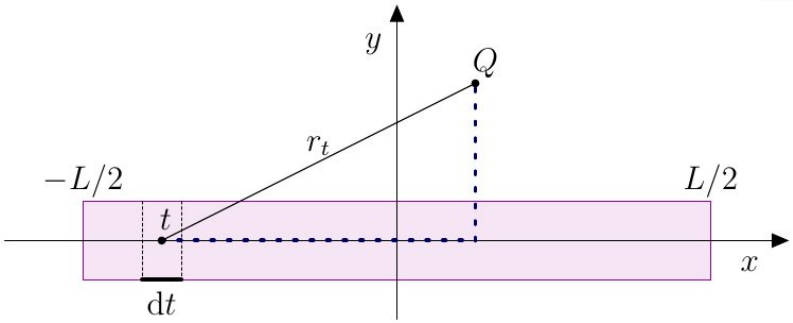
Lampada visibile



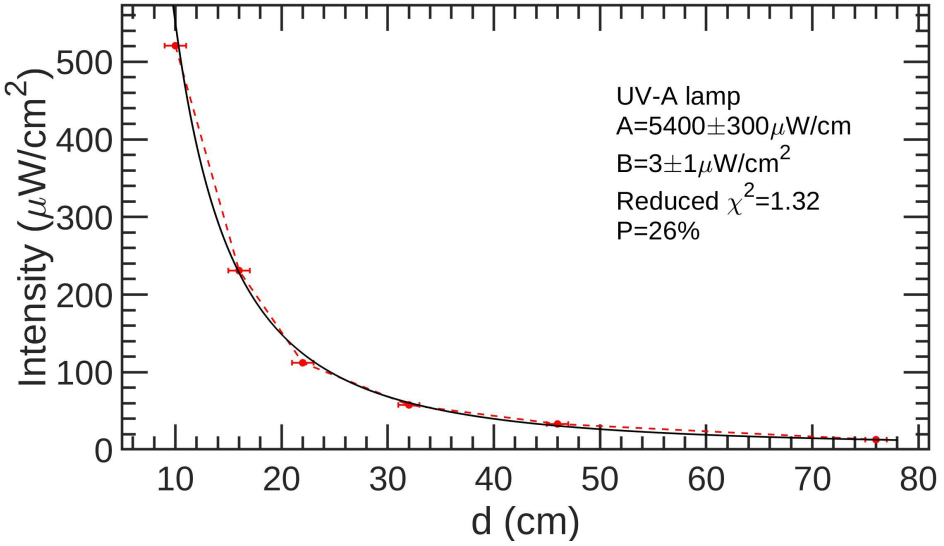
$$E(d) = \frac{A}{d^2} + B$$

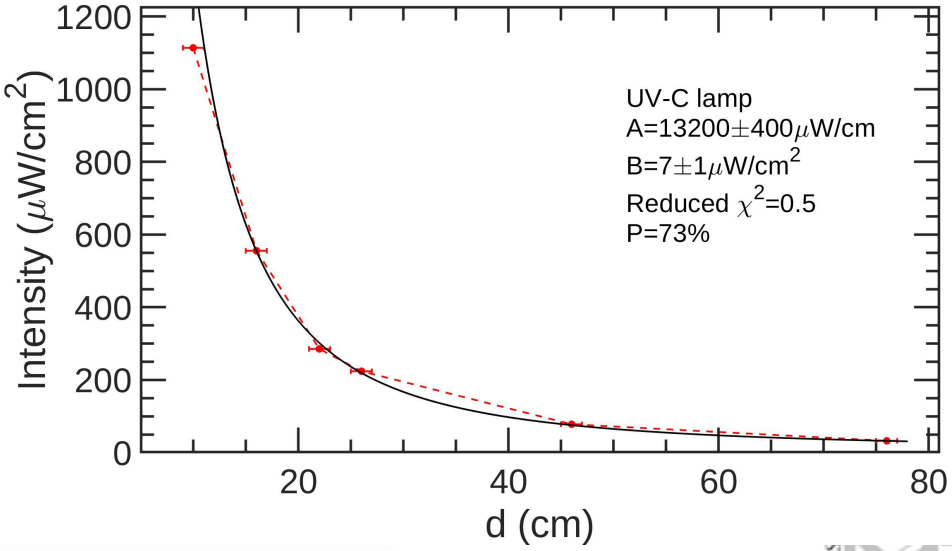


Lampade UV



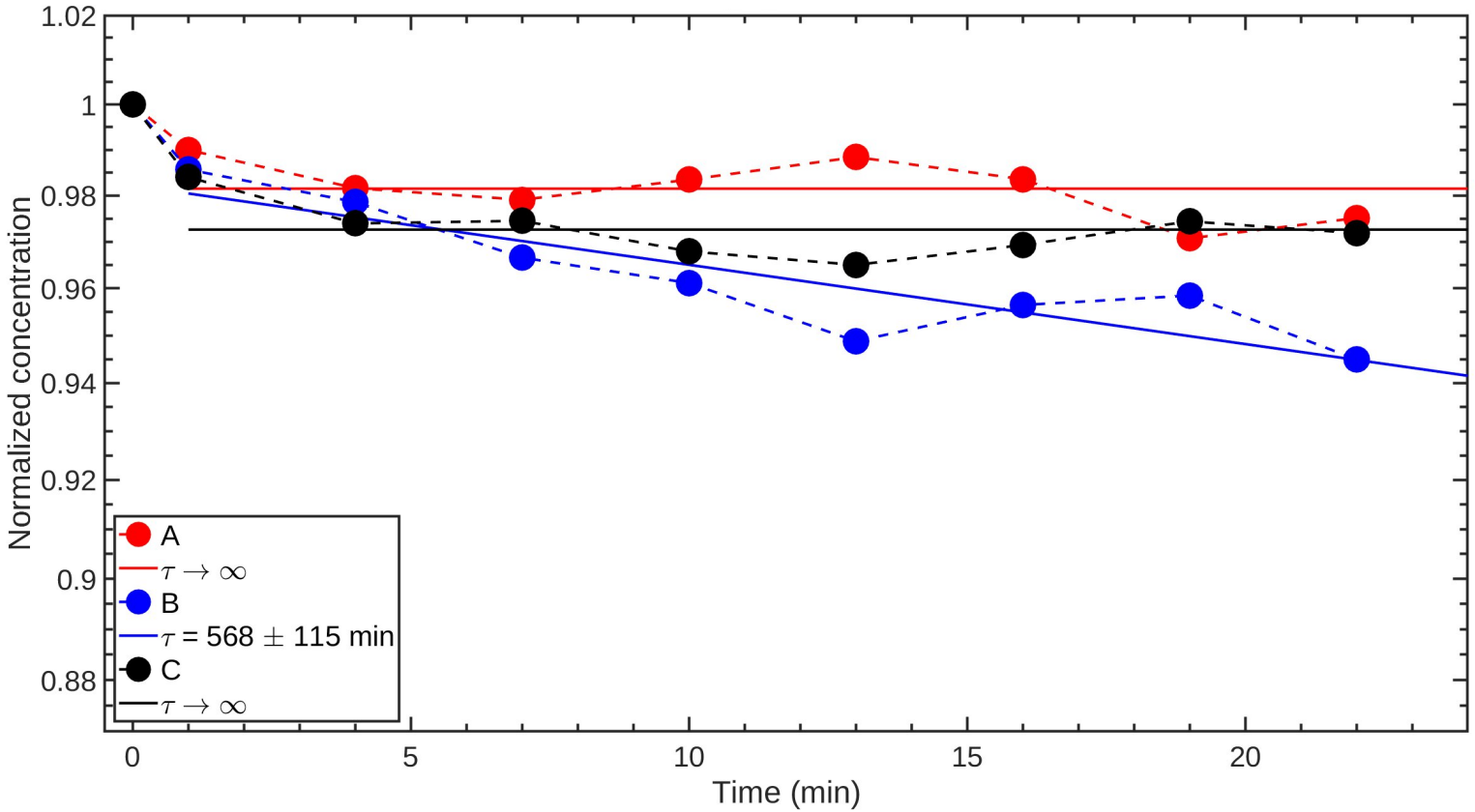
$$E(d) = \frac{2A}{d}\left[\tan^{-1}\left(\frac{L/2}{d}\right)\right] + B$$





Differenti catalizzatori - Lampada UV-C

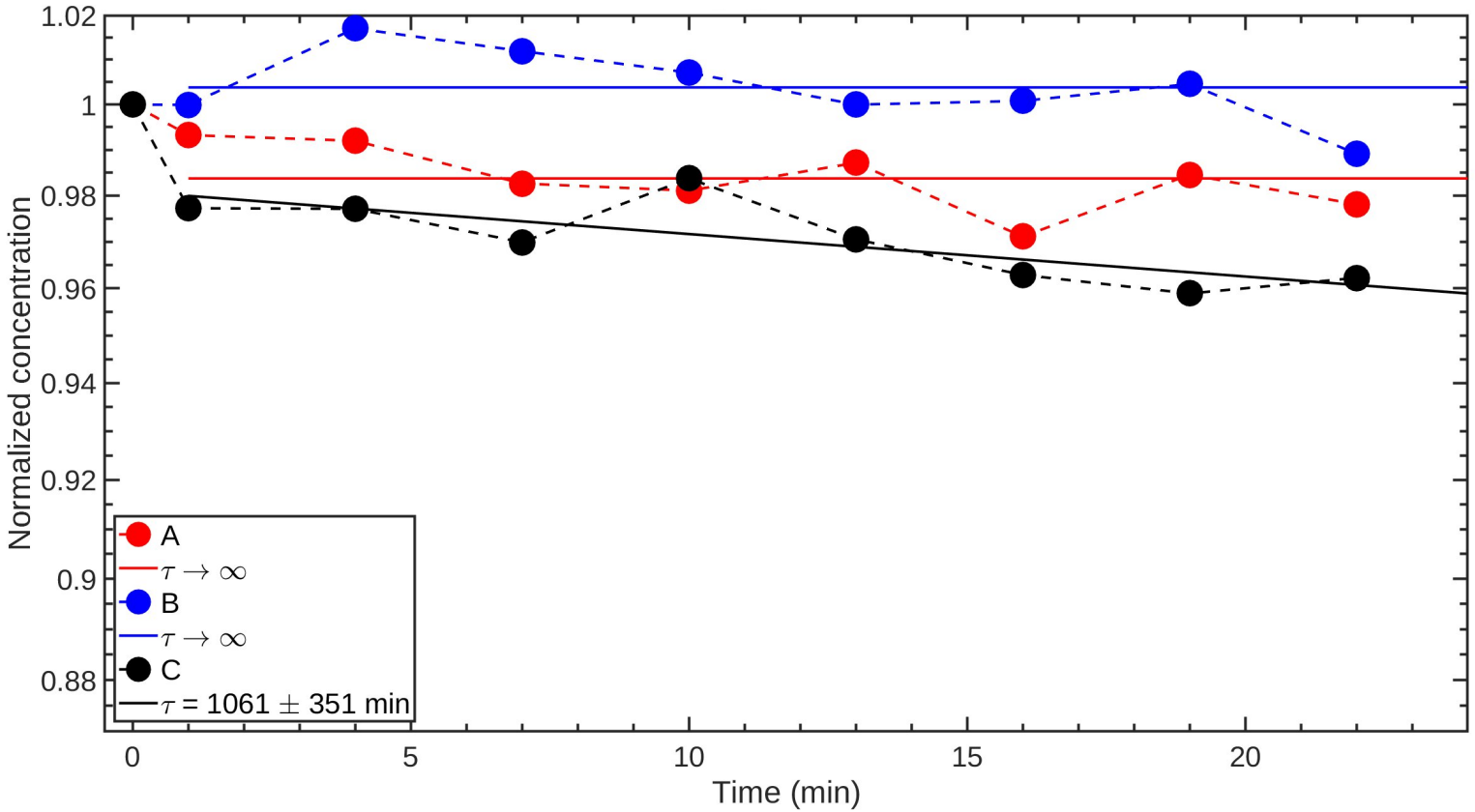
Concentrazione iniziale 1200 ppm



$$\frac{\rho_3(t)}{\rho_3(0)} = e^{-\frac{t}{\tau}}$$

Differenti catalizzatori - Lampada visibile

Concentrazione iniziale 1200 ppm



$$\frac{\rho_3(t)}{\rho_3(0)} = e^{-\frac{t}{\tau}}$$