Fotocatalisi e membrane fotocatalitiche

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Aula Napoleonica - UniMI

Membrane-Assisted Charge Separation and Photocatalytic Activity in Embedded TiO_2: A Kinetic and Mechanistic Study

Journal of Physical Chemistry C 2010, 114, 37, 15755–15762

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Photocatalytic membrane processes, and respective modelling, for removal of pharmaceutical residues in wastewaters. A case study with 2-[2,6-(dichlorophenyl) amino]phenyl acetic acid as model molecule

Ignazio Renato Bellobono and Flavia Groppi

International Journal of Photoenergy, 2009, Article ID 631768

Influence of Irradiance, Flow Rate, Reactor Geometry, and Photopromoter Concentration in Mineralization Kinetics of Methane in Air and in Aqueous Solutions by Photocatalytic Membranes Immobilizing Titanium Dioxide

International Journal of Photoenergy, 2008, Article ID 283741

Ignazio Renato Bellobono,[1] Mauro Rossi,[1] Andrea Testino,[2] Franca Morazzoni,[2] Riccardo Bianchi,[3] Giulia de Martini,[4] Paola Maria Tozzi,[4] Rodica Stanescu,[5] Cristina Costache,[5] Liliana Bobirica,[5] Mauro Luigi Bonardi,[6] and Flavia Groppi[6]

Nonlinear Modelling of Kinetic Data Obtained from Photocatalytic Mineralisation of 2,4-Dichlorophenol on a Titanium Dioxide Membrane

Current Opinion in Green and Sustainable Chemistry, 2017, 6, 69-77

Ignazio Renato Bellobono,[1] Roberto Scotti,[2] Massimiliano D'Arienzo,[2] Franca Morazzoni,[2] Riccardo Bianchi,[3] Rodica Stanescu,[4] Cristina Costache,[4] Liliana Bobirica,[4] Gabriela Cobzaru,[4] Paola Maria Tozzi,[5] Mauro Rossi,[6]

Nonlinear modelling of data in photomineralization kinetics of organic micropollutants by photocatalytic membranes immobilizing titanium dioxide in membrane reactors†

Ignazio Renato Bellobono ✉, Riccardo Bianchi, Giulia de Martini, Paola Maria Tozzi, Mauro Luigi Bonardi, Flavia Groppi, Mauro Rossi

Journal of Chemometrics, 2008, 22, 425-435

Classification of membrane techniques

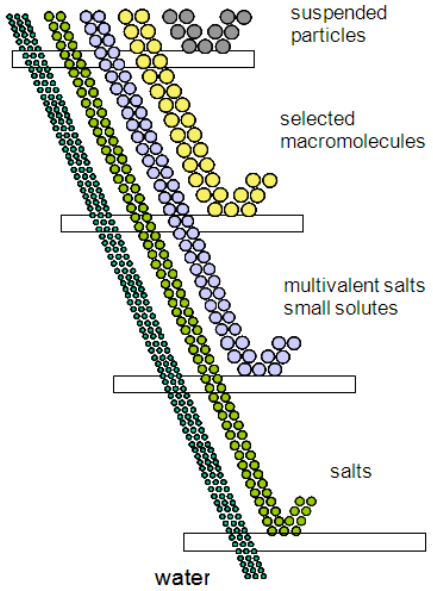
Pressure driven

Microfiltration 0.1 - 3 bar, 0.1 - 5 µm

Ultrafiltration 2 - 10 bar, 20 nm - 0.1 µm

Nanofiltration 5 - 30 bar, » 1 nm

Reverse Osmosis 10 - 100 bar, 0.1 - 1 nm (close)



Concentration gradient driven

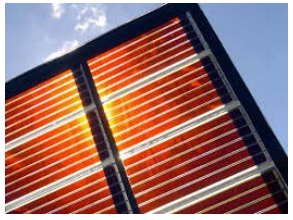
Dialysis

Pervaporation

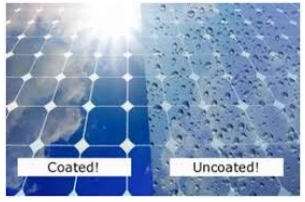
Direct Contact Membrane Distillation

Fotocatalisi eterogenea

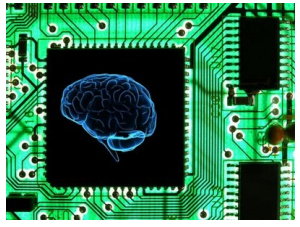
DSSC
corrente elettrica

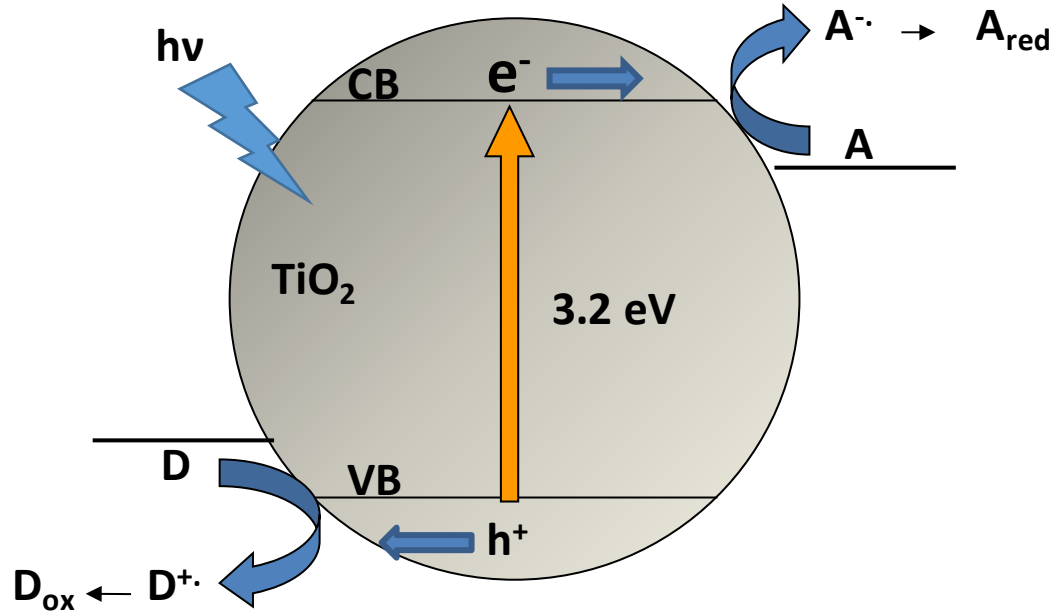


COATINGS



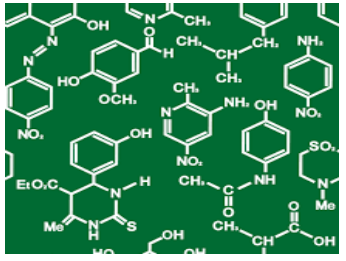
MEMRISTORI



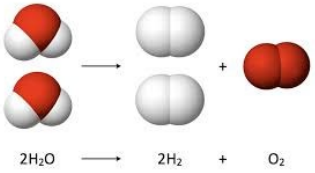


APPLICAZIONI AMBIENTALI

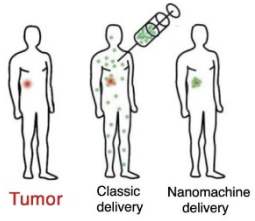
SINTESI ORGANICA



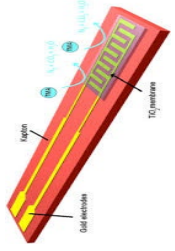
WATER SPLITTING
H_2



APPLICAZIONI BIOMEDICHE



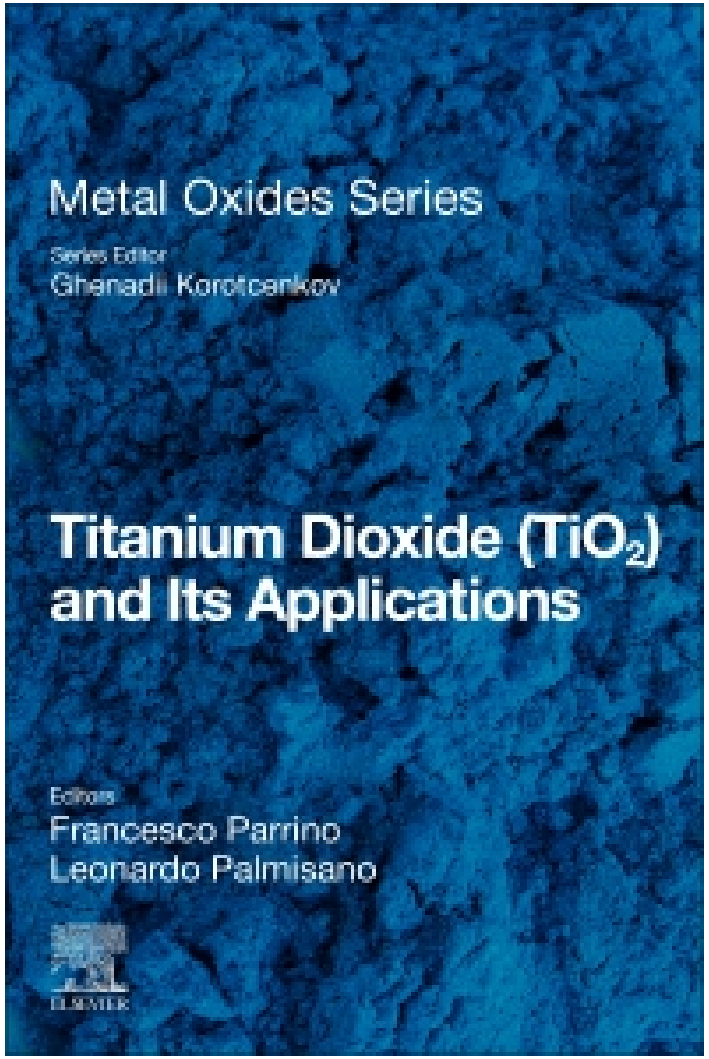
SENSORI



Titanium Dioxide (TiO_2) and Its Applications

1st Edition - November, 2020

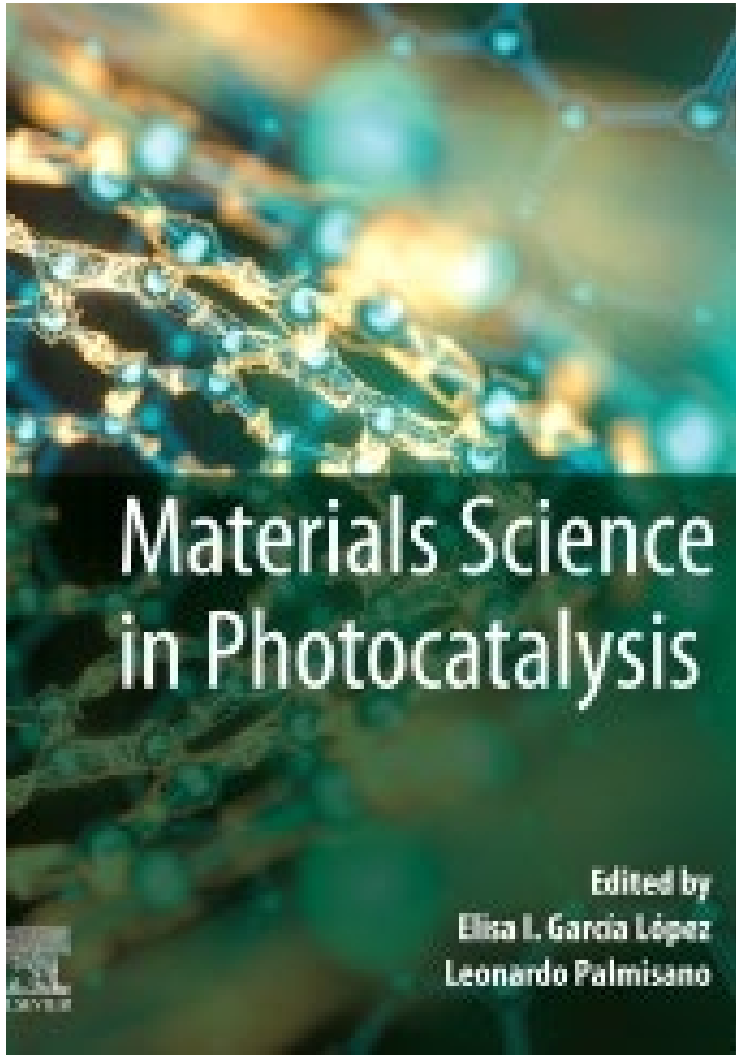
•Editors: Francesco Parrino, Leonardo Palmisano



Materials Science in Photocatalysis

1st Edition - August 15, 2021

•Editors: Elisa Garcia Lopez, Leonardo Palmisano



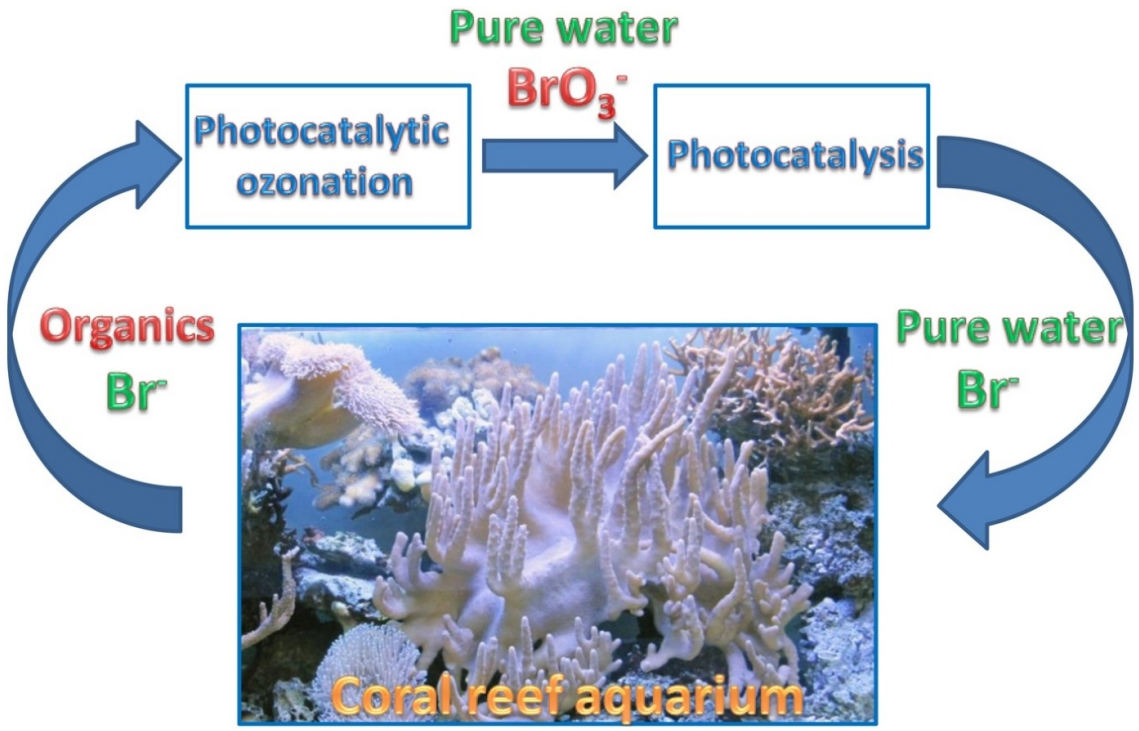
Fotocatalisi + O_3

Problema:
depurazione di effluenti inquinati contenenti
ioni bromuro tramite fotocatalisi e/o ozonizzazione

FC + O_3

Strategia di purificazione

[Br^-]
in acqua potabile**: 0.01 – 3 mg L^{-1}**
in acqua di mare: **67 mg L^{-1}**



O_3

Degradazione efficace…ma
$Br^- + O_3 \rightarrow BrO_3^-$
Bromato cancerogeno
Concentrazione massima consentita: **10 µg L^{-1}**

FC

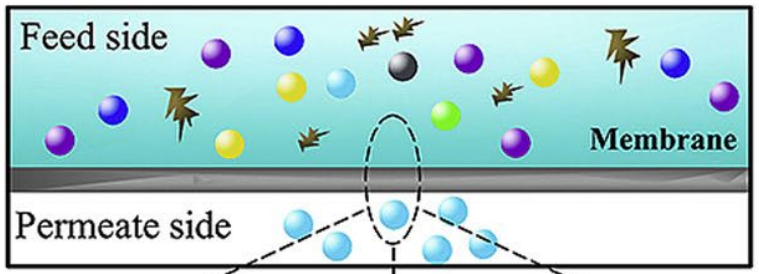
Degradazione lenta…ma
$BrO_3^- \rightarrow Br^-$

Parrino et al. Photocatalytic ozonation: maximization of the reaction rate and control of undesired by-products, Appl. Catal. B: Environ. (2015) 178, 37-43

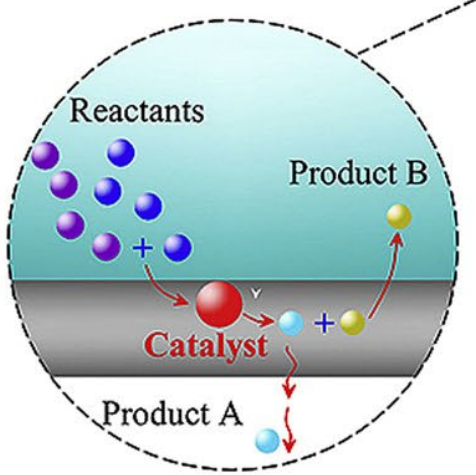
Camera Roda et al. Photocatalytic ozonation for a sustainable aquaculture: A long-term test in a seawater aquarium, Appl. Catal. B: Environ. (2019) 253, 69-76

Reaction-Separation coupling by catalytically active membrane

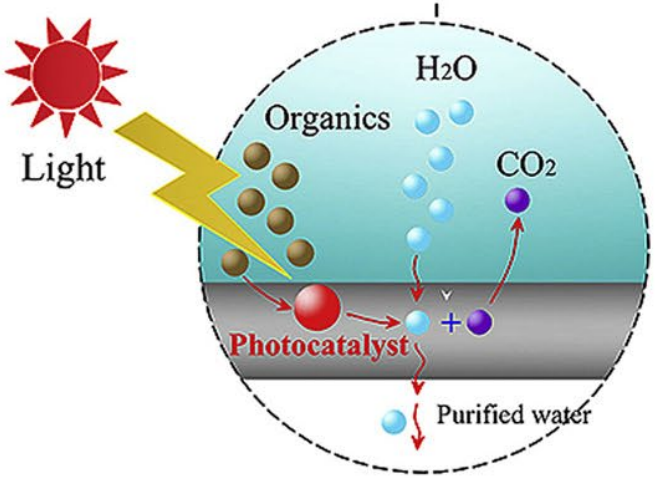
- Multidiscipline



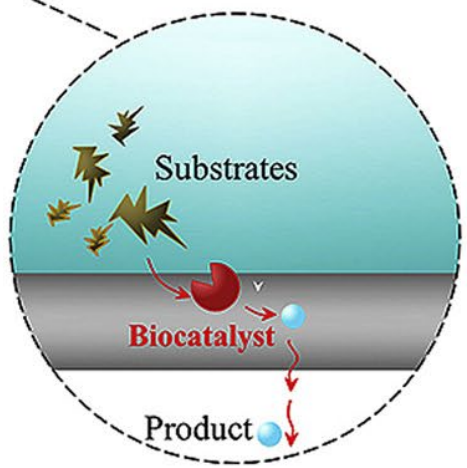
- Liquid Phase Reactions:
  - Fine Chemical Synthesis Reactions
  - Photocatalytic Reactions
  - Biocatalytic Reactions
  - Other Reactions
- Gas Phase Reactions



Synthesis - Separation Coupling



Photocatalysis - Separation Coupling

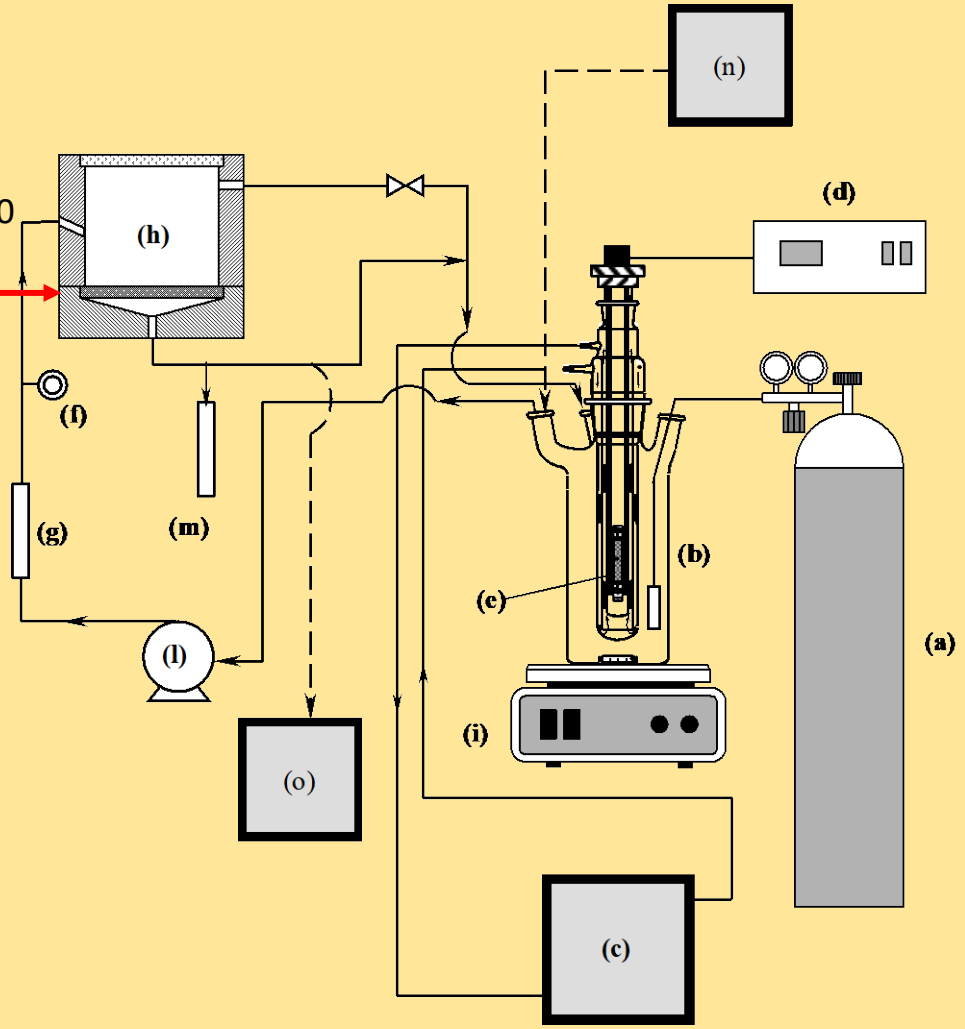


Biocatalysis - Separation Coupling

The catalyst can be **suspended** in the reacting medium or **supported** by the membrane

Photocatalytic membrane reactors for water purification

Commercial nanofiltration membrane NTR 7410 (sulphonate polyethersulphone polymer, 600/800 Da cut-off, Nitto, Denko, Tokyo)



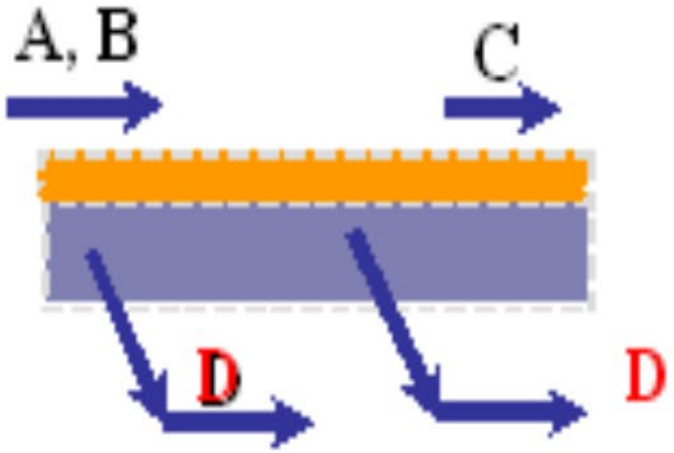
R. Molinari, M. Mungari, E. Drioli, A. Di Paola, V. Loddo, L. Palmisano, M. Schiavello, Study on a photocatalytic membrane reactor for water purification Catalysis Today 55 (2000) 71–78.

R. Molinari, F. Pirillo, M. Falco, V. Loddo, L. Palmisano, Photocatalytic degradation of dyes by using a membrane reactor, Chemical Engineering and Processing 43 (2004) 1103–1114.

(a) oxygen cylinder; (b) photoreactor; (c) thermostatic bath with cooling water; (d) power supply; (e) medium pressure Hg lamp with cooling jacket; (f) manometer; (g) rotameter; (h) pressurised cell containing the membrane; (i) magnetic stirrer; (l) pump; (m) graduated cylinder for permeate sampling; (n) feed tank (continuous regime); (o) waste tank (continuous regime).

MEMBRANE REACTORS

i.e. separating during reaction



Increased conversion

By shifting the equilibrium towards the products

Increased selectivity

By limiting further reaction of D (i.e. undesired overoxidation)

Photocatalytic membrane reactors for the synthesis of high added value compounds

The case of vanillin

- Vanillin is the most popular aroma in the world (the demand is more than 14000 t/y)
- Widely used in mass produced foodstuffs from biscuits to beer, from chocolate to ice cream.
- Utilized in the food, cosmetic, pharmaceutical, nutraceutical and fine chemicals industry.
- Important health benefits (antioxidant and anti-tumoral activity).

Vanilla flower

Vanilla pods

Natural vanilla extract
from vanilla planifolia
(**long and expensive procedure**)

The problem with vanilla…

- **Natural Vanillin** can supply less than 1 % of the demand and is very expensive.
- **Synthetic Vanillin** (mainly from guaiacol) costs one hundredth of the natural vanillin, but the process is not “green” and the product is of lower quality (less pleasant “bouquet”)
- The **green and/or sustainable production** of vanillin has **marketing importance**, in particular for consumers of certain types of goods (food, cosmetics, pharmaceuticals)

“After vowing to go natural, food brands, face a shortage of the favored flavor”

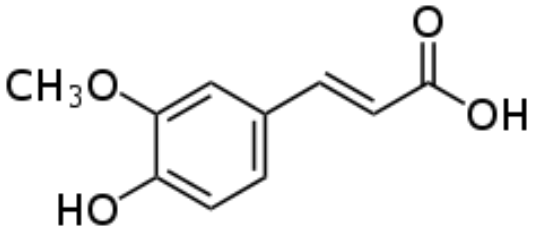
(from “The problem with vanilla” by Bomgardner, Chem. Eng. News, 94 (2016) pp. 38-42)

«Dopo la promessa di diventare naturali, i marchi alimentari devono affrontare una carenza del gusto preferito»

Alternative green processes needed

We need sustainable innovative processes which can represent a green and sustainable alternative of the traditional production.

In aqueous solution and starting from natural cheap precursors the **biotechnological and the photocatalytic synthesis** of vanillin satisfy the requirements of **sustainability and green chemistry**.



❖ Acido ferulico
❖ Scarto industriale
❖ Componente lignina

❖Processo lungo.
❖ Necessaria purificazione.
❖ Ceppi batterici selezionati.
(Streptomyces, E. Coli, Actinomyces)

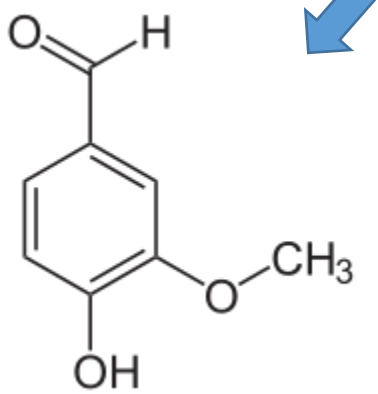
❖ Prodotto di bassa qualità.
❖ Solventi e ossidanti tossici.
❖ Prodotto non alimentare.

TiO_2

1500 $ / Kg

15 $ / kg

2400 $ / Kg

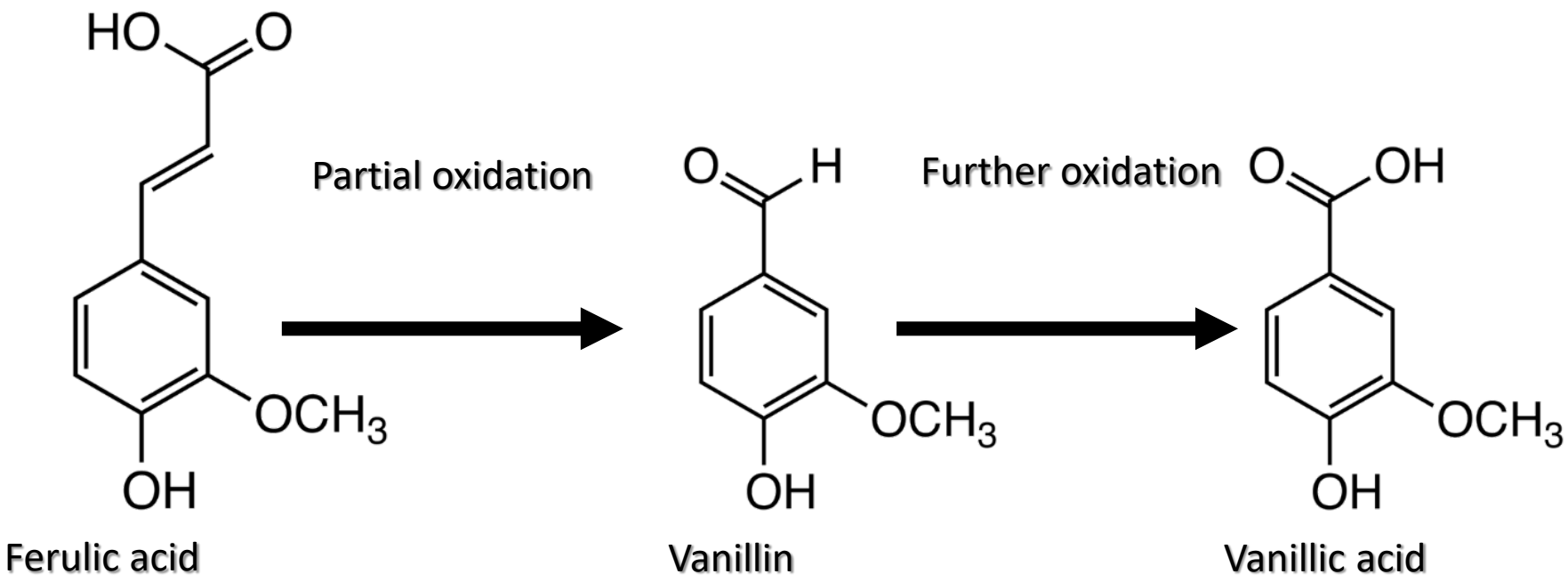


vanillina

Problems

1) Vanillin degradation in the reacting solution

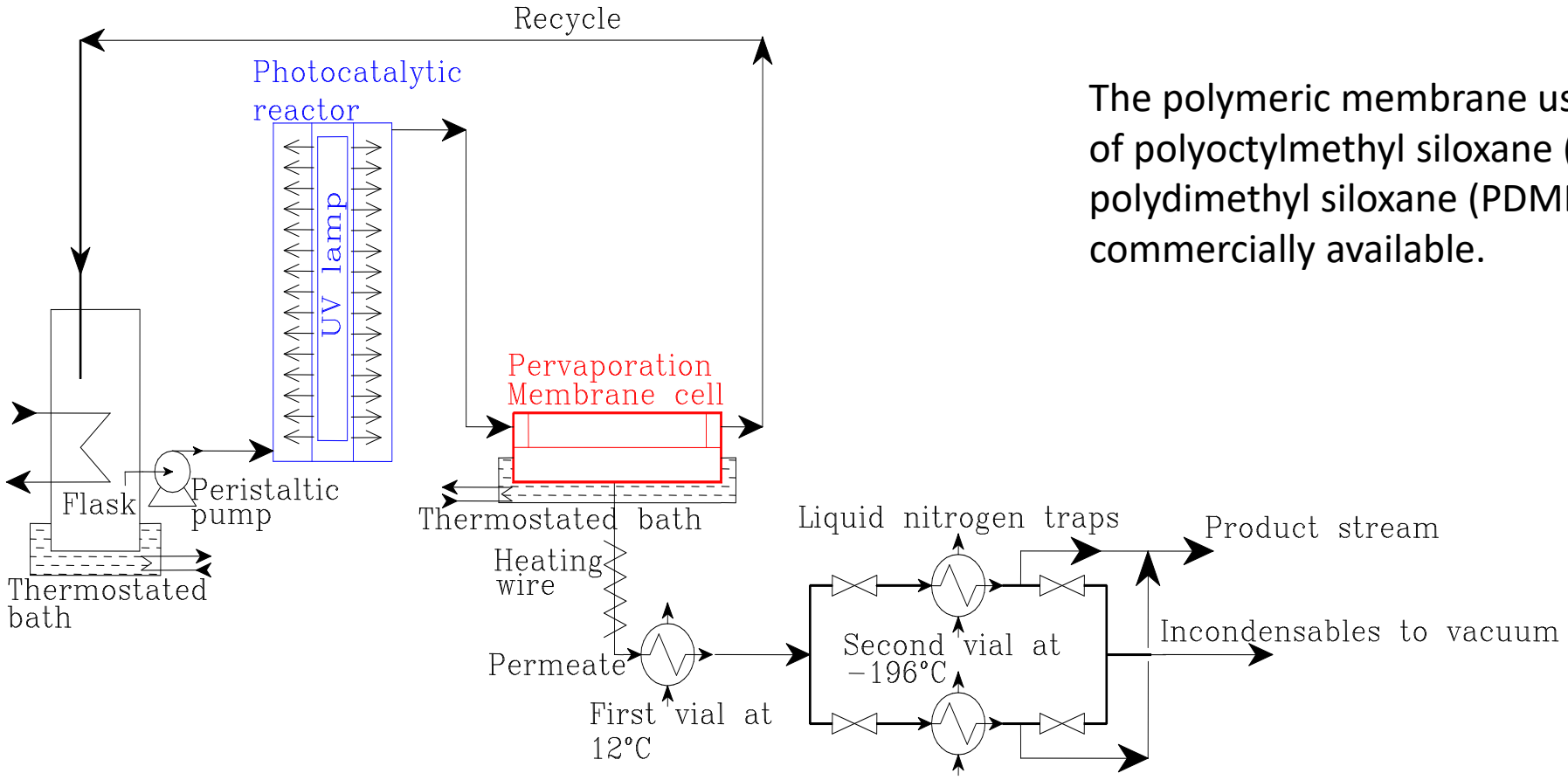
2) the build-up of vanillin hinders or slows down the process



Ferulic acid Vanillin Vanillic acid

These problems can be solved by
recovering vanillin directly from the reacting solution **during** (not after) the reaction.

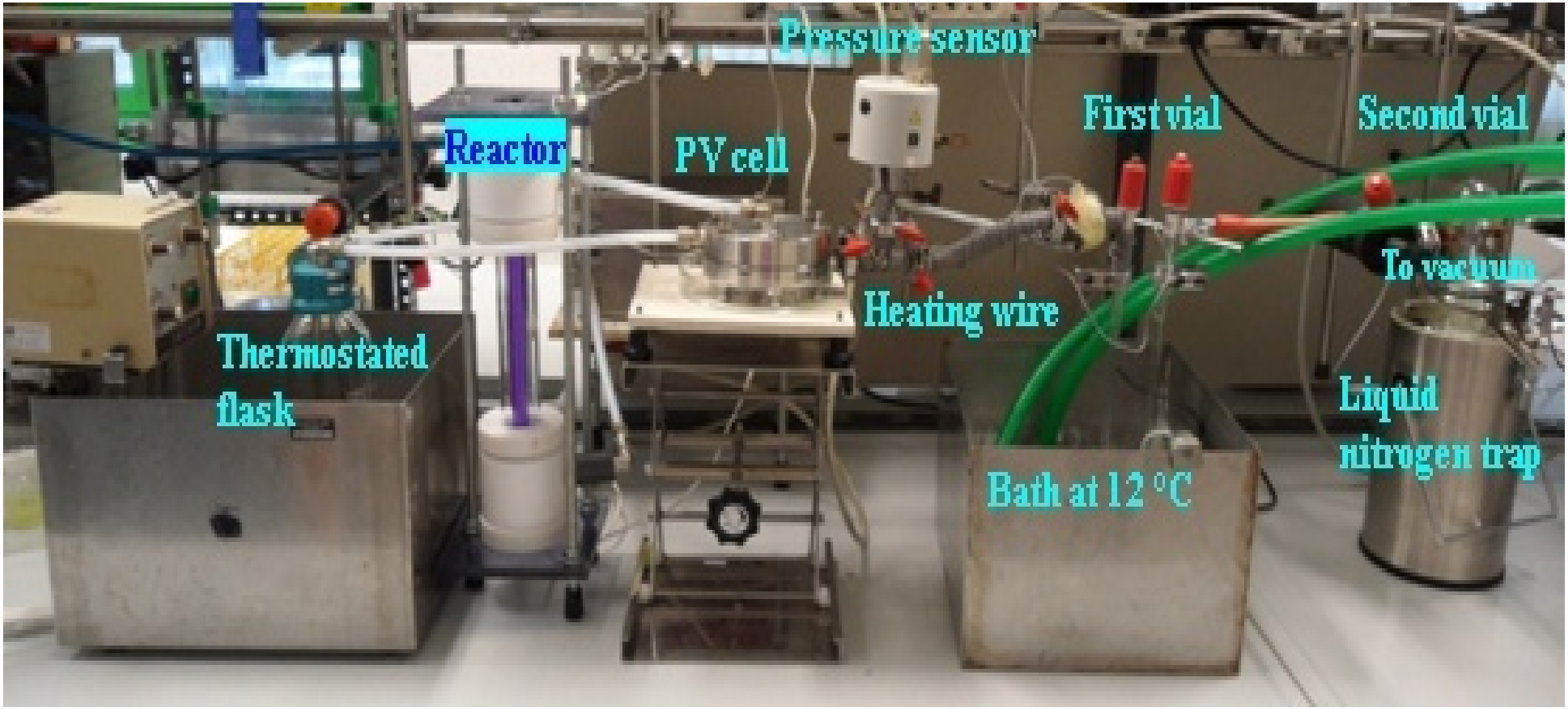
Estrazione e purificazione della vanillina tramite pervaporazione



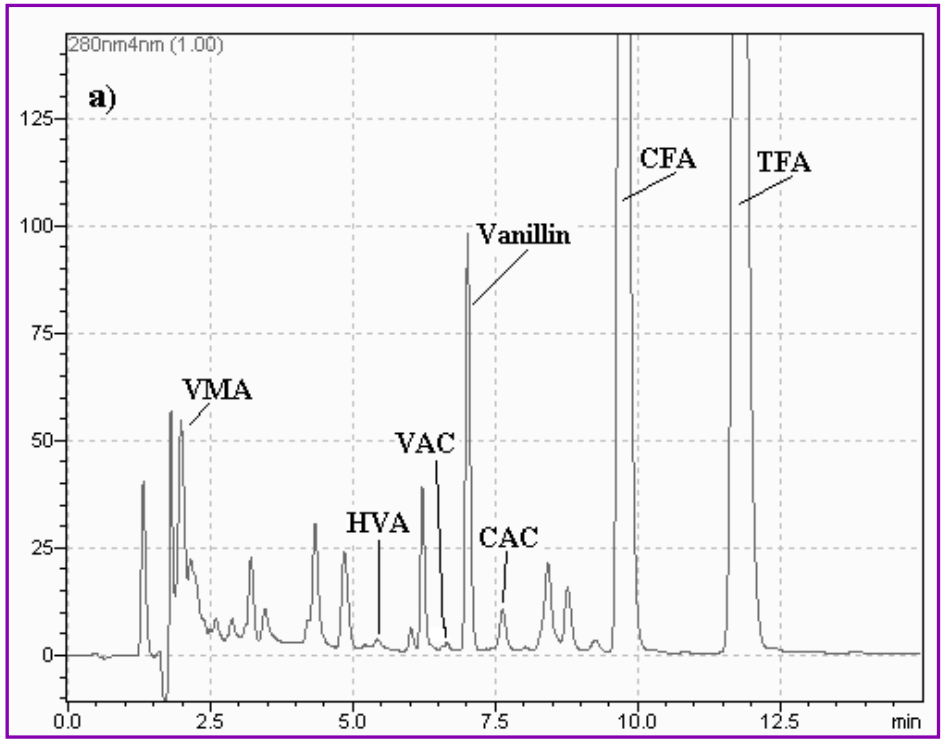
The polymeric membrane used is made of polyoctylmethyl siloxane (POMS) or polydimethyl siloxane (PDMDS), commercially available.

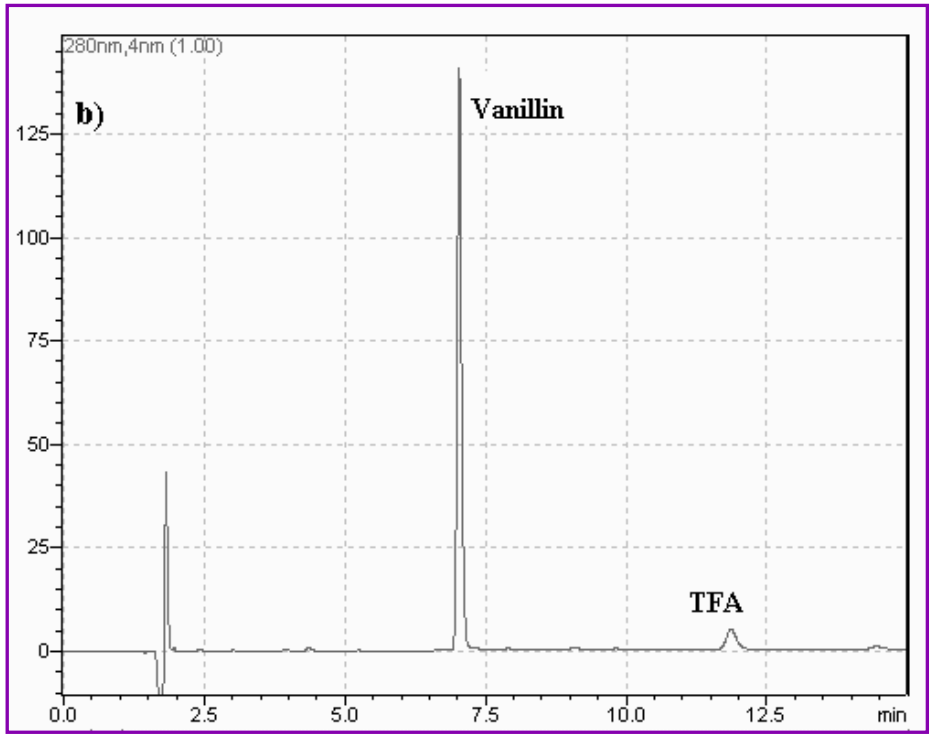
V. Augugliaro, G. Camera Roda, V. Loddo, G. Palmisano, L. Palmisano, F. Parrino, M.A. Puma,
Synthesis of vanillin in water by TiO_2 photocatalysis
Appl. Catal. B: Environ. (2012) 111-112, 555-561

Experimental set-up



After 2h UV-irradiation…

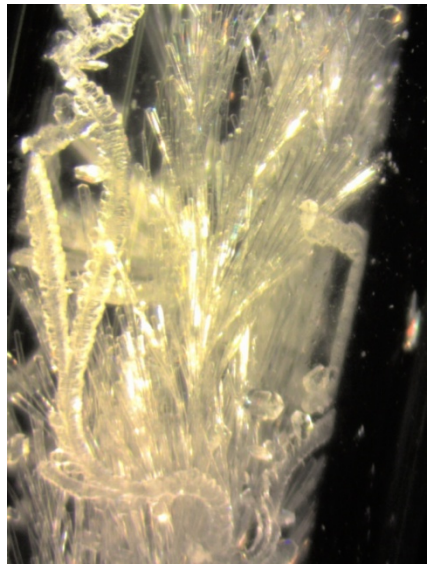




In the reacting solution

In the permeate

VMA: Vanillyl mandelic acid
HVA: Homovanillic acid
VAC: Vanillic acid
CAC: Caffeic Acid
CFA: *Cis* ferulic acid
TFA: *Trans* ferulic acid



Cristalli di vanillina 99.8%

Conclusions

- **Heterogeneous photocatalysis (HP) for the abatement of pollutants is suitable for niche applications, at least in liquid-solid systems, the larger-scale application appears more problematic.**

- **An alternative use of HP is in the formation of high added value molecules such as aldehydes from alcohols or vanillin from ferulic acid.**

- **The coupling of HP with other methods can be useful for many purposes, see for example coupling with membranes.**

- **The presence of a membrane can have beneficial effects both on conversion of the initial species and selectivity towards one or more products.**

Thanks for your kind attention