



**UNIVERSITY OF ROME “LA SAPIENZA”  
NANOTECHNOLOGIES ENGINEERING**

# **NANOPARTICLES IN WASTEWATER TREATMENT**

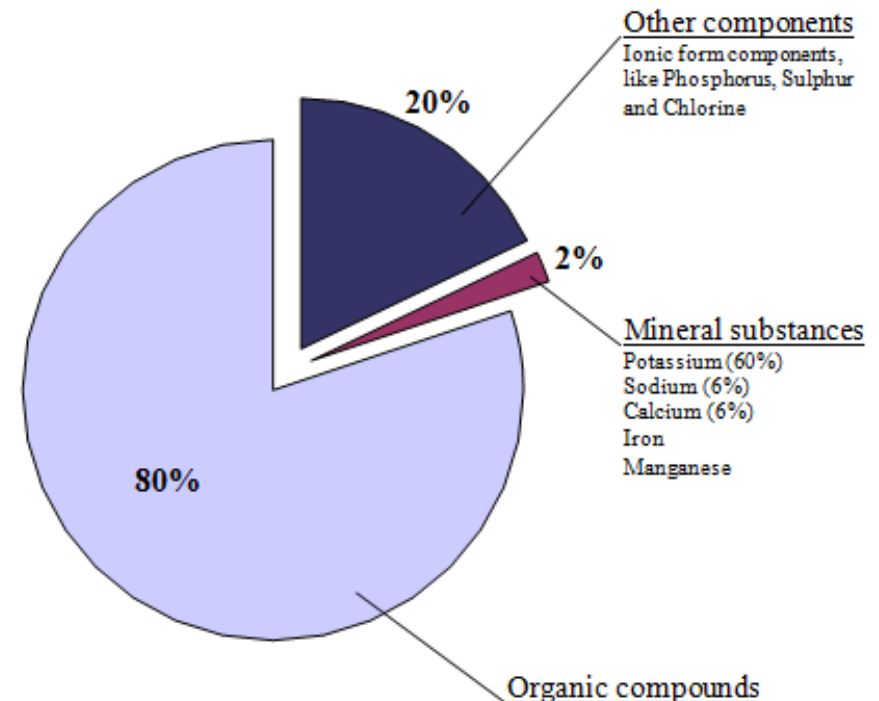
# INTRODUCTION

**PHOTOMEM project** was realized under the *Seventh Framework Program for Research and Technological Development (FP 7)*.

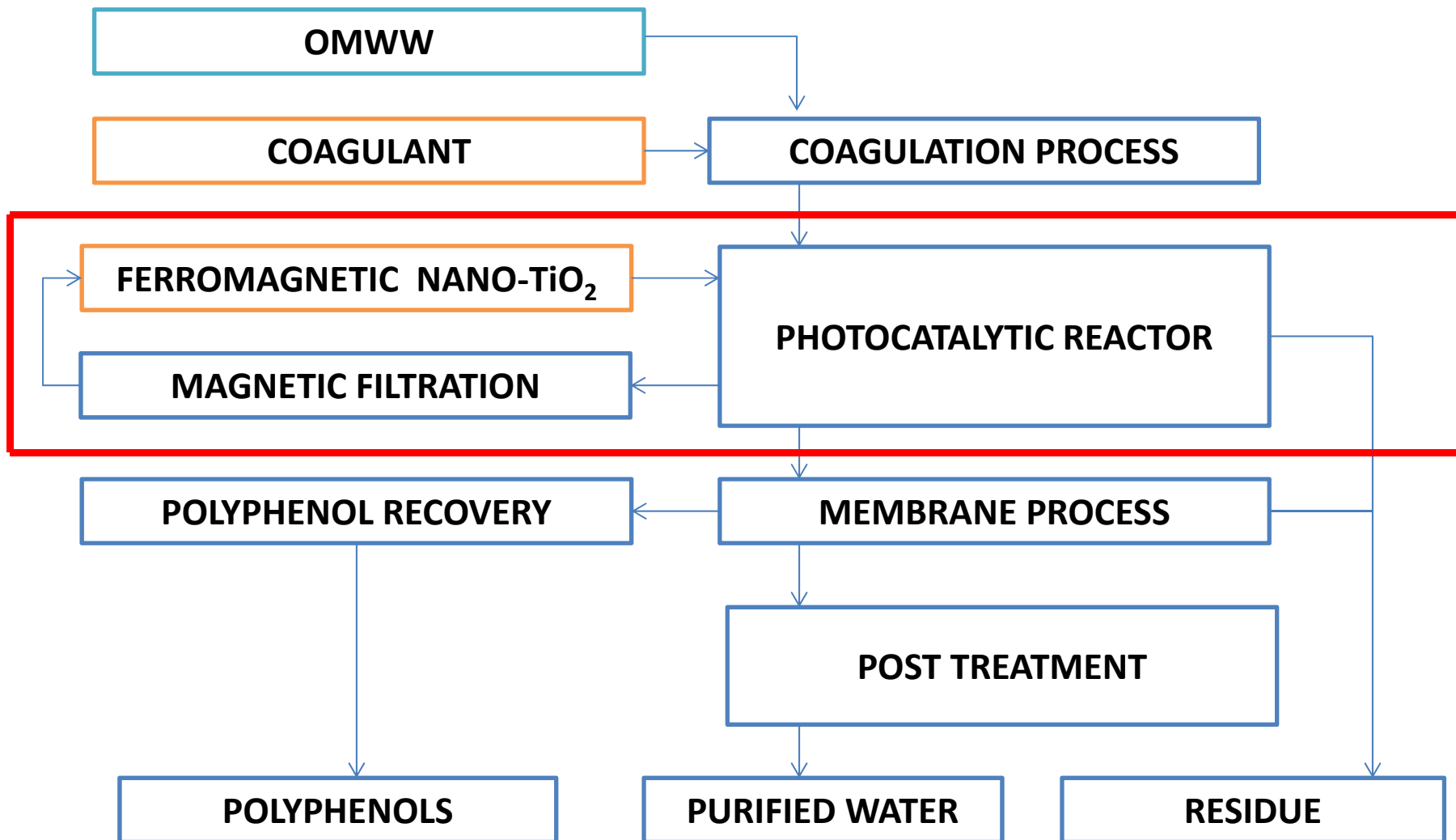
**The aim** of PHOTOMEM is to define and implement an innovative process for the treatment of wastewater derived from agro-food processing, in particular olive mill wastewater (OMWW).

**OMWW is a strong pollutant** generated in the production of olive oil:

- Mass ratio 0.8 ton per ton of olive
- COD value in the range 40 – 150 g/l
- Phytotoxicity due to the presence of phenolic compounds



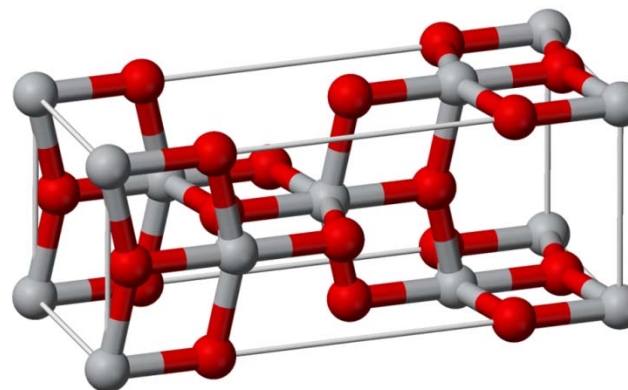
# PHOTOMEM OMWW TREATMENT SCHEME



# TITANIUM DIOXIDE AS A CATALYST

*TiO<sub>2</sub> in its anatase phase has deserved particular interest due to its*

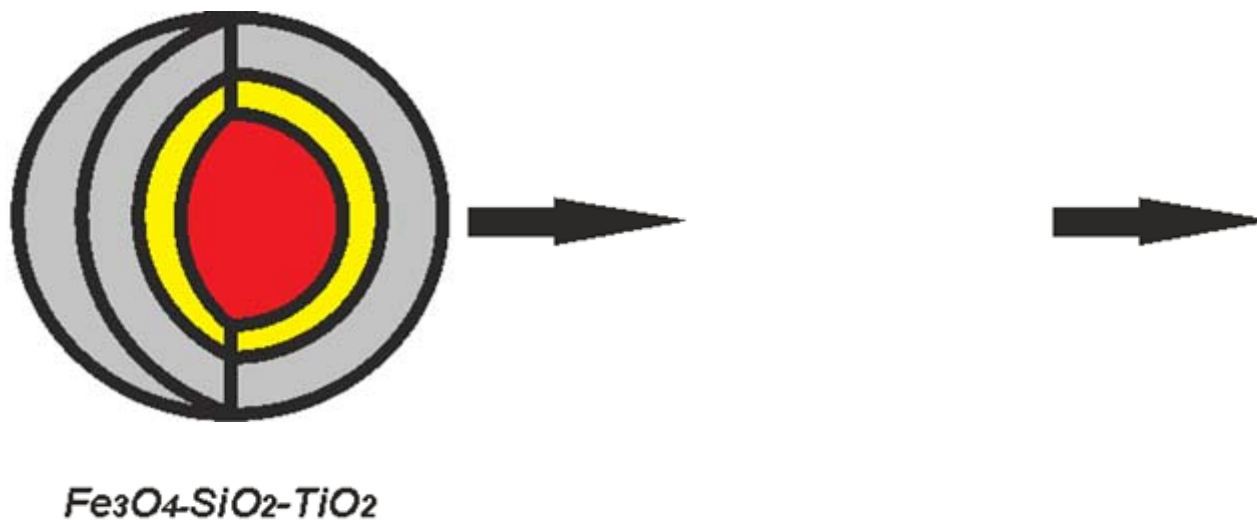
- excellent photo catalytic properties
- chemical stability
- relatively low cost



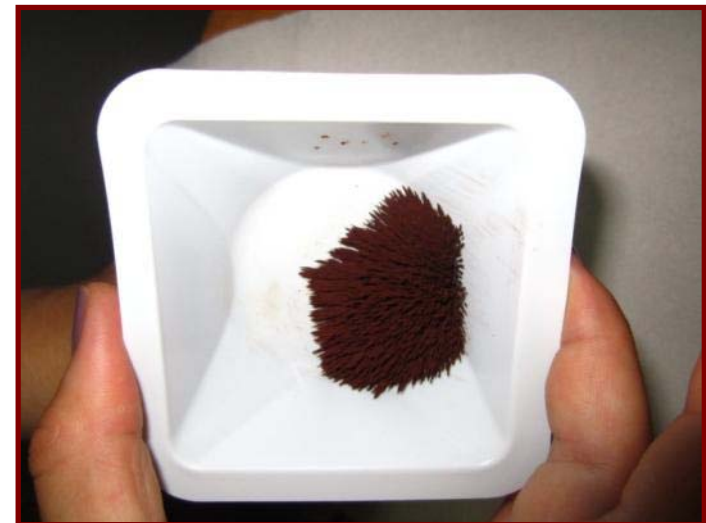
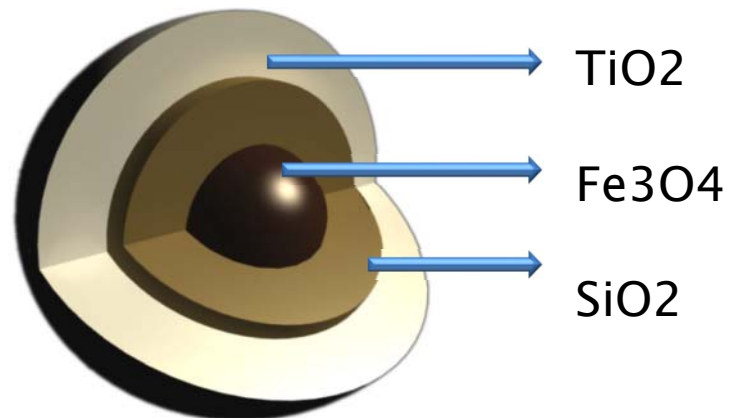
*The crystalline structure  
anatase of TiO<sub>2</sub>*

**Technological problem** in the application of the TiO<sub>2</sub> for wastewater treatment is the presence in the purified water of TiO<sub>2</sub> powder dispersion.

# COMPOSITE CORE-SHELL-SHELL NANOPARTICLES STRUCTURE



Core-shell-shell particles of magnetite, silica and titania were produced for photocatalytic application for the treatment of OMWW.

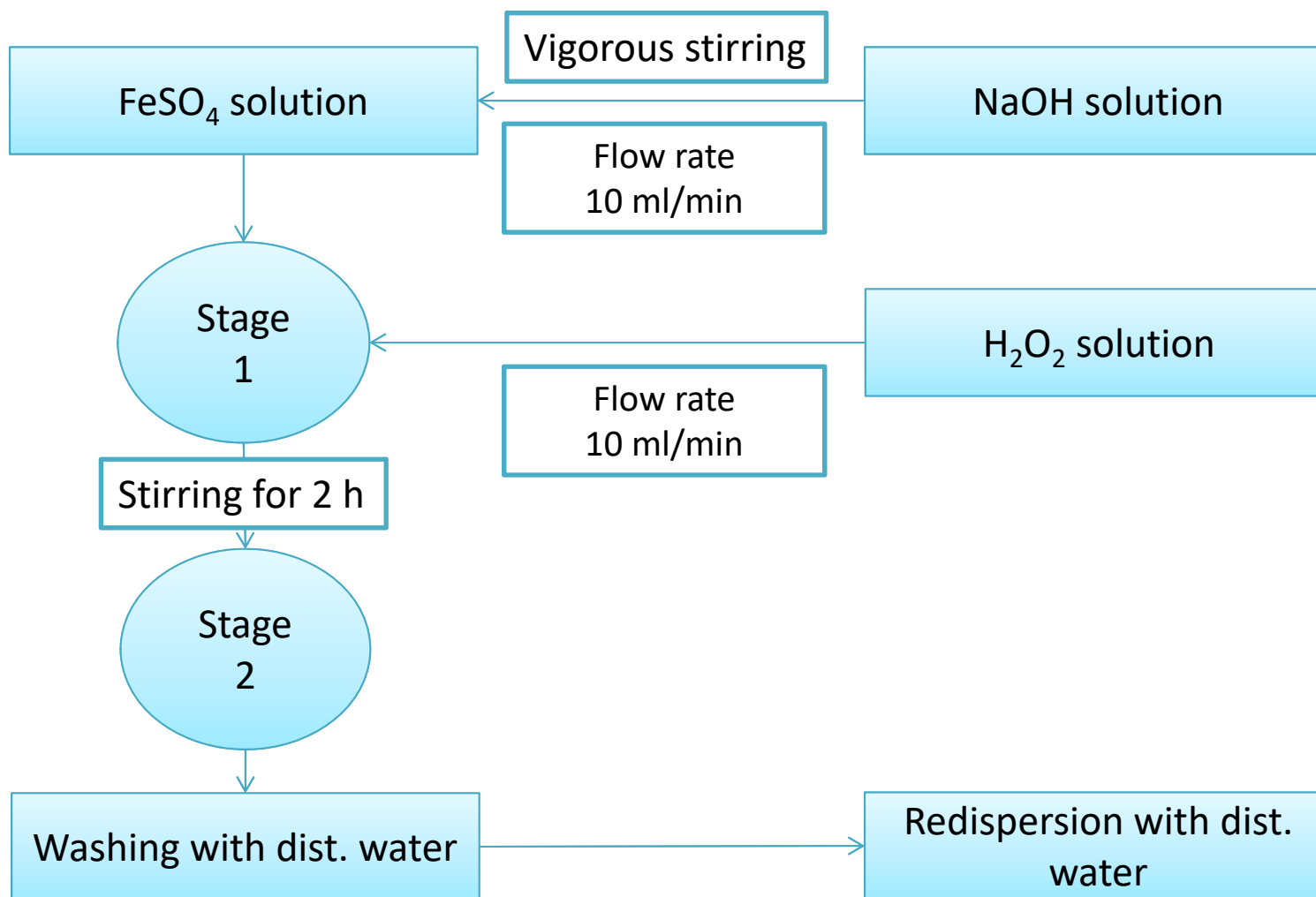


Dimension	$\Delta$ COD	Recovery	$\Delta$ COD	Recovery[%]
	First treatment	[%]	Second treatment	
	[%]		[%]	
40 nm	88%	95%	44%	90%
80 nm	60%	90%	59%	88%

**Experimental runs have demonstrated that it was possible to achieve constant performances for 10 consecutive batches.**

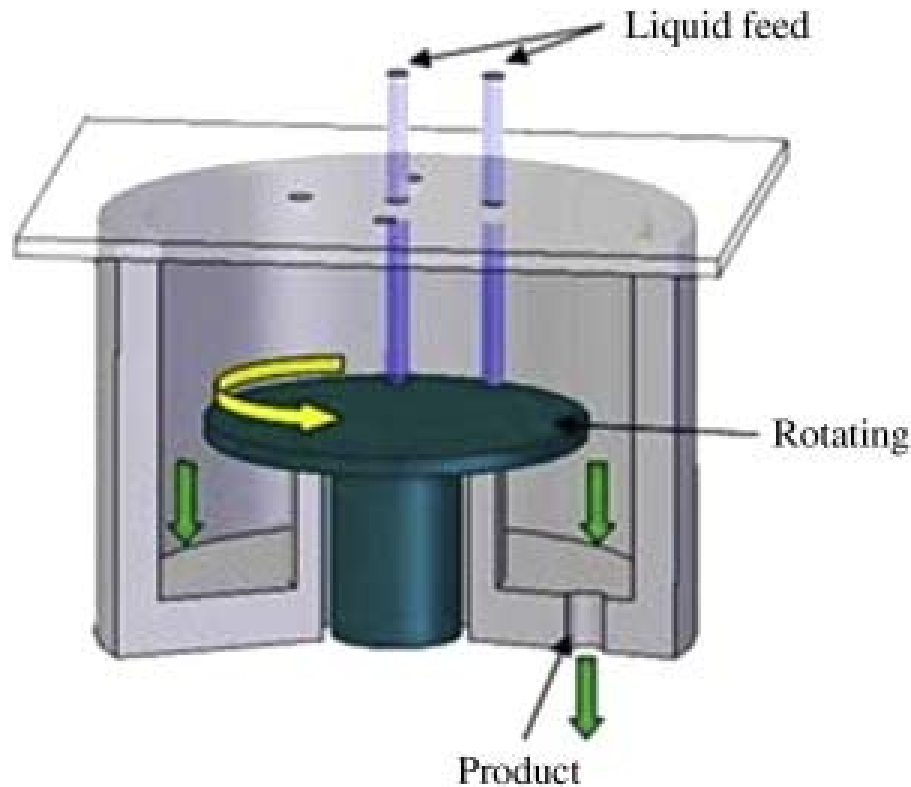
**Moreover, fouling of the subsequent membrane processes is strongly inhibited.**

# $\text{Fe}_3\text{O}_4$ MAGNETIC CORE SYNTHESIS



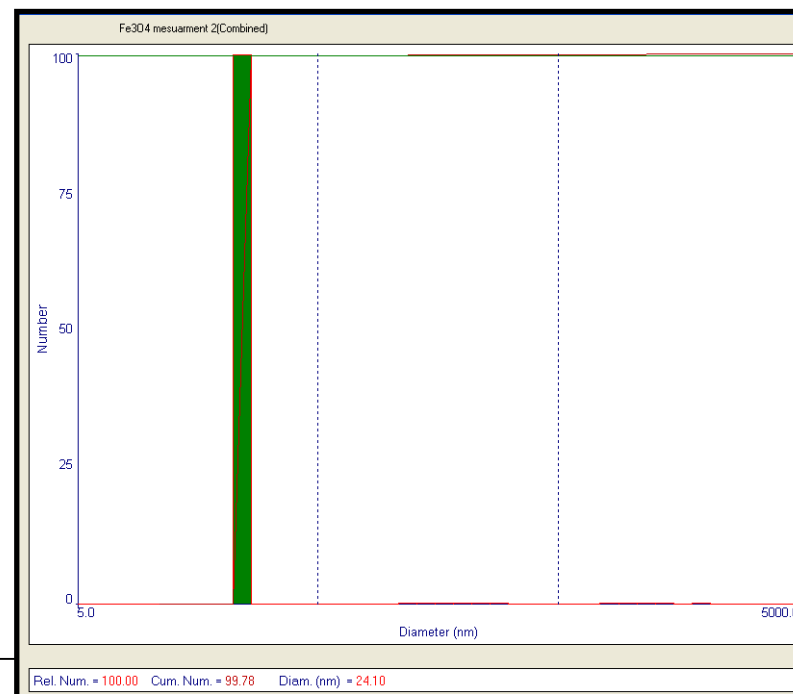
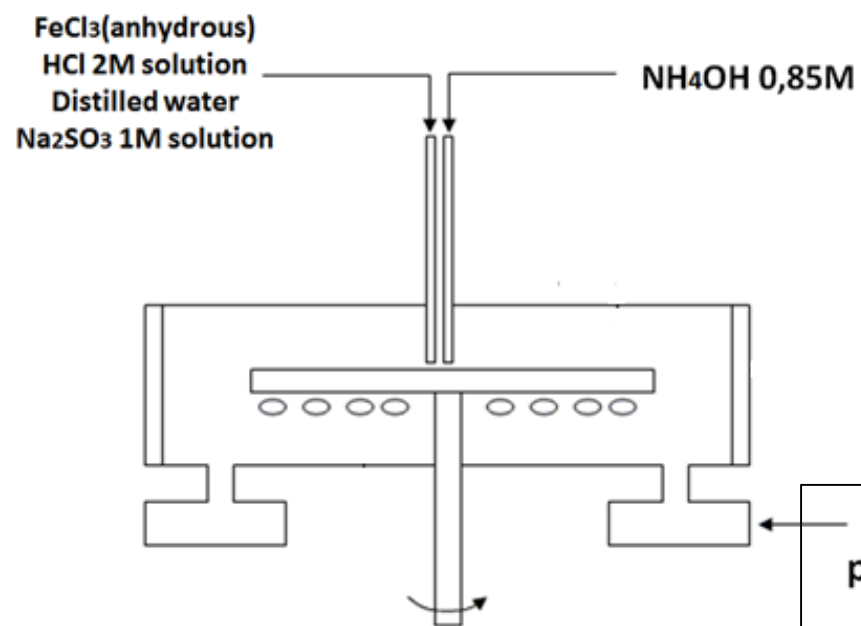


# Set up for the $\text{Fe}_3\text{O}_4$ magnetic core NP production: Spinning Disc reactor



- Disc diameter – 8.5 cm
- Rotational speed (max) – 1400 rpm
- Ambient temperature
- Disk material: PVC

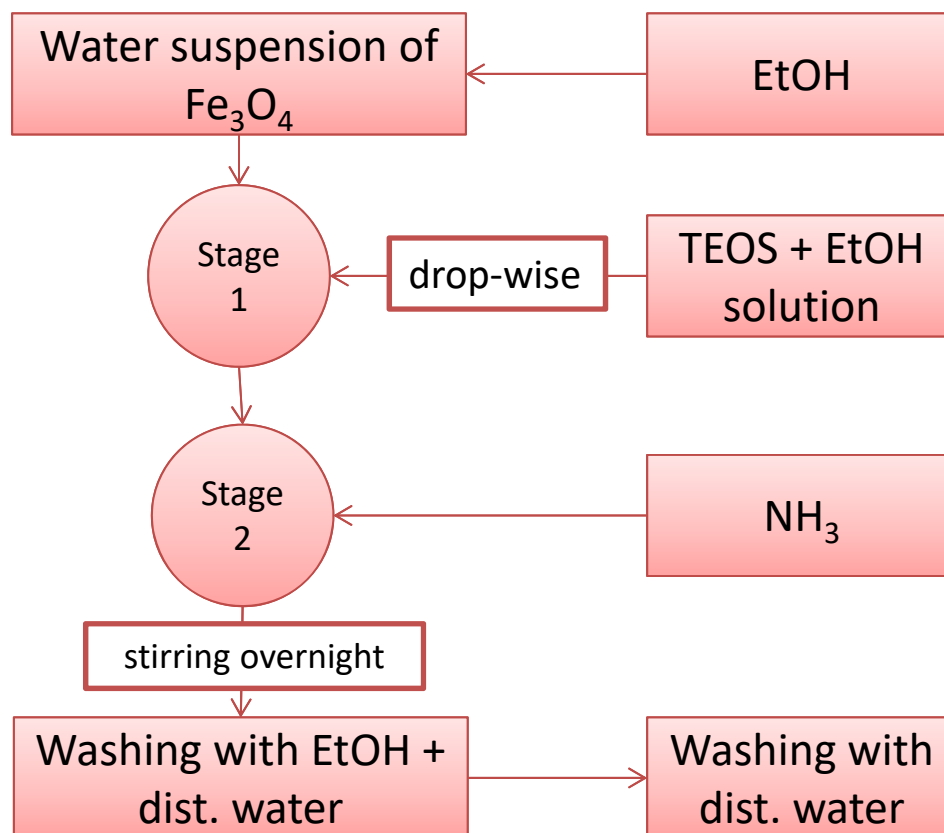
# $\text{Fe}_3\text{O}_4$ magnetic core NP production process: Reaction precipitation



Final  
product

Size distribution of  $\text{Fe}_3\text{O}_4$   
Nanoparticles (24 nm)

# Production process of the SiO<sub>2</sub> intermediate layer

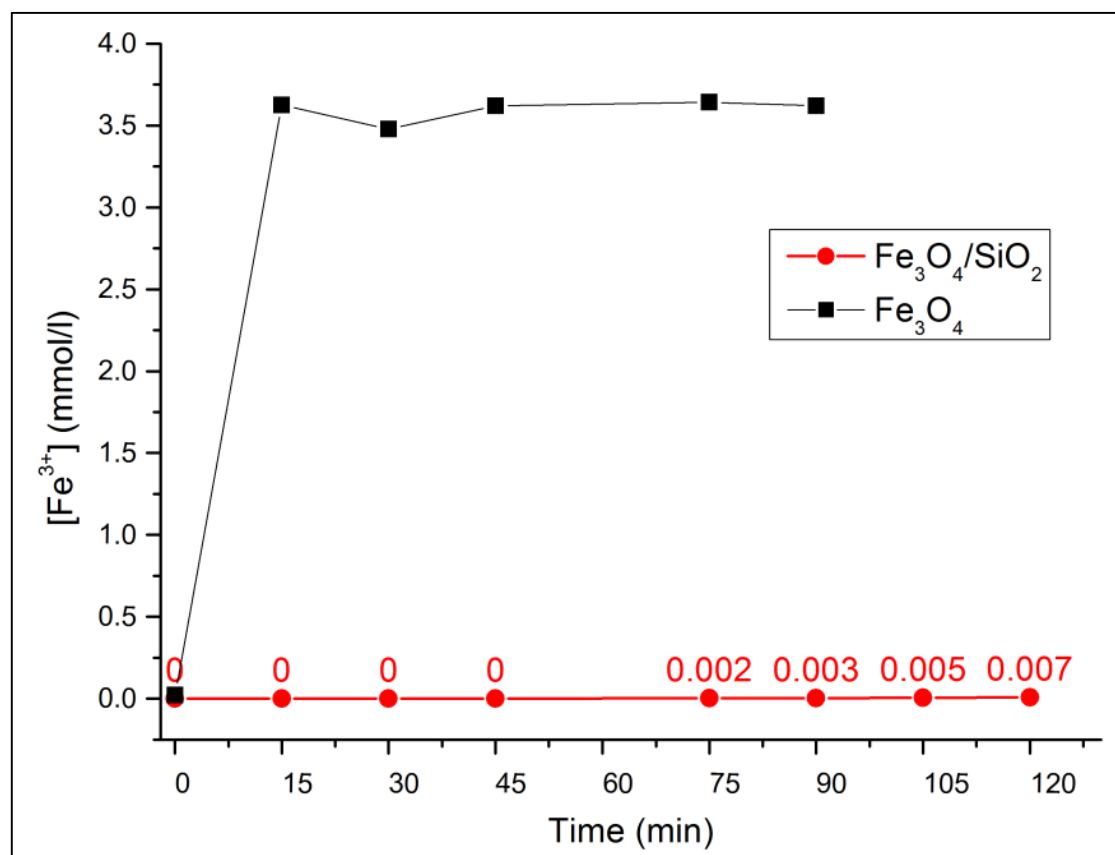


Parameters	Stöber method
SiO <sub>2</sub> precursor	TEOS
Reactants ratio	EtOH : H <sub>2</sub> O : NH <sub>3</sub> = 20 : 5 : 1

# SiO<sub>2</sub> intermediate layer: coating check

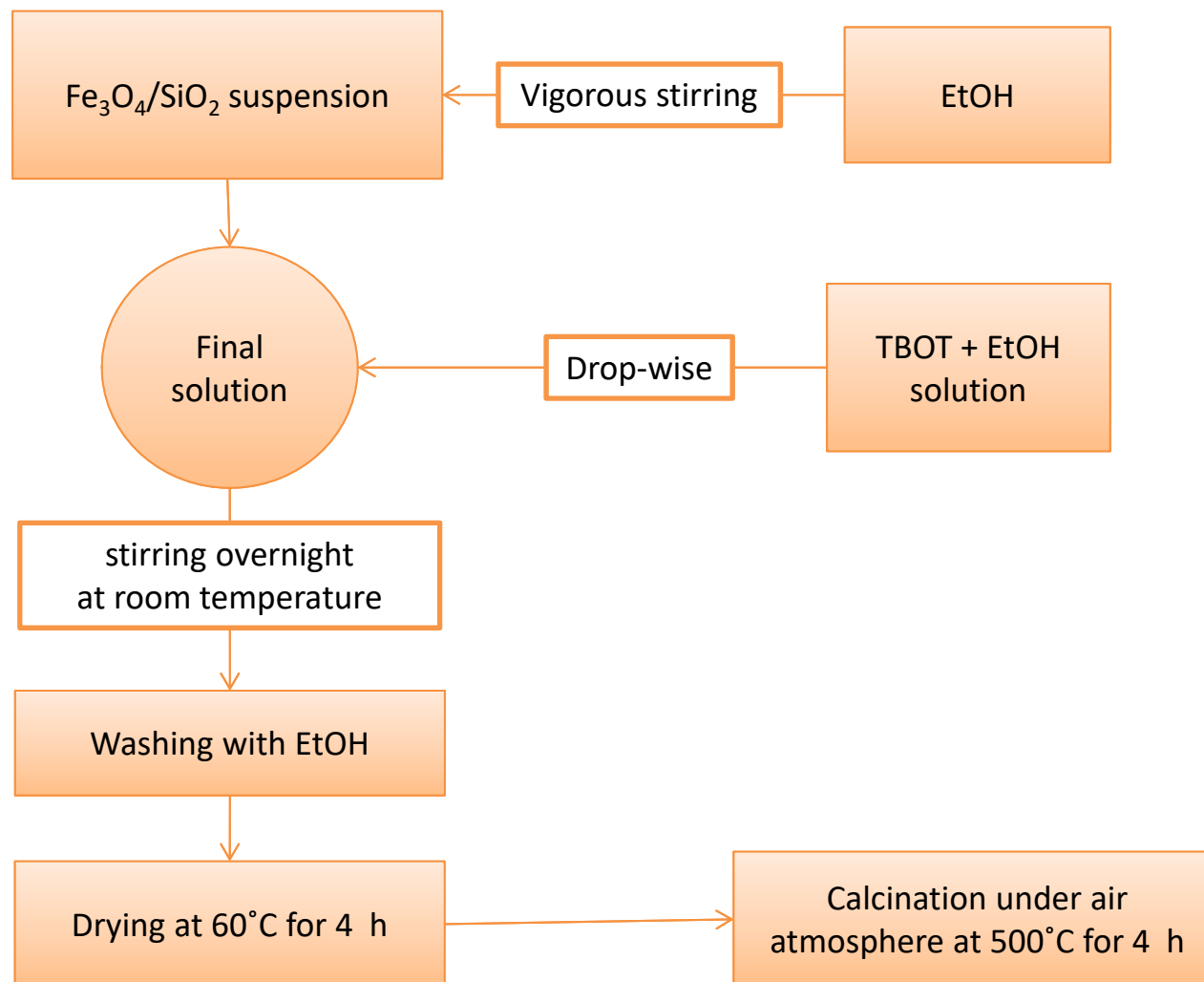
Estimated silica layer thickness: 22 nm

The check was based on the dissolution of the magnetite core by HCl acidification.

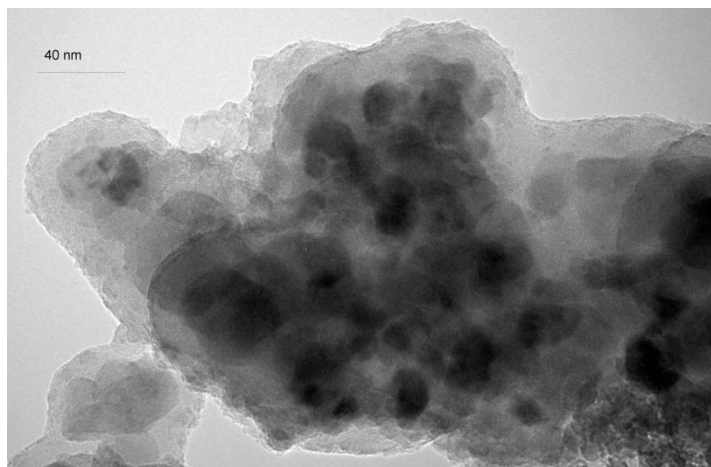


**Silica coating avoids any HCl attack of the core**

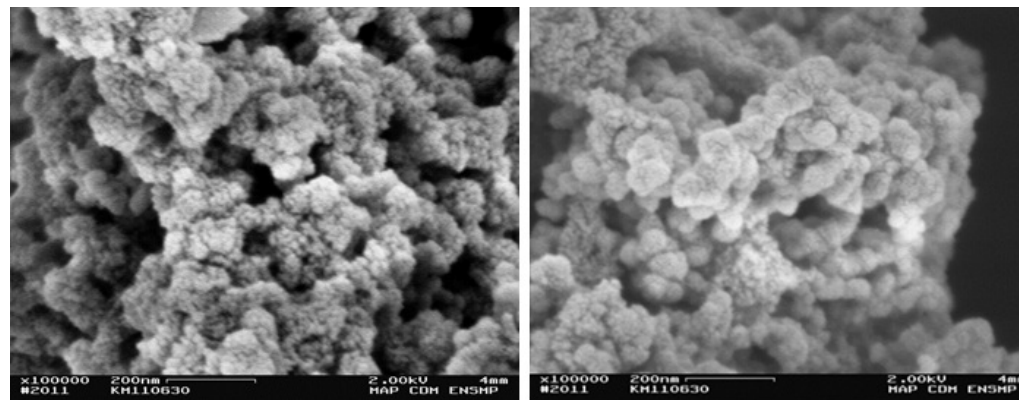
# Production process of the $\text{TiO}_2$ external layer



# TiO<sub>2</sub> COATING (Sol-gel method - TBOT)

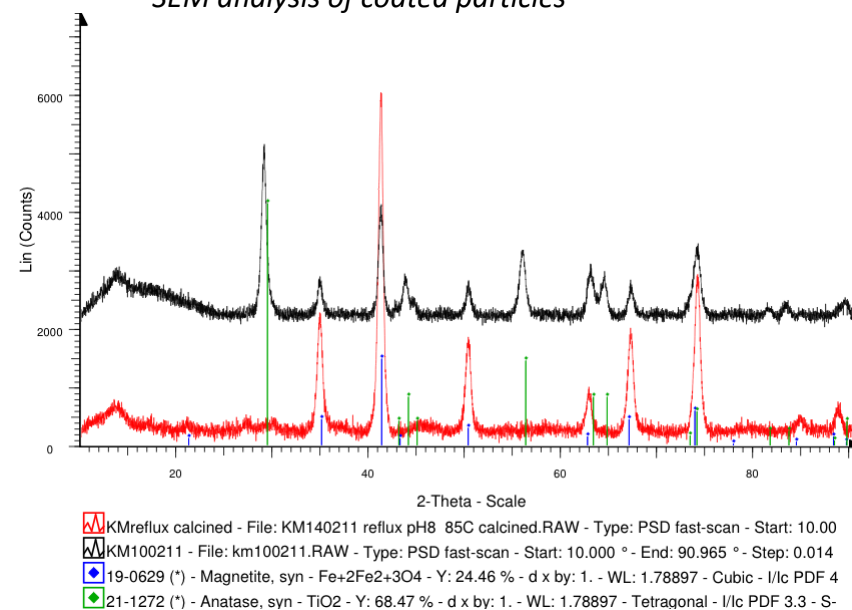


TEM analysis of coated particles



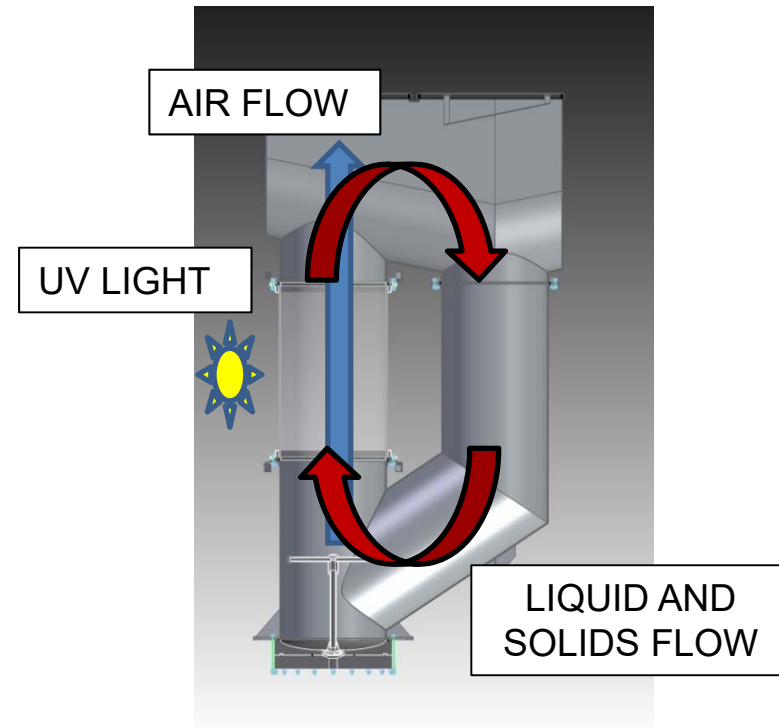
SEM analysis of coated particles

BET summary	
Surface area	105.9 m <sup>2</sup> /g
Equivalent spherical diameter	70 nm



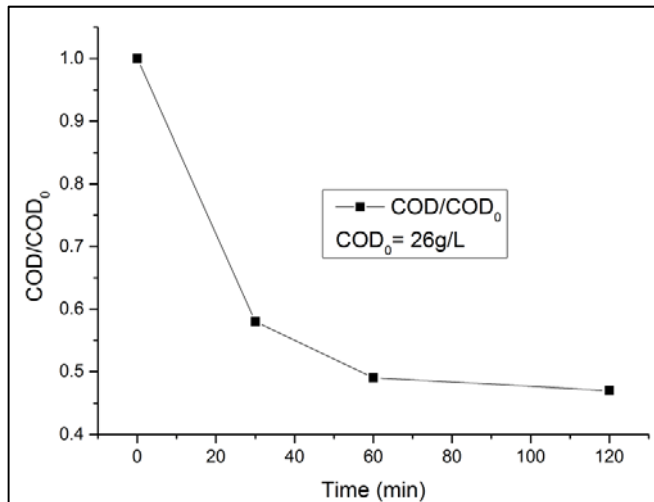
X-Ray diffractograms of silica and titania coated magnetite particles

# PHOTOCATALYSIS EXPERIMENTS (LAB SCALE SET UP)

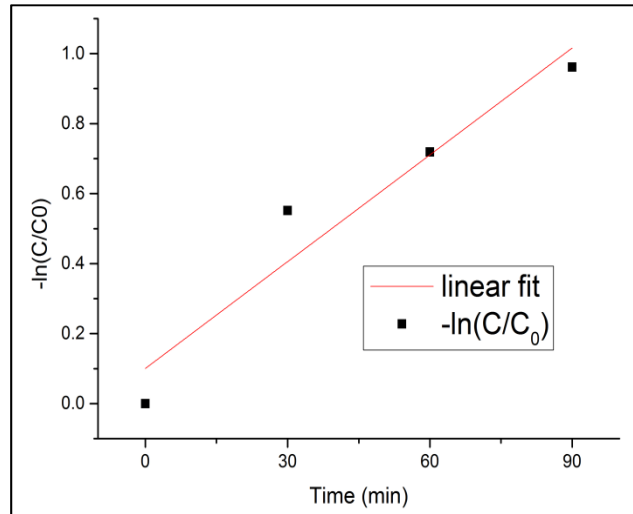
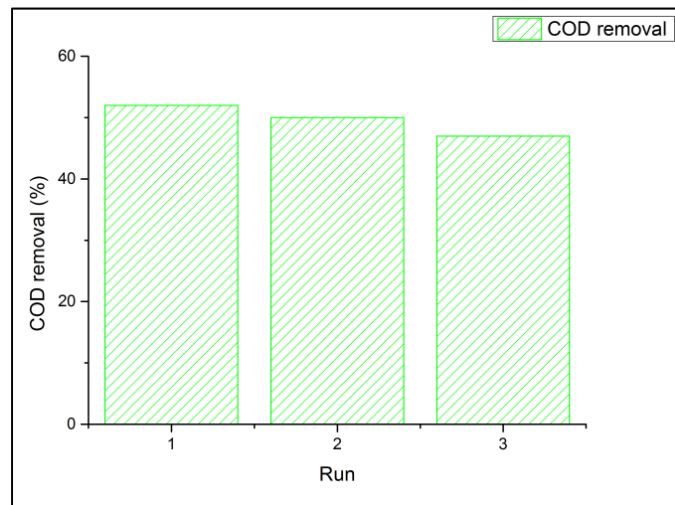


*Airlift reactor adopted for the lab tests (reactor volume 0,5 L)*

# PHOTOCATALYTIC TESTS ON THE AIRLIFT REACTOR



Repeatability Test, after TiO<sub>2</sub> removal

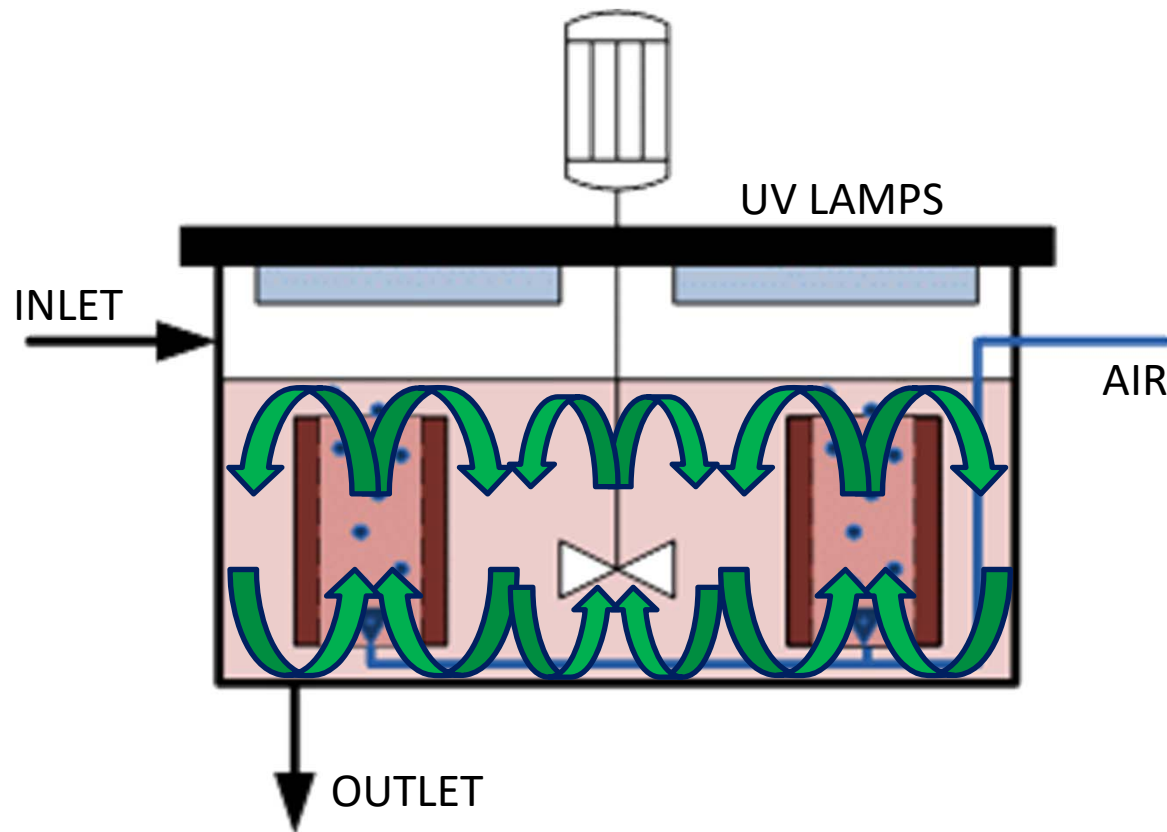


Reaction order	Pseudo-first
Reaction constant, k	0.0116
R <sup>2</sup>	0.902

Photocatalysis parameters	
Solution	Flocculated OMWW
COD	26 g/L
Catalyst dose	1.5 g/l
Air flow rate	4 LPM
Irradiation	UV light 365 nm 40 W lamp
Irradiation time	2 h



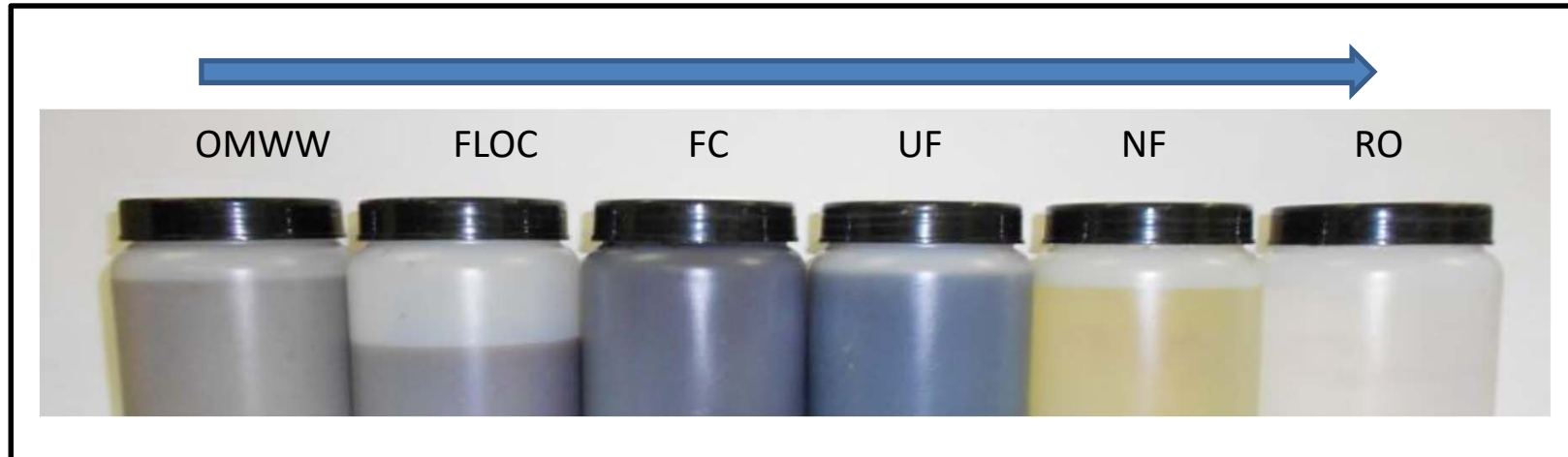
# PILOT REACTOR



# PHOTOCATALYTIC TESTS ON THE PILOT REACTOR

	Measured value
<b>Inlet stream</b>	Flocculated wastewater
<b>COD [mg/l]</b>	19350
<b>Organic degradation</b>	35 %
<b>Photocatalyst dose</b>	1.5 g/l
<b>Reactor Volume</b>	0,5 m <sup>3</sup>

# PHOTOMEM PROCESS PERFORMANCES



	COD [mg/l]	pH [-]	TSS [g/l]	Volume [l]
OMWW	34360	4.62	221.3	251
Purified water	412	6.5	0.0	189
Legal limit in Italy for municipal sewer system	500	5.5 – 8.5	0.0	-

# CONCLUSIONS

- ✓ In this study the technique for the production of composite core-shell-shell  $\text{TiO}_2$  nanoparticles is presented and the relevant photocatalytic results are discussed.

**The preparation process** goes in 3 steps:

- Synthesis of core magnetic particles based on  $\text{Fe(II)}$  precipitation followed by oxidation with  $\text{H}_2\text{O}_2$
  - Production of silica coating based on Stöber process
  - Production of titania coating based on titanium tetrabutoxide hydrolysis
- ✓ The NP photocatalytic activity tested on the organic degradation of OMWW gave satisfactory results either in a lab plant or in a pilot plant .
  - ✓ A very high recovery grade of the NP was obtained thanks to the magnetic core > 95 %.
  - ✓ By using photocatalysis in the treatment process of OMWW it was possible to reach the required OMWW purification ( $\text{COD} < 500 \text{ mg/l}$ ) and to reduce the membrane fouling.

## N-doped magnetic titania nanoparticles ???

