

# Photocatalytic Treatment of Olive Mill Wastewater by Magnetic Core Titanium Dioxide Nanoparticles

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The photocatalytic degradation of organic compounds of olive mill wastewater (OMWW) was investigated by using core-shell-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles as catalyst. The preparation of nanoparticles was performed by coating onto magnetic nanoparticles a  $\text{SiO}_2$  layer, using Stober method and  $\text{TiO}_2$  layer, using sol-gel method. The photo catalyst was characterized by dynamic light scattering (DLS), zeta-potential measurement, UV-visible spectroscopy, energy-dispersive X-ray diffraction (EDX), scanning electron microscopy (SEM). Batch photo reactor, irradiated by an UV lamp of 45 W, was used to check the photocatalytic activity of the produced nanoparticles. The organic content of OMWW was evaluated by COD measurements.

The photo degradation process was optimized by using 1.5 g/L core-shell-shell nanoparticles. The obtained results showed a high activity of synthesized nanoparticles for photocatalytic degradation of the OMWW organic compounds. Moreover, the recovery of the magnetic core photo catalyst by using a magnetic trap was proven.

## 1. Introduction

The use of heterogeneous photo catalysis to solve global pollution problems has been increasing in the last decades owing to its great potential to remove aqueous and air pollutants through complete mineralization (Valencia et al., 2011). Among the known semiconductor photo catalysts ( $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{CdS}$ ,  $\text{ZnS}$ ,  $\text{SrTiO}_3$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ),  $\text{TiO}_2$  in its anatase phase has deserved particular interest due to its high oxidizing power of organic contaminants, chemical stability and low cost (Tieng et al., 2011). The possibilities of application of this material are being investigated since early 1970s of the 20<sup>th</sup> century after a pioneering work by Fujishima et al. (1972). Titanium dioxide is nowadays a well-known and commercially used photo catalyst (Tyrpekl et al., 2011). Nanocrystalline  $\text{TiO}_2$  immobilized on supporting materials such as glass, sand, or zeolite can improve the separation efficiency. Magnetic separation provides a very convenient approach for removing and recycling magnetic particles (such as magnetite, ferrite, and barium ferrite) by applying external magnetic fields. The incorporation of magnetic components into  $\text{TiO}_2$  nanoparticle-based catalysts may, therefore, enhance the separation and recovery of nanosized  $\text{TiO}_2$  (Ye et al., 2010). Very recently, a large scale synthesis of discrete and uniformly sized super paramagnetic  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  has been developed (Schatz et al., 2009). The silica shell thickness can be controlled from 12.5 nm to 45 nm by varying the operating parameters. The reaction time, the ratio of TEOS/ $\text{Fe}_3\text{O}_4$ , and the concentration of hydrophilic  $\text{Fe}_3\text{O}_4$  seeds were found to be very important parameters in the control of silica shell thickness (Hui et al., 2011). However, there are currently very few literature which report on the synthesis of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  core-shell nanoparticles and their photocatalytic properties. Gad-Allah et al. (2009) reported the preparation of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanocomposites. However,  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  core-shell nanoparticles prepared by him were in the form of patches and not discrete nanoparticles. As such, these core-shell nanoparticles exhibited a reduction of their surface area and photocatalytic properties, as well. Abramson et al. (2009) produced core-shell-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles of few tens nanometers by successively coating onto magnetic nanoparticles a  $\text{SiO}_2$  layer and a  $\text{TiO}_2$  layer, using sol-gel methods. In this work, firstly the production procedure of core-shell-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles is presented, then the effectiveness of the photocatalysis assisted by such nanoparticles to degrade the organic

compounds of olive oil mill vegetation wastewater (OMWW) is reported. This latter wastewater is characterized by high organic load, with COD values up to 80 g/L, high salinity, acid pH values and a high content of polyphenols, when it comes out from a tree-stages olive oil production process. It results to be strongly phytotoxic and thus its disposal on the terrain is not advisable. As a consequence OMWW represents a serious environmental threat, in particular for the Mediterranean countries, which requires an urgent solution from a technical and economical point of view. Membrane technologies appears the most promising technique to treat different kind of wastewater streams of agricultural origin containing organic matter, such as OMWW exiting the 2-phase and 3-phase production processes or the tomato industry (Stoller et al., 2006; laquinta et al., 2009; Ochando-Pulido et al., 2012). One of the main problem in applying this technique is membrane fouling, and to understand the complex undergoing phenomena leading to this (Stoller, 2011; Stoller and Chianese, 2006; Stoller and Bravi, 2010). Methods to inhibit membrane fouling involves both the search of optimal operating conditions as well as the application of suitable pretreatment processes such as photocatalysis, flocculation, gridding, coagulation, biotech and others (Stoller and Chianese, 2007; Stoller, 2008; Stoller, 2009; Stoller et al., 2013). Photocatalysis appears to be a very efficient pretreatment process for wastewater streams containing organic matter and for fouling inhibition purposes on membranes purifying wastewater streams containing organic matter, thus increasing both productivity and longevity of the membrane modules (Stoller et al., 2011; Sacco et al., 2012).

## 2. Experimental procedure

The core-shell-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles were prepared by three steps. Firstly,  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were synthesized using spinning disk reactor (SDR) by the application of an optimized protocol (Stoller et al., 2009; Parisi et al., 2011). Then,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  core shell nanoparticles were prepared by Stober method, and, finally, a  $\text{TiO}_2$  sol-gel material was used for the external coating of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  nanoparticles.

### 2.1 Materials

Materials which were used in the experimental procedure are submitted below.

Table 1: The chemicals used in the experimental procedure

Chemicals	Formula	Brands	Purity, (%)
Iron (III) chloride	$\text{FeCl}_3$	Sigma Aldrich	>97
Hydrochloric acid	HCl	J.T. Baker	36 - 38
Sodium sulphite	$\text{Na}_2\text{SO}_3$	Sigma Aldrich	98
Ammonium hydroxide solution	$\text{NH}_4\text{OH}$	Sigma Aldrich	33
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	Carlo Erba	96
TEOS	$\text{Si}(\text{OC}_2\text{H}_5)_4$	Sigma Aldrich	98
2-propanol	$\text{C}_3\text{H}_8\text{O}$	Fluka	
Hydrogen peroxide	$\text{H}_2\text{O}_2$	Sigma Aldrich	$\geq 35$
TTIP	$\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$	Sigma Aldrich	97

### 2.2 Synthesis of $\text{Fe}_3\text{O}_4$ magnetic nanoparticles

$\text{FeCl}_3$  were dissolved in a 2 M aqueous solution of HCl under gentle stirring. Afterwards, in two subsequent steps distilled water and 1 M aqueous solution of  $\text{Na}_2\text{SO}_3$  were added. The obtained solution was maintained under stirring mixed for 20 min. The so produced solution is yellow in color, hereafter named "1". Beside, a 0.85 M aqueous solution of  $\text{NH}_4\text{OH}$ , called "2", were prepared.

The  $\text{Fe}_3\text{O}_4$  nanoparticles were precipitated by means of a spinning disc reactor, reported in details elsewhere (de Caprariis et al., 2012). The solution "1" was injected on the spinning disk at 2 cm from the center, whereas the solution "2" was fed at the disc center. The rotation velocity of the disc was set at 1400 rpm. The precipitate was immediately collected from the bottom of the spinning disc reactor. The obtained slurry was mixed by means of a mechanical stirrer for 12 h. The produced particles were separated from liquid by applying a magnet field then they were submitted to several washing with distilled water and dried at 105 °C.

### 2.3 Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticles

The magnetite particles were suspended in distilled water. Then  $\text{C}_2\text{H}_5\text{OH}$  was added to that suspension. TEOS, preliminarily diluted in  $\text{C}_2\text{H}_5\text{OH}$ , was added drop-wise to the magnetite particle suspension. Then an aqueous solution of  $\text{NH}_4\text{OH}$  (28 %) was added and the TEOS hydrolysis and condensation was allowed

under overnight gentle stirring. The obtained magnetite particles covered by a silica layer were washed in a centrifuge using firstly water/ethanol mixtures then distilled water. Finally, they were dried and calcinated at 450 °C for 30 min.

#### 2.4 Synthesis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> core-shell-shell nanoparticles

In order to produce the TiO<sub>2</sub> sol material, titanium tetraisopropoxide was dissolved in 2-propanol and then hydrolyzed with distilled water. The white precipitate of hydrous oxide was instantaneously produced, then the mixture was stirred for 10 min. The amorphous precipitate was separated by centrifugation and washed three times with distilled water for complete removal of alcohol. Afterwards, hydrogen peroxide was added to the obtained slurry drop-wise (Jagdale et al., 2008). The precipitate was completely dissolved by the reaction with hydrogen peroxide and a transparent orange sol of titanium-hydrogen peroxide complex was formed. Then Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanoparticles were added into the sol. This transparent orange sol slowly thickened and transformed into the gel. The obtained nanoparticles were dried under the visible-light lamp and calcinated for 4 h at 500 °C.

### 3. Characterization of the produced nanoparticles

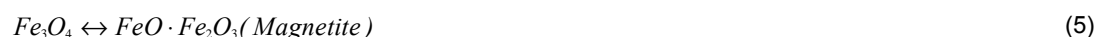
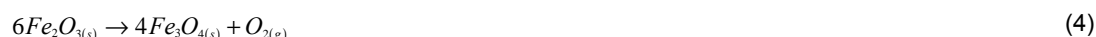
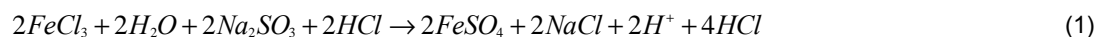
The size distribution of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles was measured by a dynamic light scattering supplied by Brookhaven. This instrument was also used to measure the Z-potential of all the produced nanoparticles suspensions. An energy-dispersive X-ray diffraction (EDX) analysis was performed to determine the presence of the atoms of silicon and titanium. Simple dissolution test was carried out to check the effectiveness of the silica coating insulation: a small amount of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanoparticles were dispersed in an aqueous solution of HCl (37 %) and the suspension was kept under stirring. Every 15 min samples of solution were withdrawn, centrifuged and UV-visible spectra of supernatants were measured. The UV-visible spectroscopy measurements were performed in an UV-1800 PC spectrophotometer. Scanning electron microscopy performed by an Auriga Zeiss instrument was used to observe the overall morphology of the nanoparticles.

### 4. Photocatalytic activity

Photocatalytic tests on the degradation of organic compounds in OMWW were performed in batch mode. OMWW was flocculated and centrifuged before photocatalytic process and the clarified solutions were used for the experiments. The COD of the clarified OMWW was equal to 26.1 g/L. The set-up consisted of a 1 L Pyrex-glass beaker, 10 cm in diameter and 14 cm in height. 3 × 15 W UV mercury lamp (λ=365 nm) was placed under the beaker at 5 mm from the bottom to continuously irradiate the slurry. 300 mL of olive mill wastewater (OMWW) and 1.5 g of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles were used for each 2 h experiment. Air was purged into the solution by bubbling. The slurry was agitated by a three blade marine stirrer. All experiments were carried out at ambient temperature. Samples were taken every 30 min. Every sample was centrifuged, diluted with distilled water, and its COD was measured by Dr. Lange Lasa-100 analyzer.

### 5. Results and discussion

The SDR was used to precipitate Fe<sub>3</sub>O<sub>4</sub> ferromagnetic nanoparticles. The synthesis of Fe<sub>3</sub>O<sub>4</sub> core is described by the following equations.



The resulting particles were highly agglomerated and before using light scattering instrument to measure their size the agglomerates were carefully dispersed by using an ultrasound bath. Figure 1 shows the obtained particle of magnetite and of the composite Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>, respectively. The Fe<sub>3</sub>O<sub>4</sub> size distribution was quite narrow with an average size of 18.7 nm. The core magnetic particles was nanometric in size, exhibiting an average size of 70.5 nm. The z-potential values of the magnetite, silica covered and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles were also measured. The z-potential value of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was -

37.5 mV, which means the magnetite solution are electrically moderate stabilized. The z-potential values of  $Fe_3O_4/SiO_2$  and  $Fe_3O_4/SiO_2/TiO_2$  nanoparticles, was equal to - 46.4 mV and 40.0 mV, respectively, showing a good electrical stability.

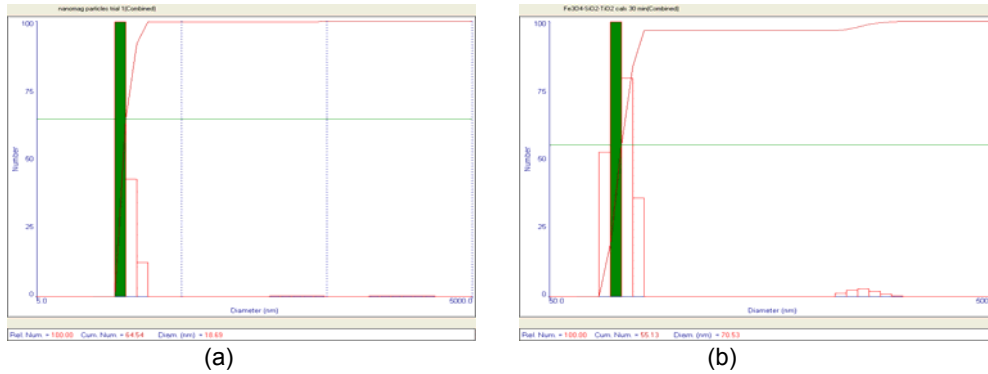


Figure 1: Size distribution of  $Fe_3O_4$  magnetic nanoparticles (a) and  $Fe_3O_4/SiO_2/TiO_2$  (b).

Simple dissolution test was carried out to check a silica coating insulation function. The results, reported in Figure 2 with those on magnetic nanoparticles for comparison, showed a very good surface protection of  $SiO_2$  layer. It means that all ferromagnetic nanoparticles are homogenously covered by  $SiO_2$  and silica coating is dense.

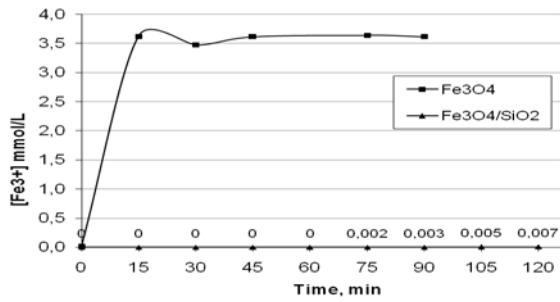


Figure 2: dissolution kinetics of magnetite nanoparticles

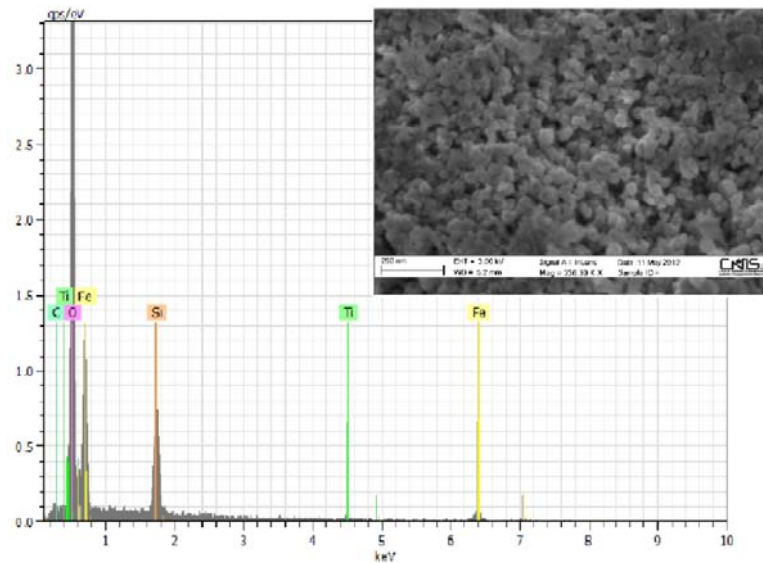


Figure 3: SEM picture and EDX spectrum of the  $Fe_3O_4/SiO_2/TiO_2$  nanoparticles

TiO<sub>2</sub> nanoparticles were synthesized by sol-gel method. The process is described by the following equations.



SEM image of the nanoparticles, reported in Figure 3, was carried out to observe the overall morphology of the particles, which appears quite regular. Moreover, EDX analysis was performed to determine the composition of the composite nanoparticles. The EDX spectrum shows that the composition of the obtained nanopowder consisted of Fe, Si and Ti elements, which confirms the presence of both the silica and TiO<sub>2</sub> layers. Figure 3 shows SEM picture and EDX spectrum of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles.

The OMWW sample used for the photocatalytic runs was preliminarily submitted to flocculation and centrifugation to eliminate the suspended solid. The COD and pH of the clarified solution was equal to 26.1 g/L and 3.0, respectively. Three subsequent runs were made in order to evaluate the effectiveness of the catalyst after its recovery. The results, reported in Figure 4 shows a COD reduction of about 50 % after two hours for the first run. The second and third runs showed a moderate loss of catalyst effectiveness, due to adsorption of heavy organic compounds over the nanoparticles surface. The results proven a high photocatalytic activity of the produced nanostructured catalyst and the possibility of its re-use.

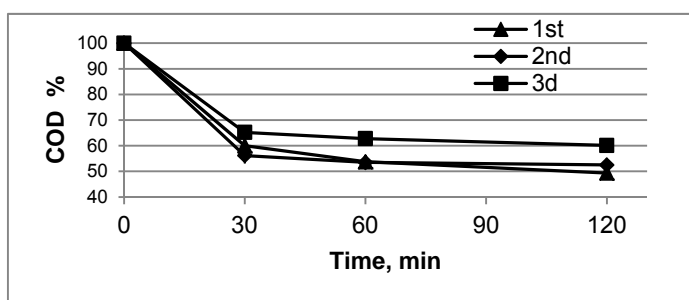


Figure 4: Reproducibility of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> nanoparticles

For comparison, 58 % removal of COD (initial COD value 1,960 mg/l) was determined after 24 h exposure to 365 nm UV light (Baransi et al., 2012) and 70 % removal COD (initial value 117.8 mg/L) was determined after 60 min of UV-irradiation by using 2 g/L of TiO<sub>2</sub> (Badawy et al., 2009). The relatively smaller COD removal is largely justified by the higher value of the initial COD, i. e. 26.1 g/L, of the treated OMWW.

## 6. Conclusions

In this paper firstly the procedure to produce a magnetic core-shell photocatalyst was carefully described, then its characterization and effectiveness in degradation of organic compounds present in an OMWW sample was reported. The produced nanoparticles were 70 nm in size and its compositions, proven by a microanalysis, was in agreement with their three steps structure. The efficiency of the OMWW organic degradation was around 50 %. The composite nanoparticles were easily recovered by their magnetic core and re-used without significant reduction of efficiency. The use of such nanoparticles is very interesting for photocatalysis applications, since they join a good catalytic efficiency with the possibility of their recovery, thus dramatically cutting the catalyst cost.

## Acknowledgements

This research work was carried out in the framework of the European project PHOTOMEM (Grant agreement 242670).

## References

Abramson S., Srithammavanh L., Siaugue J-M., Horner O., Xu X., Cabuil V., 2009, Nanometric core-shell-shell  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> particles, Journal Nanopart Res 11, 459-465.

- Badawy M.I., Gohary F.El., Ghaly M.Y., Ali M.E.M., 2009, Enhancement of olive mill wastewater biodegradation by homogeneous and heterogeneous photocatalytic oxidation, *Journal of Hazardous Materials* 169 (1-3), 673-679.
- Baransi K., Dubowski Y., Sabbah I., 2012, Synergetic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater. *Water Research* 46,789-798.
- de Caprariis B., Di Rita M., Stoller M., Verdone N., Chianese A. 2012, Reaction-precipitation by a spinning disc reactor: Influence of hydrodynamics on nanoparticles production, *Chem. Eng. Sci.* 76, 73-80.
- Fujishima A., Honda K., 1972, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 283, 37-38.
- Gad-Allah T.A., Kato S., Satokawa S., Kojima T., 2009, Treatment of synthetic dyes wastewater utilizing a magnetically separable photocatalyst ( $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ ): Parametric and kinetic studies, *Desalination* 244, 1-11.
- Hui C., Shen C., Tian J., Bao L., Ding H., Li C., Tian Y., Shiab X., Gao H-J., 2011, Core-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  nanoparticles synthesized with well-dispersed hydrophilic  $\text{Fe}_3\text{O}_4$  seeds, *Nanoscale* 3, 701-705.
- Iaquinta M., Stoller M., Merli C., 2009, Optimization of a nanofiltration membrane process for tomato industry wastewater effluent treatment, *Desalination* 245, 314-320.
- Jagdale T.C., Takale S.P., Sonawane R.S., Joshi H.M., Patil S.I., Kale B.B., Ogale S.B., 2008, N-Doped  $\text{TiO}_2$  Nanoparticle Based Visible Light Photocatalyst by Modified Peroxide Sol-Gel Method, *Journal Physical Chemistry* 112, 14595-14602.
- Ochando-Pulido J.M., Stoller M., Bravi M., Martinez-Ferez A., Chianese A., 2012, Batch membrane treatment of olive vegetation wastewater from two-phase olive oil production process by threshold flux based methods, *Separation and Purification Technology* 101, 34-41.
- Parisi M., Stoller M., Chianese A., 2011, Production of nanoparticles of hydroxyapatite by using a rotating disk reactor", 2011, *Chemical Engineering Transactions* 24, pp. 211-216, DOI: 10.3303/CET1124036
- Sacco O., Stoller M., Vaiano V., Ciambelli P., Chianese A., Sannino D., 2012, Photocatalytic Degradation of Organic Dyes under Visible Light on N-Doped Photocatalysts, *Int. J. Photoenergy*, Article ID 626759, 8 pages. DOI:10.1155/2012/626759
- Schatz A., Hager M., Reiser O., 2009, Cu (II)-Azabis (oxazoline)-Complexes Immobilized on Superparamagnetic Magnetite/Silica-Nanoparticles: A Highly Selective and Recyclable Catalyst for the Kinetic Resolution of 1,2-Diols, *Advanced Functional Materials* 19, 2109-2115.
- Stoller M., 2008, Technical optimization of a dual ultrafiltration and nanofiltration pilot plant in batch operation by means of the critical flux theory: a case study, *Chem. Eng. Proc. J.* 47, 1165-1170.
- Stoller, M., 2011, Effective fouling inhibition by critical flux based optimization methods on a NF membrane module for olive mill wastewater treatment, *Chem. Eng. J.* 168, 1140-1148.
- Stoller M., Bravi M. 2010, Critical flux analyses on differently pretreated olive vegetation waste water streams: some case studies, *Desalination* 250, 578-582.
- Stoller M., Bravi M., Chianese A., 2013, Threshold flux measurements of a nanofiltration membrane module by critical flux data conversion, *Desalination* 315, 142-148.
- Stoller M., Chianese A., 2006, Optimization of membrane batch processes by means of the critical flux theory, *Desalination* 191, 62-70.
- Stoller M., Chianese A., 2006, Technical optimization of a batch olive wash wastewater treatment membrane plant, *Desalination* 200, 734-736.
- Stoller M., Chianese A., 2007, Influence of the Adopted Pretreatment Process on the Critical Flux value of Batch Membrane Processes, *Ind. Eng. Chem. Res.* 8(46), 2249-2253.
- Stoller M. 2009, On the effect of flocculation as pre-treatment process for membrane fouling reduction, *Desalination* 240, 209-217.
- Stoller M., Miranda L., Chianese A., 2009, Optimal feed location in a spinning disc reactor for the production of  $\text{TiO}_2$  nanoparticles", *Chemical Engineering Transactions* 17, pp. 993-998, DOI: 10.3303/CET0917166.
- Stoller M., Movassaghi K., Chianese A., 2011, Photocatalytic degradation of Orange II in aqueous solution by immobilized nanostructured titanium dioxide, *Chemical Engineering Transactions* 24, pp. 229-234, DOI: 10.3303/CET1124039
- Tieng S., Kanaev A., Chhor K., 2011, New homogeneously doped Fe (III)- $\text{TiO}_2$  photo catalyst for gaseous pollutant Degradation, *Applied Catalysis A: General* 399, 191-197.
- Tyrpekl V., Poltiero V., Roca A.G., Murafa N., Szatmary L., Niznansky D., 2011, Magnetically separable photocatalytic composite  $\gamma\text{-Fe}_2\text{O}_3/\text{TiO}_2$  synthesized by heterogeneous precipitation, *Applied Surface Science* 257, 4844-4848.
- Valencia S., Catano F., Rios L., Restrepo G., Marin J., 2011, A new kinetic model for heterogeneous photo catalysis with titanium dioxide: Case of non-specific adsorption considering back reaction, *Applied Catalysis B: Environmental* 104, 300-304.
- Ye M., Zhang Q., Hu Y., Ge J., Lu Z., He L., Chen Z., Yin Y., 2010, Magnetically Recoverable Core-Shell Nanocomposites with Enhanced Photocatalytic Activity, *Chemistry a European Journal* 16, 6243-6250.