# Comparison of Catalytic Efficiency of Some Industrial Nanosized Titanium Dioxides in Heterogeneous Photodegradation by Chemometric Analysis

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## Introduction

Recently, chemical and pharmaceutical industries have imposed higher quality standards for their products and therefore they can produce more complex purer molecules. There is a bigger demand for high quality, ultrapure products, especially in the chemical industries of dyes, pigments, reagents, food additives, for example. Furthermore, the distribution chain of chemical products has globalised and delocalized, so it is important to have molecules with a long shelf life. This kind of production cycle has a huge environmental impact because toxic wastes are more difficult to dispose and have longer lasting after-effects; hence the need for new technologies to cope with this kind of pollution. To suit industrial applications these technologies must be efficient, fast, inexpensive, ready to use and, most importantly, harmless.

The technology that best fits these requirements is based on advanced oxidation processes (AOPs) [1]; developed during 1970s, AOPs rely on advanced homogeneous oxidation and heterogeneous photocatalysis of organic molecules in order to transform them into $CO_2$ and $H_2O$ or into oxidation products with a lower environmental impact.

Due to its high intrinsic efficiency, heterogeneous catalysis is widely utilized in wastewater treatment [2] using mixed catalysts. However, in this kind of catalysis it is extremely difficult to separate the suspension catalyst from the solution at the end of the procedure. Titanium dioxide-based catalysts are most frequently used in these processes, especially in environmental applications, because they are easily treated, are characterized by very low toxicity, and principally for the dimension of their particles as well as their crystalline structure.

## Materials & Methods

In this study, five different brands of $TiO_2$ corresponding to five different particle dimensions were used. Using SEM analysis, we have found minimum diameter values for Degussa at 20nm, Nanomaterials 33nm, Aldrich 60nm, Merck 120nm and Hombikat show 10nm.

The catalytic efficiency of the five $TiO_2$ samples has been estimated using an experimental apparatus based on UV irradiation from two different light sources: 1) a germicidal lamp with a maximum emission at 254nm; 2) a overvoltaged dichroic halogen lamp with a simulated solar spectrum and UV emission extended to 330nm. Five industrial textile dyes were used for target molecules: Acid Blue 29, Alizarin Red S monohydrate, Procion Red MX-5B, Acid Green 25 and Reactive Blue 2. These substances constitute a diffuse kind of organic pollution, especially in superficial waters.

We establish two contact time, 45 and 90 minutes, able to reduce the concentration but not so high to produce mineralisation. The residual concentration [3] was measured after these exposition times by measuring the absorbance value at the wavelenght of maximum absorbance (in the visible range of the spectrum), by means of Perking Elmer Lambda 16 UV-Vis spectrophotometer.The solution is clarified after illumination with a double pass in cooled centrifuge, at 4000 and 18000 RPM.

The calibration curves, from a L.O.D. to initial concentration, were produced analyzing the solutions obtained dissolving an opportune quantity of the pure dyes.

As comparison, the photolysis obtained without the use of any catalysts is shown. These simple data will be successively analysed by chemometric methods in a future work, using Factor Analysis and PCA. We will try to highlight the different recalcitrance of the molecules used, the influence of the catalyst concentration, and the different efficiencies of the catalysts considered, by using these pattern recognition methods.

The components of the experimental apparatus are standard laboratory equipment, such as flasks, pipettes, glassware, an analytical balance at 0.01 mg, a magnetic stirrer, beakers, etc. The special components are:

- halogen, dichroic coating, (without front glass lens) Osram Decostar 35 lamp, 35mm, 12V, 20W, GU 4;
- germicidal UV-C, Hg vapour GTL3 lamp, 60mm, 3W, E17 (Sankyo Denki Co.Ltd, Hiratsuka city, Japan);
- UV/Vis double beam spectrophotometer (and Suprasil 300, 10mm cuvettes by Hellma, Germany), (Perkin Elmer Lambda 15 from Perkin Elmer, Wellesley, MA, USA);
- catalyst, $TiO_2$, Aldrich n. 24857-6, Titanium(IV) oxide, pore size -325 mesh, principally anatase (Aldrich Chem. Co. Inc., Milwaukee, WI, USA);
- catalyst, $TiO_2$, Nanomaterials Research Corporation, lot# PT90019-4F (N.R.C. Longmont, CO, USA);
- catalyst, $TiO_2$, Merck, 100808 Titanium(IV) oxide for analysis (Merck GmbH, Darmstadt, Germany);
- catalyst, $TiO_2$, Degussa P25, new industrial size, 10Kg package (Degussa AG, Frankfurt, Germany);
- catalyst, $TiO_2$, Hombikat, Fluka 53450, 250g package (Germany);
- 40 mg/L dye solutions are prepared starting (Aldrich products: Acid Blue 29 [5850-35-1], Alizarin Red S monohydrate [130-22-3], Procion Red MX-5B [17804-49-8], Reactive Blue 2 [12236-82-7] (Aldrich Chem. Co. Inc., Milwaukee, WI, USA), Acid Green 25 [4403-90-1] (Acros Organics, New Jersey, USA);

## Experimental apparatus

The experimental apparatus consists principally of two cells containing the solution under investigation and the two light sources acting on all the cells. The two cells are connected by a system of little tubes fed by a peristaltic pump. The cell irradiated by the halogen dichroic lamp is built of Suprasil quartz, a material transparent to UV-A, UV-B and UV-C wavelength. A membrane air pump continuously forces air into this cell by means of a small teflon tube: 1) to provide the solution with a sufficient amount of oxygen promoting the oxidation reactions; 2) keep the catalyst in suspension; and 3) remove the carbon dioxide produced in the process.

In order to obtain a partial immersion of the GTL3 lamp in the target solution, the second cell has been made of Perspex; this material is easy to be shaped in our mechanical workshop. The bottom of the cell is built with a parabolic profile to place a magnetic stirrer, which avoids the deposition of the catalyst. We have planned a cool air flow system to avoid an overheating of the solution (temperature always lower than 40°C). In fig. 1 the scheme of the apparatus is shown.

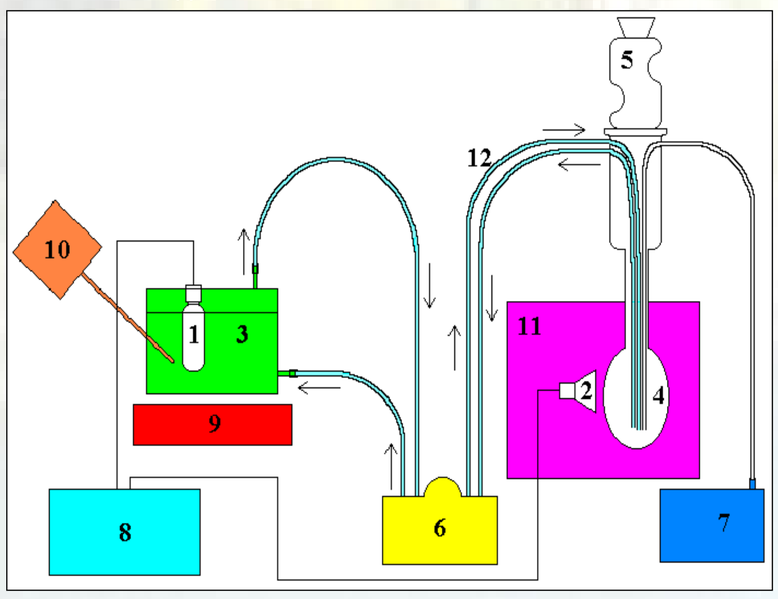
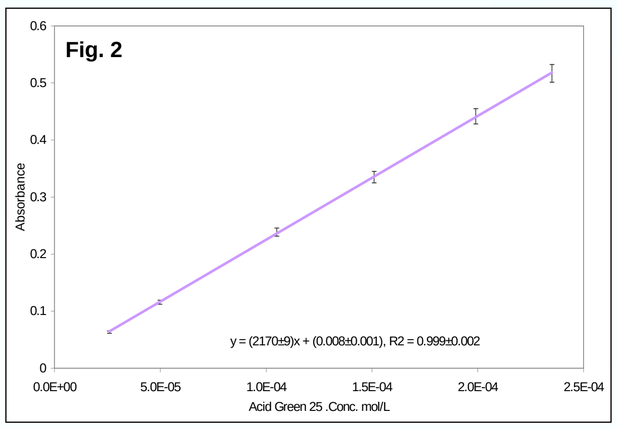
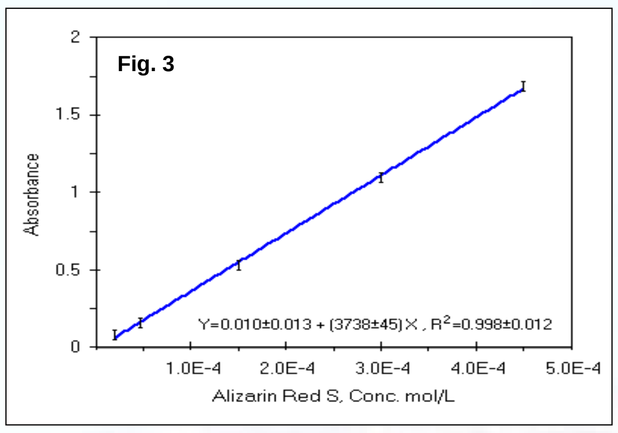


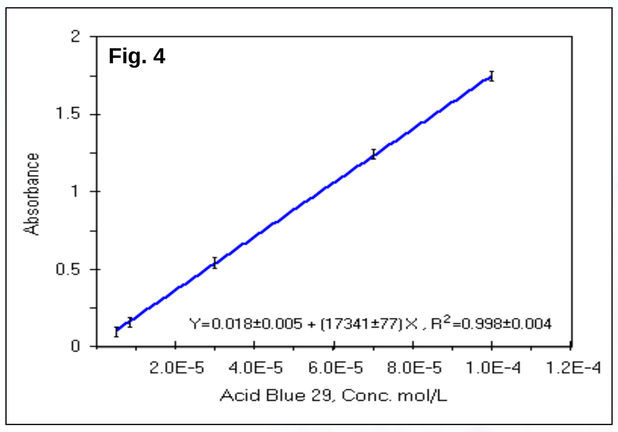

**Fig. 1:** Experimental apparatus 1) UV lamp, 2) halogen lamp, 3) Perspex cell, 4) quartz cell, 5) condenser, 6) peristaltic pump, 7) membrane pump, 8) dual power supply, 9) magnetic stirrer, 10) thermometer, 11) cool air flow chamber, 12) teflon tubes.

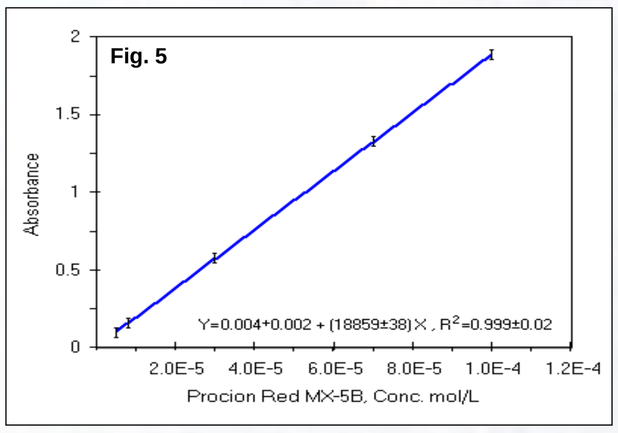
## Results and discussions

The first result of this work confirms that heterogeneous photocatalysis with $TiO_2$ is affected by the dimensions of the particles. In particular the catalysts with nanometer dimensions exhibit the greatest efficiency. The second result shows how the choice of labile (Acid Blue 29 and Procion Red MX-5B) and recalcitrant (Reactive Blue 2 and Acid Green 25) molecules facilitates a good photocatalytic activity classification of the catalysts. The figures 7, 8, 9, 10 and 11 show the degradation efficiency of a selected catalyst, comparing the five dyes with the two exposure time and different concentration of $TiO_2$ in solution (0.0 g/l means no catalyst, i.e. photolysis). It can be noted that Degussa P25 and Hombikat have the highest photocatalytic activity but the last one has lesser efficiency even if it has a great surface area (about 300 $m^2/g$ against 60 $m^2/g$ for the Degussa P25) and smaller particles dimension.



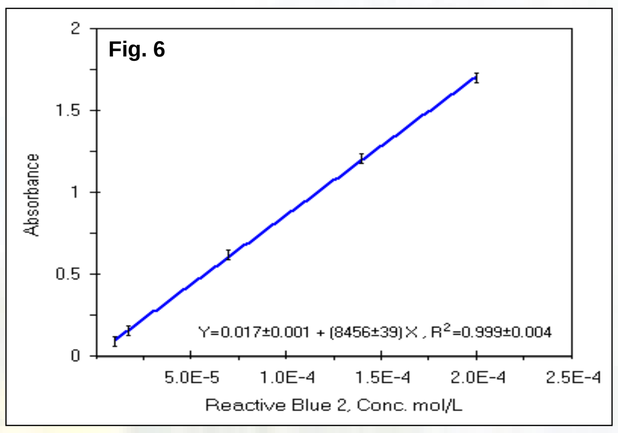
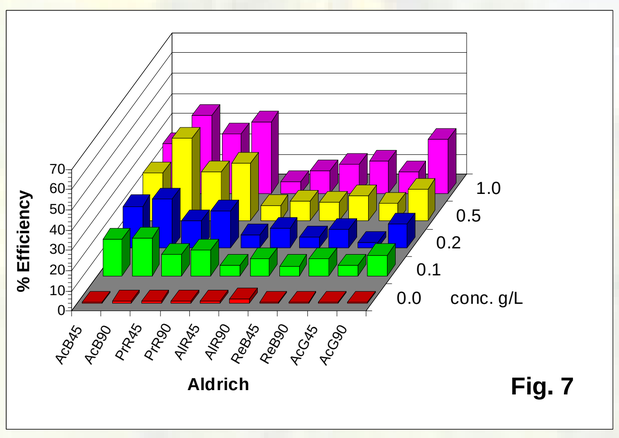
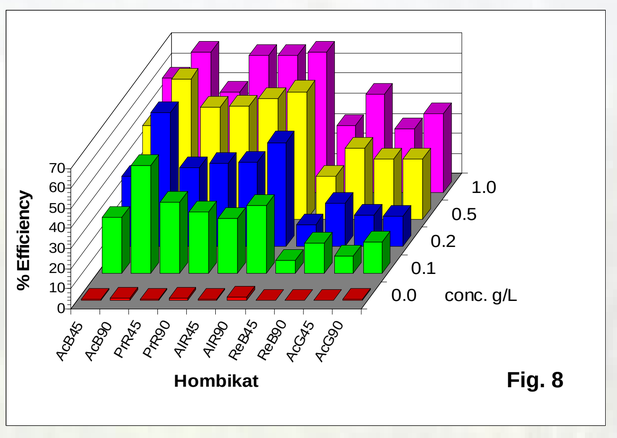
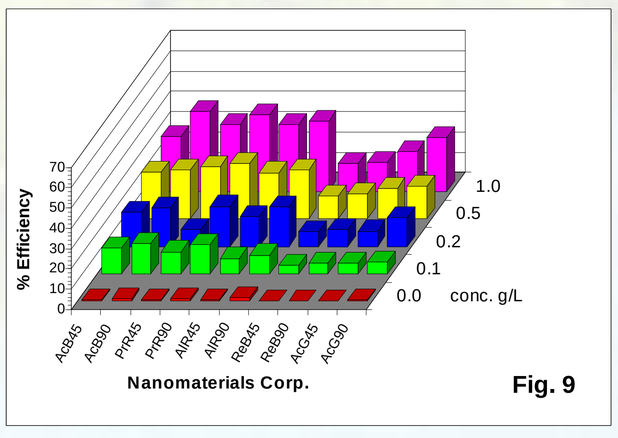
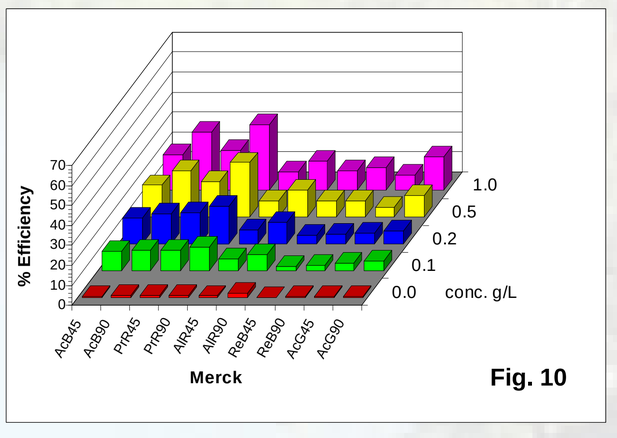




**Fig. 2, 3, 4, 5, 6:** Calibration curves of the five considered dyes by spectrophotometry.



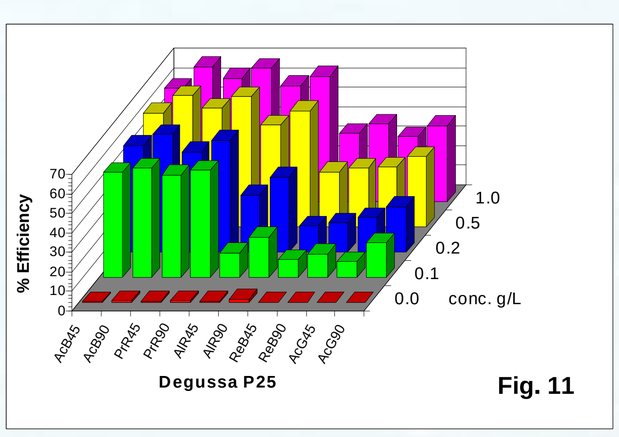




**Fig. 7, 8, 9, 10, 11:** 3D representation charts of the matrix values of each catalyst with the addition of photolysis line.

## Conclusions

The focus of this work is to evaluate the possibility of using non-nanoparticled catalysts that are easily separable from the suspension and to obtain similar efficiencies by changing the specified parameters is not quite obtained. The catalytic efficiency will be compared in future using the Factor Analysis looking for the components of the first factors. As previous the size of the particles, and of course, the exposed surface have main roles but industries can use this study to obtain a cost balance taking in account the expense of clarification.

### References

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