



# Nanosized TiO<sub>2</sub> compared according to chemometric analysis with other titanium dioxides for photodegradation application



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## Introduction

Recently the chemical and pharmaceutical industries have become very capable of marking products with higher quality standards, that means that they can produce more complex, purer and stronger molecules. In fact, in the Western market, there is a bigger demand for high quality and ultrapure products, especially in the chemical industry specialising in dyes and pigments, reagents food additives, e.g. Furthermore, the chain of distribution of chemical products has been globalised, so it is important to have molecules with a long shelf-life.

Unfortunately this kind of production cycle has a huge environmental impact because toxic wastes are more difficult to be disposed and have longer lasting after-effect hence; the need for new technologies to cope with this kind of pollution. These technologies, to suit industrial applications, must be efficient, fast, cheap, ready to go and, above all, harmless.

A technology that best fits these requirements is based on advanced oxidation processes (AOPs): developed during 1970s, AOPs rely on advanced homogeneous oxidation and on heterogeneous photocatalysis of organic molecules in order to transform them into CO<sub>2</sub> and H<sub>2</sub>O or into oxidation products with a lower environmental impact [1].

Advanced homogeneous oxidation utilisation, depending mostly on the addition of H<sub>2</sub>O<sub>2</sub> and Fe(II) acid solutions (Fenton's reagent), has limitations and causes after-effects which are difficult to be avoided. Thus research is now oriented to the study of heterogeneous photocatalysis.

## Heterogeneous Photocatalysis

Heterogeneous photocatalysis is an oxidative process that by means of some suspended or immobilised solid phase semiconductor, under the effect of a source of light, is able to catalyse photodegradation reactions. The exploitation of this technology has a lot of positive aspects because it is largely successful with recalcitrant molecules, makes photodegradation reactions faster and is cheap.

As shown by bibliography, among all the semiconductors used in the experiments, the best is titanium dioxide. In the natural state TiO<sub>2</sub> is available in crystalline forms of Anatase and Rutile (tetragonal structure) or Brookite (orthorhombic structure). It has been well established that the most active crystalline form for the catalytic process is Anatase.

TiO<sub>2</sub> has the properties of a semiconductor because the band-gap between unoccupied electronic levels and occupied electronic levels is low. Occupied electronic levels represent the valence band (vb) as well as unoccupied electronic levels represent the conductivity band (cb). If an energy equal or higher than the band-gap is supplied to electrons, they come into the valence band, generating a rise in electrical conductivity.

TiO<sub>2</sub> energy corresponding to the band-gap is 3.23eV (384nm) for Anatase and 3.02eV (411nm) for Rutile: corresponding to UV light, to activate this semiconductor, therefore, an UV light source must be used.

We can split the whole heterogeneous oxidation process into five steps: **1**) the transfer of the reagent (in this case the pollutant) to the liquid phase on the surface of the catalyst; **2**) adsorption of reactives on the catalyst, **3**) reaction, on the adsorption phase, between reactive and catalyst, **4**) desorption of reaction's products, **5**) removal of reaction's products from interface between liquid phase and catalyst.

The success of the process relies mostly on the amount of the absorption of pollutants on the catalytic surface; it follows that a titanium dioxide that has a higher surface generation works better. TiO<sub>2</sub> production is highly oriented to powders with smaller and smaller diameters, which go down as far as nanometers.

## Mineralisation process

The common characteristic of every AOP is the generation of extremely reactive free radicals, in particular, hydroxy-radicals. The whole heterogeneous photocatalysis process is characterised by a complex sequence of reactions. The mineralisation process, by definition, is the complete degradation of organic matter, soluble or suspended in solution, following the later equations:

The efficiency of the whole process, shown on the right, depends very much on the entity of the adsorption of the polluting on the surface, it is clear, therefore, that a titanium dioxide characterised by a greater superficial development has a greater efficiency.

For this research work 4 industrial dyes, as target molecules, have been chosen: extremely diffuse in the environment, they are characterised by a high recalcitrance to the photodegradation [2]. These substances, besides, also present an intense colouring to low concentrations, making easier, so, their detection with simple analytical methods such as UV/Vis spectrophotometry.

Concentrations of the solutions of dyes have been chosen all equal to 40 mg/L, so that the corresponding absorbance values were included in the range of linearity of the spectrophotometer. In the table below we show the molecules characteristic.

Commercial Name	Acid Blue 29	Procion Red MX-5B	Alizarin Red S monohydrate	Reactive Blue 2
Structural formula				
IUPAC name	2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3-[(3-nitrophenyl)azo]-6-(phenylazo)-disodium salt	2,7-Naphthalenedisulfonic acid, 5-(4-(6-dichloro-3-triazin-2-ylamino)-9,10-dioxo-2-(phenylazo)-1,3,5-triazin-2-ylamino)-disodium salt	3,4-Dihydroxy-9,10-dioxo-2-anthracenesulfonic acid sodium salt monohydrate	1-amino-4-[[4-[[4-chloro-6-[(2-sulphophenylamino)-1,3,5-triazin-2-ylamino]-9,10-dioxo-2-anthracenesulfonic acid sodium salt
C.A.S. number	5850-35-1	17804-49-8	130-22-3	12236-82-7
Color Index name	Acid Blue 29	Reactive Red 2	Mordant Red 3	Reactive Blue 2
Color Index number	20460	18200	58005	81211
Color Index category	Acid Dye	Reactive Dye	Mordant Dye	Reactive Dye
Class	Disazo	Monoazo (reactive system: dichlorotriazinyl)	Anthraquinone	Anthraquinone (reactive system: monochlorotriazinyl)
Synonyms	Acid Blue 2BS, Bernacil Navy BL, Cettile Black M	Brilliant Red SSKH, Cerven reaktivni 2 (Czech), Chemitive Brilliant Red 5B, Mikacion Brilliant Red 5BS, Brilliant Red 5B, Procion Brilliant Red 5BS, Procion Brilliant Red M 5B	Alizarin Carmine, Alizarin sulfonate sodium, Sodium alizarin sulfonate sodium salt	Basilen blue E-3G, Cibacron blue F3G-A, Procion blue H-B
Formula weight	616.50	615.34	380.28	840.12
Formula hill	C <sub>22</sub> H <sub>17</sub> N <sub>6</sub> Na <sub>2</sub> O <sub>7</sub> S <sub>2</sub>	C <sub>19</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>6</sub> Na <sub>2</sub> O <sub>7</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>7</sub> NaO <sub>7</sub> S	C <sub>29</sub> H <sub>22</sub> ClN <sub>6</sub> O <sub>7</sub> S <sub>2</sub>
Absorb,max UV/Vis (in water)	600 nm	538 nm	556-596 nm	540 nm
Melting point	N.A.	300°C	287-288°C	-
Boiling point	N.A.	430°C	-	-
Solubility in water (L.D.50 oral (in rat))	20 mg/L	70 g/L	20 g/L	Yes
Use	Textile use: dye for wool, nylon and silk Non textile use: dye for leather, paper, casein surface dyeing	Textile use: dye for cellulose, nylon, silk and wool Non textile use:	Textile use: dye for wool, silk and nylon Non textile use: drugs and cosmetics. Indicator pH 3.7-5.2 (yellow to violet). Lakes. Microscopic stain.	Textile use: dye for cellulose, nylon, silk and wool Non textile use:

## UV Sources

In this work two luminous sources characterised by different emission spectra have been used:

- germicidal lamp GTL3: Emission at 254 nm. The energy associated to this wavelength was necessary both to the activation of the catalyst and the break of intramolecular bonds of the dyes.
- survaltage dichroic halogen lamp: emission in the entire solar spectrum, with extent to UV up to 300 nm. This source has contributed to the break of intramolecular bonds of dye agents, besides this is sufficient to activate the TiO<sub>2</sub> rutile form [3].

## Catalysts

Aim of this work is to compare the efficiency of four different kinds of TiO<sub>2</sub>, focusing the attention on the dimensions of the particles.

TiO <sub>2</sub> brand	diameter	surface area
Degussa new P25	20 nm	50
Nanomaterials Corporation	40 nm	33
Aldrich	1.0 µm	6
Merck	0.75 µm	11

Estimated values for diameter and surface area (m<sup>2</sup>/g) for catalysts

## Experimental apparatus

The experimental apparatus is composed principally by two cells containing the solution under investigation, on everybody of which the two luminous sources mentioned before act. 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 in Suprasil quartz, material transparent to the UV issued by the source radiation. Inside this cell, through a thin tube, insufflated air coming from one pump, to the triple purpose to provide the solution a sufficient amount of oxygen to promote reactions of oxidation, to keep in suspension the catalyst and remove the CO<sub>2</sub> produced.

The cell irradiated by the GTL3 lamp is built in Perspex, material of easy manufacturing which has allowed to fix the luminous source in such a way to be partially dipped in the solution contained there. Under this cell a magnetic stirrer which avoids the deposition of the catalyst in the cell bottom is positioned.

## Materials and methods

The main components of the experimental apparatus are:

- halogen, dichroic coating, (without front glass lens) MR11 lamp, 35mm, 12V, 20W, GZ/GU 4, from Fluorimport S.r.l., Milan, Italy
- germicidal UV-C, Hg vapor GTL3 lamp, 60mm, 3W, E17, from Sankyo Denki Co.Ltd, Hiratsuka city, Japan.
- hand made Perspex and quartz cells, one with Suprasil quartz from Hellma GmbH, Müllheim, Germany
- standard laboratory equipments; peristaltic pump, Teflon tubes, magnetic stirrer, analytical balance, flask and spectrophotometer
- catalysts from: Aldrich Co., USA; Degussa Ag, Germany; Merck GmbH, Germany; Nanomaterials Corporation, USA
- Q-Parvus chemometrics software, freeware, written 25 years ago from Prof. Forina, a father of chemometrics in Italy, member of Chemometrics Society, full professor at Genova University. This modular software are, firstly, mathematical correctness, second, continuous update. On contrary for full use we think useful follow an annual school of chemometrics at Genova University.
- multivariate analysis software MVSP, from dr. W. Kowak, born in paleontological study, this inexpensive software have a lot of easy and useful feature but leak a little in validation.
- graphs, calculation, data collection are performed by Lotus 123, the story of Spreadsheet unfortunately not upgrade yet by new brand.

## Monitoring of the Photodegradation Process

For a quick, simple, cheap, but reliable monitoring of the photodegradation we have chosen spectrophotometric UV/Vis method. The purpose of the detection, in fact, was to verify the decrease of the concentration of the dyes; the detection of the nature of substances formed as product of the degradation was lying outside our aims.

Therefore we used a Perkin-Elmer Lambda 15 double beam spectrophotometer, with quartz cuvettes. To detect the entity of the photodegradation the spectrum of the colouring agent in exam before and after every test was registered: from the difference of the values of the

absorbance concerning the characteristic peak of the substance, we have obtained the efficiency of the photodegradation expressed as "photodegradation percent".

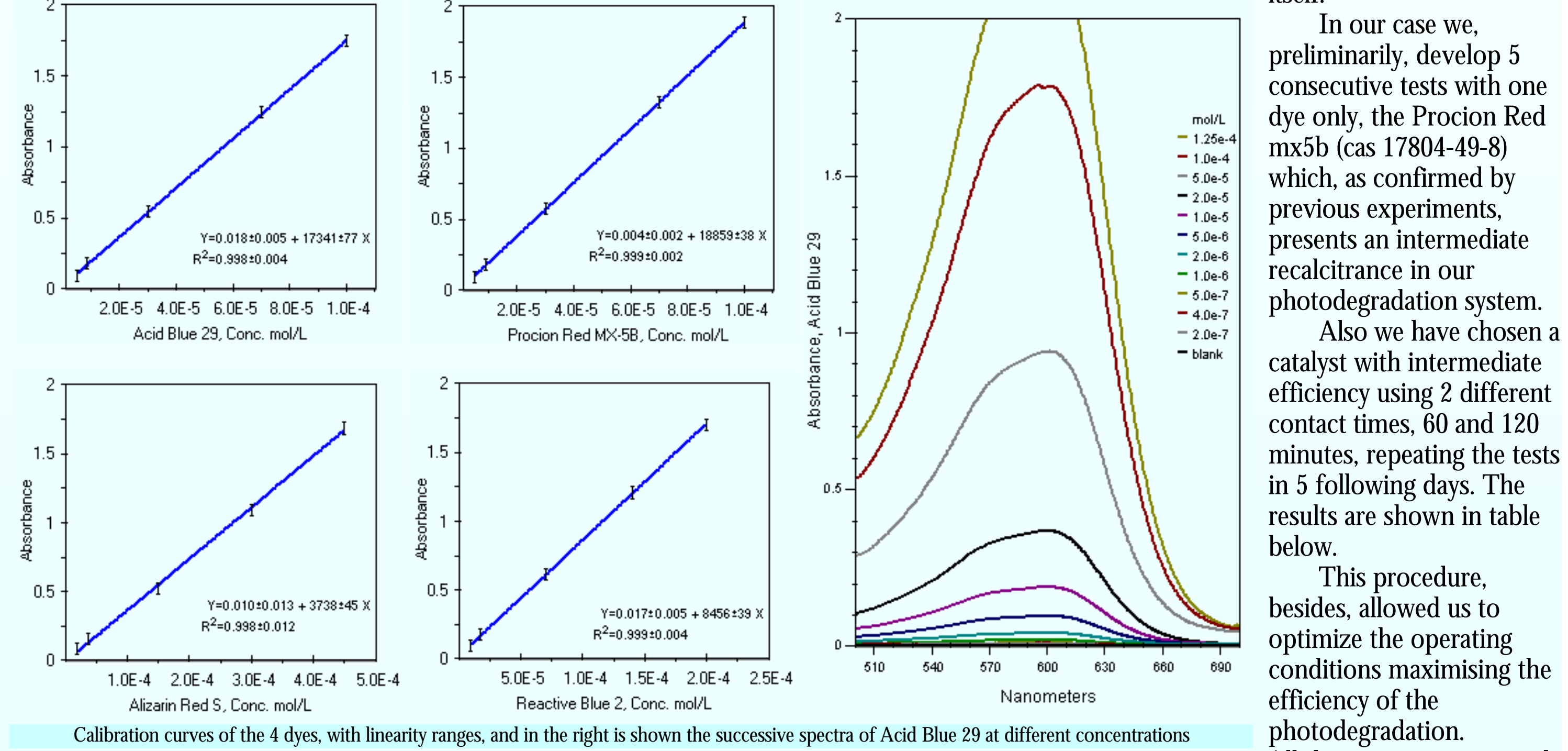
Two steps, 15 minutes of 6000 rpm centrifuge, sovranatant accurate extraction, other 15 minutes at 6000 rpm are able, in this case to remove the TiO<sub>2</sub> suspension.

$$\text{Photodegradation \%} = 100 \left( 1 - \frac{\text{Abs}_y}{\text{Abs}_x} \right)$$

where: Abs<sub>y</sub> is the value of the absorbance of the solution after the photodegradation and Abs<sub>x</sub> is the value before

## Results and Discussion

The analysis of the efficiency of catalysts cannot leave out of consideration the preventive analysis of the reproducibility. Photodegradation process is much affected by parameters as the temperature, the reflecting power of the involved surfaces, the power of the lamps, the lamp's life itself.



Calibration curves of the 4 dyes, with linearity ranges, and in the right is shown the successive spectra of Acid Blue 29 at different concentrations

three times, consecutively and the averages and the standard deviations have been calculated obtaining distributions like that of table on the right. For the statistical elaboration the mediane has been used, that is a center value really measured among three available.

We obtain so, for every catalyst, for every concentration, for every dye, for the two contact times and lighting, a value of reduced concentration measured by spectrophotometer.

## Experimental Evidence

The matrix of the obtained data is shown on the left, it is built to allow an easier chemometric treatment. In this matrix it is possible to highlight the 8 variables composed from the 4 catalysts everyone with the two times of contact.

The lines of the matrix are composed from 4 catalysts, everyone with the 4 possible concentrations in suspension, with added the photolysis object.

Many chemometrics recommend an objects/variables ratio of 3 to 1; increase the number of the objects to respect this ratio, however, would have lengthened in heavy way the times of the research: in fact, a reconditioning of all the experimental device before every test has been necessary.

From the matrix one can obtain various 2D and also 3D representations. The two graphs 3D shown in figure 1 et 2 highlight the different trend of two catalysts characterized by very different efficiencies among them.

The objects to classify are so the catalysts, or rather, their concentration in solution, with, for comparison, the photolysis also (the absence of catalytic effect).

In fig. 1 we show the 3D representation of the zone of the matrix concerning the Degussa catalyst, with addition the line of photolysis. Even if in their simplicity these graphs are unbelievably explanatory if read with attention, and they are able to give several information. It is possible to highlight at least two trends.

The first is the pronounced jump between the photolysis and the concentration 0.1 g/L, which shows the efficiency of the catalyst at so low concentrations, jump that is then reduced passing from 0.1 to 1 g/L.

We can see outlined well the trend of the efficiency both for two recalcitrant dyes and for that more labile changing of the concentration of the catalyst. In the case of the two catalysts Alizarin Red and Reactive Blue the trend is always growing, for which the saturation is not neither reached with 1 g/L.

The second trend is the change of the efficiency in function of the time: reading also the only line of the photolysis a continuous improvement is observed passing from 45 to 90 minutes, improvement that however is always different changing the target molecules.

In fig. 2 the Aldrich catalyst shows a true different trend: the total efficiency is lower and the trend to the change of concentration is less pronounced and with some uncertainty. Also passing from 45 to 90 minutes a different improvement is noticed from that seen in the previous figure.

Various 2D and 3D graphs could be produced but however the study of the efficiency relationships among the catalysts and therefore the study of the recalcitrance of the two couples of used molecules cannot leave out the consideration from a careful multivariate and/or chemometric analysis.

## Chemometric Analysis

Chemometry is defined as the science that allows putting in relation, through the application of mathematical and/or statistical multivariate methods, the measures done on a system or a process, with the state of the system itself.

The characteristic that makes it very interesting and useful for the demand of the research is really the possibility of checking and studying the effect of the descriptive variables changing them all together. That allows to always extract the maximum information from any data set, independently from the complication level.

The 136 experimental efficiency measures, median, obtained for the four catalytic systems show values from 6.7% of the AcB45 photolysis to 68.9% of photocatalysis of PrR90 obtained with Degussa TiO<sub>2</sub>. Analysing the averages of every catalyst we obtained values which change from 7.6% of the Merck 0.1 g/L up to 57.6% of the Degussa 1 g/L.

In this work we have chosen to elaborate the data by one of more long-lived method of pattern recognition: the **Principal Component Analysis**. The P.C.A. is useful to redistribute the information present on numerous descriptive variables in few variables known as note principal components, without information loss with variance accumulated in the prime P.C..

After autoscaling (subtraction of column average and division by sample standard deviation) we calculate the correlation matrix and finally the Eigenvector and Eigenvalues.

No preventive classification of the objects has been done, placing them, in only one category; a help to the interpretation, however, is provided by the colour graphic representation on the Cartesian plan. So this method can view as "Pattern Cognition".

We use R-mode PCA. The component loadings are scaled to unity, so that the sum of squares of an eigenvector equals 1, and the component scores are scaled so that the sum of squares equals the eigenvalue.

The correlation matrix, after autoscaling, supplies values included between a maximum of 0.99 among the two AIR45 et AIR90 variables and a minimum of 0.78 among the two AcB90 and AIR45 variables. For our choice we consider everybody the eight variables assigning to the interpretation of the graphs of the loading the interpretation of the themselves ones.

The "scree plot" of eigenvalues show only two components. For this two one we obtain a explained variance of 90.2% for the first component, and 6.6% for the second component, with a total of 96.8%. The values for the first two eigenvalues are 7.2 and 0.5.

Graphing, in Fig. 3, the "loading" (the original variable even if after transformation of the coordinates) of eigenvector it is possible to highlight the contribution on the axis of the P.C. of the original variables. The graph show relation from, practically only, PC2 and dye molecules. We obtain two molecules easy to mineralise with low values of PC2 and two molecules with recalcitrance with high value of PC2. This distribution is exactly what expected.

Finally Fig. 4 shows the replay at our question, it is possible to notice as the PC1 is already, by oneself, sufficient to separate the behaviour of the catalysts among them, which highlights the superior efficiency of the nanoparticled catalysts, and in particular of the new one Degussa P25. From the Fig. 4 we notice that all the catalysts show a growing efficiency trend when their concentration increase in solution. All the catalysts show values almost constant on the PC2 used as efficiency indicator changes.

A completely different behaviour is that of the Degussa catalyst, which shows a strong variation also on the PC2. We can assume a different crystalline structure of the catalyst that places his efficiency in strong correlation with the target molecule (as also suggested from the fig. 1), catalyst, which the producer declares to be mainly in the form Anatase.

## Reference

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