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

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Abstract

For more than thirty years the so-called Advanced Oxidation Processes (AOPs) have been continuously studied. They are based on photochemical reactions catalysed by suitable metal oxides with semiconductor properties. For more incisive processes we coined a new acronym High Performance O.P. (HPOP) [1].

A particular attention was always paid to the reaction mechanisms and to the interaction with the energy source. One of most critical parameters ruling the efficiency of the photo-catalytic process is constituted by the interface between the liquid solution and the solid catalyst, generally coming to the conclusion that the surface area of the catalyst is a determining parameter as directly related to the process efficiency.

On the other side the nanosized catalysts are difficult to remove from the "cleaned" solution and a less efficient catalyst but easy to remove from waste is very useful for industries. Comparison must be done by chemometrics method, if possible using a costs evaluation.

Introduction

Recently, chemical and pharmaceutical industries have imposed higher quality standards for their products and therefore they can produce more complex and purer molecules. There is a bigger demand for high quality, ultrapure products, especially in the chemical industries of dyes, pigments, reagents, food additives,. Furthermore, the distribution chain of chemical products has globalized 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) [2]; developed during 1970s, AOPs rely on advanced homogeneous oxidation and heterogeneous photocatalysis of organic molecules in order to transform them into CO₂ and H₂O or into oxidation products with a lower environmental impact.

Due to its high intrinsic efficiency, heterogeneous catalysis is widely utilized in wastewater treatment [3] 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 20 nm, Nanomaterials 33 nm, Aldrich 60 nm, Merck 120 nm and Hombikat show 10 nm.

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The catalytic efficiency of the five TiO₂ samples has been evaluated using an experimental apparatus based on UV irradiation from two different light sources: 1) a germicidal lamp with a maximum emission at 254 nm; 2) a overvoltaged dichroic halogen lamp with a simulated solar spectrum and UV emission extended to 330 nm. 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. Using these times we can measure the reduction of concentration [4] using the absorbance value of the colour peak, by means of Perkin Elmer Lambda 16 UV-Vis spectrophotometer. The solution is clarified after illumination with a double pass in cooled centrifuge, at 4000 and 18000 RPM.

Opportune calibration curves, from a L.O.D. to initial concentration, are produced by direct weight and dissolution of pure dyes.

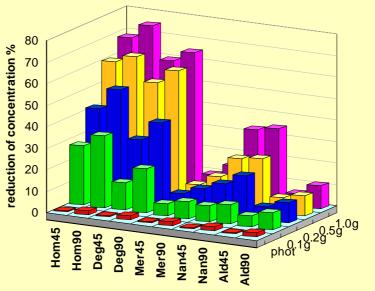


Fig.1, Concentration of Alizarin Red S dyes after degradation with exposure of 45 and 90 minutes. Catalysts as in the text.

In fig. 1 are shown the values obtained for the ancient dye

Alizarin Red with different exposure and dyes. As comparison, is shown the photolysis. After those simple representations the data were analysed by chemometry, using Factor Analysis and PCA to highlight the different recalcitrance of the molecules used (already known), the influence of the catalyst concentration, and the different efficiencies of the catalysts considered.

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 is compared using the Factor Analysis looking for the components of the first factors. As expected the size of the particles, and of course, the exposed surface have the main roles but industries can use this study to obtain a cost balance taking in account the expense of clarification.

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