Environmental permanence and TOC sensors based on TiO_2

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Summary: *A TiO_2 photosensor is assembled in order to determine TOC and environmental permanence of different compounds and solutions. The proposed method is based on measuring CO_2 produced by TiO_2 catalysed photodegradation and the occurring acidification.*

Keywords: *titanium dioxide, photosensor, photocatalysis, alarm device, TOC, environmental permanence*

Introduction

Potentially chemicals able to be completely degraded to water and carbon dioxide are leastly dangerous compared with others which produce many different products each one able to react with ecosystem. The ability to be completely degraded is not an easily measured property [1].

The setting up of photosensors based on titanium dioxide seems to allow to get this kind of information [1,2,3], basing on the property of TiO_2 to simultaneously act as catalyst and as pH indicator [2,3,4].

Really during mineralisation acidification occurs: TiO_2 being a photocatalyst of the process but also behaving as pH sensor is so in the lucky position to activate a process and to monitor its proceeding as acidification is the result of mineralisation. The time needed in order to record a pH shift to more acid values can be assumed as a delay time proportional to the recalcitrancy and so the environmental permanence, the kinetic aspects being strictly related in this case to the thermodynamic ones.

Further informations are obtained by the slope of the pH decrease following the beginning of the mineralisation process denounced by the acidification after the delay time.

Mineralisation and pH

Following data shown in table 1 we can temptatively propose to assume the ratio between the delay time and the slope of pH decrease as a parameter to measure the environmental permanency of a compound, that reasonably we can assume as inversely related to ability to be mineralised.

Table 1: characteristic data of the curves such as Fig. 1 refereed to different compounds

Compound and concentration 10^{-2} mol/L	Delay time (min) RSD% ± 6	Slope (ΔpH/Δmin)
p-chlorophenol	30	0.16
m-chlorophenol	30	0.31
o-chlorophenol	60	0.22
Hydroquinone	70	0.08
p-quinone	20	0.04
Glucose	10	0.04
Carbaryl	50	0.12

In Fig 1 the time-potential trend is shown. As said the time which allows acidification to start and the slope of curve after minimum potential values are useful mineralisation indicators. Some interferences from sodium chloride able to slow the initial kinetics must be considered.

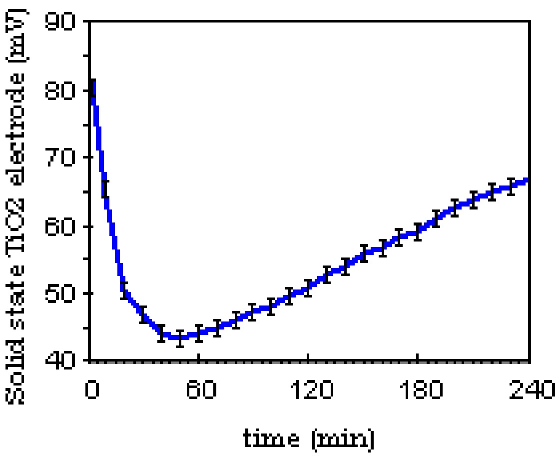

Figure 1: trend of TiO_2 electrode with the time during photodegradation of a Carbaryl 10^{-3} M solution

The suggested ratio could be of great help in the case of unknown or not characterised compound: a White Book of European Community invites scientific community to make the most of efforts in order to set up chemical test able to give informations - especially alarm advises - in real - or almost near real-time about the toxicity of a compound.

TOC

TiO_2 sensor can be profitably used also to determine TOC (Total Organic Carbon) index, well representing the pollution level of a water matrix. It can be determined by photodegrading the present compounds and determining the formed amount of CO_2 by a gaseous diffusion electrode. TiO_2 results to be active as a photocatalyst of the reaction.

Four catalysts were tested, all based on titanium dioxide in its mixed rutile-anatase form. In three cases TiO_2 was used in the P25 nanoparticled form produced by Degussa, described as an excellent catalyst for photodegradation. According to producer this oxide was in the crystalline anatase form. It was tested both supported on glass or metal grid and suspended in solution.

The use of PCA (principal component analysis) to make chemometric investigation about the results of the catalytic efficiency confirms the expectations and, despite of the used compounds, nevertheless demonstrates the superiority of TiO_2 in suspension [5].

Following these results we used TiO_2 in the nanoparticled form of anatase suspension in presence of phosphate buffer (unable to interfere with TOC value) and operating in such size model to allow to obtain a portable TOC monitor. The cells Plexiglas made and the UV radiation corresponding to 300-400 nm band are further optimised conditions. An auxiliary cell allows a good mixing and CO_2 measurement.

GC-MS was applied to determine intermediates and finally check the complete consumption of the photomineralised organic compounds. For some target compounds high degradation and mineralisation degrees were measured.

References

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