

Photosensor for chemical risk assessment: review

Abstract

The electron holes in the valence band and the electron excess in the conductive band in the structure of TiO_2 are able to trigger reductive and especially oxidative process involving substances present in the environment, in particular those ones that can be adsorbed on it. This property makes TiO_2 as an optimum photocatalyst. Its ability to be in particular conditions a pH sensor combined with the previous one makes titanium dioxide also a suitable material to be used as a sensor for measuring environmental permanency and consequent risks. In this paper we apply TiO_2 photosensor to demonstrate on target compounds both the activities.

Keywords: TiO_2 , photosensor, photocatalyst, organic carbon, pH, CO_2 , H_2O , photomineralised, photodegrading, titrations

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Introduction

Titanium dioxide is a well known photocatalyst.¹⁻⁹ Less famous are its characteristics as sensor material.¹⁰⁻¹⁴ So that in this paper we describe some recent our experimental results concerning the adoption of TiO_2 (prevailing anatase form) as component sensor of a TOC (total organic carbon) electrode, sensor of pH, sensor of environmental permanency, as related to the ability of a molecule to be completely degraded, that is mineralized.

As it concerns the last point it must be emphasized the difference between degradation and mineralization, the former bringing to a lower molecular weight compound, the toxicity of which can be also higher than that one of the original compound, the latter one ensuring the total production of CO_2 , H_2O and the mineral acids corresponding to the elements present in the mineralized molecule.

Materials and methods

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, often described in the literature¹³ as an excellent catalyst for photodegradation. Most of the oxide was in the crystalline anatase form. It was tested both supported on glass or metal grid and suspended in solution. In one of the catalysts tested the titanium grid was oxidised directly in order to enhance TiO_2 adhesion to the metal support and to obtain a more uniform surface distribution. A highly pure submillimetric titanium grid with suitable mechanical properties was supplied by Delker (CT, USA).¹⁴

According to chemometric treatment of the results, using PCA (principal component analysis), the catalytic efficiency scale we obtained confirms these expectations and, despite of the compounds used, nevertheless demonstrates the superiority of TiO_2 in suspension: so we used TiO_2 in the form of anatase nanoparticled suspension in presence of a phosphate buffer unable to interfere with TOC value and operating in such dimension model to allow to obtain a portable TOC monitor. Due to the abundance of a TiO_2 based mineral on the moon and so possible application to spatial research and to the positive action of conducting polymers added to sensor materials, we tested also these two options.

Total organic carbon content is an index of 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.^{15,16}

Table 1 Mineralisation and Photodegradation degrees by TiO_2 activated photocatalysis for citric acid and dimethoate at varying concentrations

| Sample mol/L | % mineralisation (RSD = ± 3) | % Photodegradation (RSD% = ± 8) |
|---------------------------------|-----------------------------------|--------------------------------------|
| Citric acid $0.9 \cdot 10^{-2}$ | 5 | 70 |
| Citric acid $0.9 \cdot 10^{-3}$ | 47 | 80 |
| Citric acid $0.9 \cdot 10^{-4}$ | 95 | 100 |
| Citric acid $4.5 \cdot 10^{-5}$ | 100 | 100 |
| Citric acid $0.9 \cdot 10^{-5}$ | 100 | 100 |
| Dimethoate $1.0 \cdot 10^{-3}$ | 6 | 13 |
| Dimethoate $5.0 \cdot 10^{-4}$ | 10 | 88 |
| Dimethoate $2.0 \cdot 10^{-4}$ | 22 | 100 |
| Dimethoate $1.0 \cdot 10^{-4}$ | 35 | 100 |
| Dimethoate $5.0 \cdot 10^{-5}$ | 49 | 100 |

The cell is Plexiglas made the UV radiation corresponds to 350nm. An auxiliary cell allows a good mixing. GC-MS was applied to determine intermediates and finally check the complete consumption of the photomineralised organic compounds organic carbon content is an index of 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.^{15,16} Acid base titrations were also performed with TiO_2 and the other materials on it based as indicators.

Results

TiO_2 as photocatalyst

For some target compounds the following degradation and mineralization degrees were measured (Table 1), some interference coming from sodium chloride presence able to slow the initial kinetics.

Behaviour of both the tested compounds suggest the conclusion that on increasing concentration mineralisation degree decreases compared to photodegradation one.

TiO_2 as pH sensor

In this case TiO_2 was tested both alone and in the enriched form with polyaniline (9 + 1 and 8 + 2 weight plus weight) and in the combined form as ilmenite (iron (III) titanate mineral). Acid base titrations were also performed with TiO_2 and the other materials as indicators, obtaining the values reported in Table 2, compared with the expected equivalent volumes.

Table 2 Acid-base titration monitored by different sensor materials, all based on TiO₂

| Titrating | Titrated | Experimental | Volume (mL) at Equivalenc | | Theoretical Volume (mL) at Equivalence |
|------------------|-----------------|------------------|---------------------------|----------------------------|--|
| | | TiO ₂ | Ilmenite | TiO ₂ +PA (8+2) | |
| HCl 10-1 eq/L | NaOH 10-1 eq/L | 16.5±0.2 | 16.5±0.2 | | 16.3 |
| HCl 10-2 eq/L | NaOH 10-2 eq/L | 22.0±0.2 | 21.6±0.2 | | 21.5 |
| CHCOOH 10-4 eq/L | NH4OH 10-4 eq/L | | | 20.0±0.2 | 20 |

Substantially TiO₂ and ilmenite behave similarly. Polyaniline enrichments does not bring the electrode performances any improvement.

The four materials were also characterised for their Nernstian behaviour: the calibration results furnished a quasi Nernstian behaviour for all the electrode materials (Table 3).

Table 3 Nernstian behaviour of the four tested materials based on TiO₂

| Material | Slope (mv/pH) |
|--------------------------------------|---------------|
| TiO ₂ | 59.4±0.2 |
| Ilmenite | 59.1±0.3 |
| TiO ₂ + polyaniline (9+1) | 55.6±0.3 |
| TiO ₂ + polyaniline (8+2) | 62.0±0.4 |

Compared with the theoretical one the obtained values fit very well.

TiO₂ as sensor of ability of a compound to be mineralised

During mineralization acidification occurs^{17,18} due to formed CO₂. TiO₂ 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. The time needed in order to record a pH shift to more acid values can be assumed as a delay time proportional to the recalcitrance of the compound. The slope of the potential curve after the delay time refers to the kinetics of photodegradation, it too in some way related to environmental permanency. So we assume as index of eco-permanency the ratio between the delay time and the above said slope, reasonably assumed as inversely proportional to its ability to be mineralised by a photodegradation process. The principle was applied to some common pollutants obtaining the enclosed delay time and slope values (Table 4).

Table 4 Delay times, acidification kinetics and eco-permanency indexes for some tested compounds

| Compound and concentration | Delay Time (min) (RSD%= ± 6) | Slope (DpH/ Dmin) | Index |
|----------------------------|------------------------------|-------------------|-------|
| p-chlorophenol 10-2 mol/L | 30 | 0.16 | 187 |
| m-chlorophenol 10-2 mol/L | 30 | 0.31 | 97 |
| o-chlorophenol 10-2 mol/L | 60 | 0.22 | 277 |
| Hydroquinone 10-2 mol/L | 50 | 0.08 | 625 |
| p-quinone 10-2 mol/L | 20 | 0.04 | 500 |
| Glucose 10-2 mol/L | 60 | 0.04 | 1500 |
| Carbaryl 10-2 mol/L | 50 | 0.12 | 417 |

Discussion

The photocatalytic activity of TiO₂ as such as well as of its mineral (ilmenite) or added with conducting polymer polyaniline is shown focusing on the obtained high degrees of photodegradation, but also on the failed mineralisation when the tested compound concentration is higher than a certain value (about 10⁻³ for the tested compounds). TiO₂ and its based materials resulted to be also material sensors for pH with almost Nernstian behaviour. The addition of a conducting polymer that in some cases results to improve the characteristics of a solid state sensor in this case does not act in this direction.

An index of eco-permanency is proposed based on the combination of the two above said properties of TiO₂. The calculated values of the above proposed index for the tested compounds are enough agreeing with other molecular properties related to the stability of the considered compounds. This can be considered our added value to the evaluation of the photocatalytic activity of titanium dioxide: to combine photodegradation tests - commonly present in literature (1-9) - with stability ones and with kinetics behaviour.

Conclusion

We propose an eco-permanency index based on thermodynamics and kinetics aspects of photocatalytic process, possibly of great help in the case of unknown or not characterised compound to answer European Union recommendation reported in a White Book of some years ago. There scientific community was invited to make the most of efforts in order to set up chemical tests able to give information's - especially alarm advices - in real - or almost real - time about the toxicity of a compound. A representative example is the drugs, used and abused in our society so that their presence in surface waters is a danger for environment and health. This danger increases with the stability and eco-permanence, so that their measurement can be of precious utility.

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Conflicts of interest

Author declares there are no conflicts of interest.

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