Evaluation of Photocatalytic Materials for Water Purification: Overview of the New CEN Standard Test

Triantis T.M.[1], Kaloudis T.[1,2], Hiskia A.[1,*]

[1] Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Athens, Greece.
[2] Athens Water Supply and Sewerage Company (EYDAP SA), Athens, Greece

*corresponding author: A. Hiskia: e-mail: a.hiskia@inn.demokritos.gr

Abstract
TiO_2 photocatalysis offers an attractive alternative to conventional water treatment technologies leading directly to the degradation of organic pollutants, compared to transferring them from one phase to another as in the case of membranes or activated carbon. There is an increasing interest on using photocatalysis for water treatment, rendering reliable evaluation of performance of the catalytic materials necessary. Methods for testing photocatalysts used in water treatment are generally not harmonized. Two ISO standards are available for assessing the photocatalytic activity of surfaces with regards to water purification, which are based on the photo-bleaching of methylene blue and the oxidation of DMSO, respectively. A new European standard for assessing the photocatalytic activity of materials has been developed and is under publication by the European Committee for Standardization, CEN TC386/WG3. Evaluation of the performance of photocatalytic materials in water purification is based on measurement of phenol degradation with UV irradiation under controlled conditions. The proposed standard method is applicable to materials in the form of powders (suspensions in water, slurries). İn this study, the new CEN standard test will be presented, while its differentiation from the existing ones, its applicability and the process followed for its validation, will be discussed.
Keywords: Photocatalysis, European Standard, CEN, Phenol degradation.

1. Introduction

Water purification is one of the most important issues of scientific research due to the increasing need of pure water worldwide. Alternatively to conventional methods, photocatalysis in the presence of TiO2 is of increasing attention as it can efficiently degrade persistent organic pollutants even at low concentrations in water (Pillai *et al.,* 2018). The photocatalytic degradation of organic pollutants using TiO_2 have been extensively studied for a plethora of compounds e.g. phenols, chlorophenols, pesticides, pharmaceuticals, dyes, cyanotoxins, water taste and odor compounds etc. (Antoniou *et al.,* 2016). In most of the cases, degradation proceeds to total mineralization of pollutants to CO_2 and inorganic ions.

The production of new photocatalytic materials that enter the increasing market of photocatalytic applications necessitates the use of a reliable and reproducible test method for the evaluation of their performance with relevance to water purification. Until now, although there are two ISO standards available for assessing the photocatalytic activity of surfaces with regards to water purification, improvements are necessary to include bulk photocatalytic materials (ISO-10676; ISO-10678). This gap is going to be fulfilled by the new CEN standard which is under publication by the European Committee for Standardization (CEN TC386/WG3) until the end of 2019.

2. Description of the new CEN standard test

This European standard describes a test method to evaluate the performance of photocatalytic materials in water purification by measuring phenol degradation. This test method is applicable to photocatalytic materials in form of powders (suspensions in water, slurries) under UV irradiation. The photocatalytic performance of the tested material is assessed by the observed rate of phenol degradation at specified experimental conditions as determined by HPLC-UV.

3. Configuration of the photocatalysis aparatus

Photocatalysis apparatus is consisted by an irradiation source and a batch type photo-reactor. The irradiation source shall consist of any lamp able to excite the photocatalyst in UV at an average irradiance of (10±5%) W/m^2, according to the technical specification CEN/TS 16599. The photo-reactor cell of 100 ml volume will be of pyrex glass and with ability for magnetic or mechanical stirring.

4. Photocatalytic reference Material

A photocatalytic reference material, when available should be used for comparisons and evaluation of test results especially between laboratories. An example of such a material is the NIST SRM 1898-Titanium

Dioxide Nanomaterial (National Institute of Standards and Technology, US Department of Commerce).

5. Procedure

At several time intervals samples should be taken for analysis of phenol by HPLC in order to obtain a plot of phenol degradation over time of irradiation. The samples must be of small volume, typically less than 1 ml. The samples are filtered prior to HPLC analysis, to remove the suspended material. Sampling intervals should adequately cover the whole degradation process (e.g. from 10% to 90% degradation) unless results indicate that no significant degradation of phenol is observed or that degradation proceeds very slowly.

Plots of phenol concentration (C) vs time, under irradiation, under dark, and under irradiation in the absence of the test material should be conducted and the slope k of the fitted line $\ln(C) = A - kt$, will be calculated by linear regression. C is the concentration of phenol, t is the irradiation time, A is a constant and k is the observed rate constant when first-order kinetics is observed. The same information and results for the test will be carried out with the reference material, e.g. NIST SRM 1898. The ratio ks/kf, will be calculated, where ks and kf are the observed rate constants for the sample and the reference standard material, respectively.

6. Validation of the new CEN standard test

A round-robin test was carried out in order to evaluate the method proposed in the new CEN standard that is intended for assessing the performance of photocatalytic materials in water purification by measurement of phenol degradation.

7. Conclusions

Validation of the new CEN standard test showed that the method is specific and doesn't give false positive results, e.g. due to direct photolysis or thermal reactions of phenol. Within each laboratory participated to the round-robin test, method produced reproducible results (RSD <20%). Between laboratories the range of reported k values was wider, indicating differences in experimental setup as a possible cause. However, the ratios ks/kf seem to have a normalizing effect on those differences. This means that the ratios ks/kf can be the most appropriate measure for the evaluation of photocatalytic materials.

Acknowledgements

The Authors would like to acknowledge NCSR "Demokritos", Institute of Nanoscience and Nanotechnology, Laboratory of Environmental Analysis (LEAD) for coordinating and funding the round-robin test.

References

Antoniou M., Zhao C., O'Shea K.E., Zhang G., Dionysiou D.D., Zhao C., Hanf C., Nadagouda M., Choi H., Fotiou T., Triantis T.M. and Hiskia A. (2016), Photocatalytic Degradation of Organic Contaminants in Water: Process Optimization and Degradation Pathways, in: D.D. Dionysiou, G. Li Puma, J. Ye, J. Schneider and D. Bahnemann (Eds.), RSC Energy and Environment Series No. 15 Photocatalysis: Applications, The Royal Society of Chemistry, Cambridge, UK, pp. 1-34.

Pillai S.C., McGuinness N.B., Byrne C., Han C., Lalley G., Nadagouda M., Falaras P., Kontos A.G., Gracia-Pinilla M.A., O´Shea K., Mangalaraja R.V., Christophoridis C., Triantis T.M., Hiskia A., and D.D. Dionysiou (2018), Photocatalysis as an Effective Advanced Oxidation Process, in: M.I. Stefan (Ed.), "Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications", IWA Publishing, London, UK, pp. 333-381.

ISO-10676 (2010), Fine ceramics (advanced ceramics, advanced technical ceramics) – test method for water purification performance of semiconducting photocatalytic materials by measurement of forming ability of active oxygen.

ISO-10678 (2010), Fine ceramics (advanced ceramics, advanced technical ceramics) – determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue.