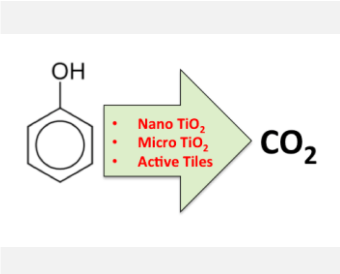
Phenol Photodegradation in Presence of Nano or Micro-TiO2: Performance Comparison and Study of the Different By-products.

C. Bianchi[a,1], *M. Stucchi*[a,1], *C. Pirola*[a,1], *G. Cerrato*[b,1], *S. Morandi*[b,1], *B. Sacchi*[a,1], *S. Vitali*[a,1], *V. Capucci*[c]. *(a) Università degli studi di Milano, Dip. Chimica - 20133 Milano, Italy, claudia.bianchi@unimi.it. (b) Università degli studi di Torino, Dip. Chimica & NIS Interdept centre - 10125 Torino, Italy. (c) GranitiFiandre SpA, 42014 Castellarano, Italy. (1) Consorzio INSTM, Firenze, Italy.*



In the present work the degradation of phenol in water was performed comparing the use of a commercial micro-sized TiO_2 (1077 by Kronos) with a nano-TiO_2 (P25 by Evonik), as well as with commercially available photoactive porcelain grés tiles; in particular, the photoefficiency of the micro-sized sample was evaluated both as powder form and immobilized on tiles, in order to make a comparison and point out the main differences and changes in term of diffusion of the pollutant, absorption, photoactivity and efficiency.

Background

Phenol and phenolic derivatives are the major pollutants of the aquatic environment because of their widespread use [1,2] and they are known as recalcitrant organic compounds or POPs (persistent organic pollutants). Phenol is also relevant in the field of environmental research because it has been chosen frequently as a model pollutant. The traditional physical techniques are only be able to transfer organic compounds from water to another phase, thus creating secondary pollution [3,4,5]. On the contrary, photocatalysis is able to induce the complete oxidation reactions, leading the most part of the elements to their higher oxidation state, namely CO_2. Titanium dioxide (TiO_2) is considered one of the best photocatalysts, owing its outstanding features including photocatalytic activity, inertness, physical and chemical stability, full availability even as commercial product, and low cost. In spite of these advantages, many authors evidenced serious problems about the use of nano-sized materials, e.g. difficulty on both sample handling, separation and collection, and the possible side-effects on human health as well [6,7,8,9].

One of the main applications of the TiO_2 is its use in the building materials, as tiles or cements: in particular in this instance, working with micro-powders instead of nano could be extremely useful and advantageous. Even if the main drawback of the use of photocatalytic tiles is the decrease of the amount of available photocatalyst, with a consequent loss of photo-activity, the final separation step between the catalyst and the depolluted water is simpler and makes this product suitable for a wide range of applications.

Objectives

In the present work the degradation of phenol in water was performed comparing the use of a commercial micro-sized TiO_2 (1077 by Kronos) with a nano-TiO_2 (P25 by Evonik), as well as with commercially available photoactive porcelain grés tiles (Active^{TM} tiles by GranitiFiandre). In particular, the photoefficiency of the micro-sized sample was evaluated both as powder form and immobilized on tiles, in order to make a comparison and point out the main differences and changes in term of diffusion of the pollutant, absorption, photoactivity and efficiency. Samples were characterized and analyzed with XRD, SEM and TEM.

Phenol photodegradation was followed over time, considering also the development of different byproducts and the mineralization, i.e. the completely conversion of phenol in CO_2, comparing different starting pollutant concentrations as well.

By means of the FT-IR analysis on the samples after the catalytic reaction, it was possible to evaluate the by-products remained on the different TiO_2 surface.

Moreover, a new phenol photodegradation pathway has been proposed, starting from the experimental data collected.

Methods

Two commercial TiO_2 powders were chosen as nano-size and micro-size photocatalysts, respectively. P25 by Evonik is usually used as reference material, while TiO_2 1077 by Kronos is commercially classified as pigment. 1077 is also used in commercially available photoactive porcelain grés tiles (named Orosei Active^{TM}) [10].

Phenol (Sigma Aldrich ≥ 99%) is purchased and used without further purifications.

Photocatalytic test using powdered nano and micro-TiO_2 catalysts

Phenol photodegradation was performed in a PIREX slurry reactor with a volume of 0.5 L. A Jelosil HG500 UV lamp (500 W, emission 310-400 nm) is placed 15 cm distant from the reactor. We kept the temperature constant by means of a glass serpentine in which water (20°C) flows, and the solution homogeneous by means a magnetic stirrer. The emitting power was verified to be 100 Wm^{-2}, evaluated in the middle of the reactor by a radiometer instrument (Delta OHM, model HD2102.2).

Samplings were executed every 60 min using a glass syringe and the solution was filtered before the analyses, performed using a HPLC instrument, a UV-VIS spectrophotometer analyzer (T60 UV-vis PG LTD instruments), and a TOC instrument.

Photocatalytic test using both powders and photoactive TiO_2 tiles

A cylindrical batch reactor of 0.5 L volume was use for phenol degradation tests in presence of photocatalytic tiles, at constant temperature.

Refrigeration was allowed by a cooling jacket and a UV lamp was directly immersed into the phenol solution (AEOPL-7913 produced by Hua Jia Electric Appliance co, 11 W power). Eight tiles 1x20 cm^2 were deposited inside the reactor, with the photocatalytic surface facing the center of the reactor and the solution was kept under magnetic stirring for all the time.

Results

P25 shows a better photoactivity compared to Kronos 1077 as expected, in particular because of the higher surface area. Through the by-products analysis (HPLC, FT-IR) it was possible to evaluate the different behavior of the photocatalysts, starting from different phenol concentrations. Interesting are also the results obtained using the photocatalytic tiles, about which a loss of activity in term of phenol photodegradation has been observed, but their effectiveness has been shown. Moreover, starting from the data collected about pollutant diffusion, photocatalytic tiles performances compared to pollutant concentration, time of reaction and more, it is possible to improve the system and optimize the chances of these building materials. The data related to the study of the by-products were useful to hypothesize a pathway for the phenol photodegradation that is different from the linear one, usually proposed.

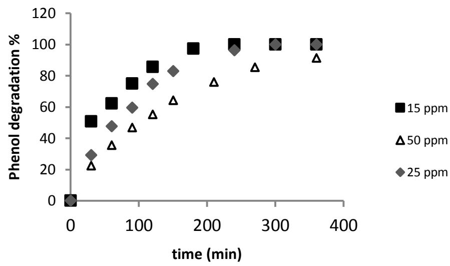


Figure 1. Phenol degradation vs. time

Conclusion

This paper proposes some results about photocatalytic tests, carried out using different titania samples, in particular for the phenol abatement in liquid phase. After the test on the powders, they were deposited on particular tiles (WGActive[10]) that were tested in the same reaction. Even if the phenol photodegradation pathway has been widely studied, this work wants to give some practical data about the by-products development, in particular in relation to the type of TiO_2 used and to the starting concentration of the pollutant, as well as a comparison between the titania powders and the performance obtained using photocatalytic tiles, on which micro-TiO_2 is deposited.

References

[1] J.W. Patterson, *Wastewater treatment technology, USA: Ann Arbor Science Pub. Inc*, 1977.

[2] T.A. Ozbelge, O.H. Ozbelge, S.Z. Baskaya, *Chemical Engineering and Processing,* 41 (2002) 719-730.

[3] Z. Aksu, F. Gonen, *Progress Biochemistry,* 39 (2004) 599-613.

[4] Z. Aksu, D. Akpinar, *Biochemical Engineering Journal*, 7 (2001) 183-193.

[5] A. Camporro, M.J. Camporro, J. Coca, H. Sastre, *Journal of Hazardous Materials*, 37 (1994) 207-14.

[6] S.M. Ruel, J.M. Choubert, H. Budzinski, C. Miege, M. Esperanza, M. Coquery, *Water Science and Technology*, 65 (2012) 1179-1189.

[7] S.M. Ruel, J.M Choubert, M.Esperanza, C. Miege, M.P. Navalon, H. Budzinski, K. Le Menach, V. Lazarova, M. Coquery, *Water Science and Technology*, 63 (2011) 2486-2497.
[8] G.C. Fonger, P. Hakkinen, S. Jordan, S. Publicker, *Toxicology* (2014).
[9] B. Trouiller, R. Reliene, A. Westbrook, P. Solaimani, R.H. Schiestl, *Cancer Research*, 69 (2009) 8784-8789.
[10] patent n. EP2443076.