Photocatalytic degradation of dyes in water with micro-sized TiO2 as powder or coated on porcelain-grès tiles

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(Article begins on next page)
Photocatalytic degradation of dyes in water with micro-sized TiO$_2$ as powder or coated on porcelain gres tiles

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ABSTRACT

Some particular drawbacks due to the industrial use of nano-sized TiO$_2$ (safety, recovery) in photocatalytic processes for water remediation can be avoided choosing micro-sized TiO$_2$. Tests on both micro-sized TiO$_2$ powder and industrially prepared photocatalytic tiles, having the surface of porcelain gres tiles hot-coated with the same photocatalyst, were performed. Good photocatalytic performance in the degradation of three organic dyes (Rhodamine B, Crystal Violet and Methylene Blue) in water phase were achieved. Photocatalytic tiles can really represent a good alternative to TiO$_2$ suspensions and pave the way for the fully industrial use of photocatalysis in environmental remediation.
Polluted water ➡️ Clear water
1. INTRODUCTION

Titanium dioxide (TiO$_2$) is worldwide considered as one of the best semiconductor to be used as photocatalyst for pollutants degradation. Exposition under UV light promotes redox reactions and charges separation that lead to oxidative processes as reported by Razavi et al.[1]. TiO$_2$ is often used in powdery form as nano-sized particles with high surface area, so as to enhance its photoactivity. Most of the literature reports consequently the use of nanometric TiO$_2$ materials for many purposes, from disinfection [2] and air purification [3] to decomposition of organic matter [4] or heavy loads metals in waste waters [5]. However, some recent papers have underlined the possible side-effects on human health due to both use and exposure to nanoparticles [6,7], as the ultra-small particles can penetrate inside human body from skin and nose especially when they are used in products like paints or simply cold-coated on materials surfaces for air purification and a loss of photoactive powder cannot be neglected.

Problems can be observed in liquid phase as well, where nano-sized powder can affect the catalyst recovering at the end of the reaction, hindering an industrial use of TiO$_2$ nanopowders, due to the extreme difficulty in the final filtering necessary to separate photocatalytic powder and the cleaned solution, as reported by Schulze et al.[8].

On this basis, a great attention is focused on the potential of TiO$_2$ micro-sized powders to be used as photocatalyst for the degradation of organic contaminants. Recent results for both NOx and VOC degradation in gas phase seem to be very promising [9] but no data are available for the degradation of pollutants in liquid phase yet.

Main target of the present work is to investigate the performance of a commercial micro-sized TiO$_2$ (1077 by Kronos) used as photocatalyst in the degradation of three different dyes (Rhodamine B, Crystal Violet and Methylene Blue) in water. Micro-sized sample was used as
recently received, so to compare the obtained results with the classical nano-sized commercial P25 by Evonik, always used as photocatalyst reference material.

Previously Marcos et al. [10] reported the deposition of TiO2 layers on common ceramic glazed tiles using the screen-printing process, which is a low cost and common technique used for decoration in the ceramic industry. Labrincha et al. [11] deposited several commercial titania powders by jet spray on ceramic tiles, then fired to stabilize the layers. In both cases a good activity of nano-sized TiO2 photocatalytic layers on ceramic tiles was demonstrated in the degradation of Orange II dye. In the present case, micro-sized 1077 was industrially hot-coated at the surface of a porcelain gres tile (Orosei Active™). Tests using photoactive tiles were carried out to verify the efficacy of the coated catalyst to degrade dyes in water media to obtain a stable and very easy way to separate the solution at the end of the reaction from the photoactive catalyst.

2. EXPERIMENTAL

2.1 Materials and Characterization

TiO2 1077 by Kronos was chosen as micro-sized photocatalyst, commercially classified as pigment. Characterization of this sample was previously carried out and elsewhere reported [12]. However, principal features (crystallographic phase and crystallites size by XRD, specific surface area (S.S.A.) by BET, and OH/O_TOT by XPS measurements) are summarized in Tab. 1. 1077 is also used in commercially available photoactive porcelain gres tiles (named Orosei Active™). TiO2 was mixed industrially with a silica-based compound, sprayed on the tiles surface, fired in industrial kiln a 680°C and cleaned with a rotating wire brush to remove the TiO2 weakly stuck at the tile surface, as already reported [13].
Rhodamine B (RhB, dye content ~95%, C₂₅N₃H₃₀Cl, PM 409 g/mol), Methylene Blue (MB, dye content ≥97%, C₂₈H₃₁ClN₂O₃, PM 479 g/mol) and Crystal Violet (CV, dye content ≥90%, C₂₈H₃₁ClN₂O₃, PM 479 g/mol) were used as organic pollutant. Each dye (Sigma Aldrich) was used without further purification.

Table 1 Physico-chemical features of either 1077 and P25 powders.

<table>
<thead>
<tr>
<th>Sample</th>
<th>crystallographic phase</th>
<th>S.S.A. (m² g⁻¹)</th>
<th>crystallite size (nm) (XRD)</th>
<th>OH/O&lt;sub&gt;TOT&lt;/sub&gt; (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>75/25 anatase/rutile</td>
<td>50</td>
<td>26</td>
<td>0.14</td>
</tr>
<tr>
<td>1077</td>
<td>anatase</td>
<td>12</td>
<td>110</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Two different dye concentrations were used in the present paper: 1x10⁻⁴ M and 1x10⁻⁵ M, depending on the reaction set-up. The most concentrated solution was used to verify the efficiency in the photodegradation of organic molecules in water of powdered micro-sized TiO₂ as stressing conditions. These results were compared to the results already obtained by P25 by several authors in the past [14,15] and reconfirmed in this text. The less concentrated solution, higher than the one reported by Marcos et al. [10], were used to test the performance of Orosei Active™ tiles.

The solutions were prepared by dissolving the dye in distilled water and without any pH adjustment, but leaving them at their spontaneous values.

1077 powder has been characterized by HR-TEM (Jeol JEM 3010 instrument, equipped with LaB₆ filament and operating at 300 kV). HR-SEM-EDX analysis were performed on as received...
Orosei Active™ tiles (Field Emission Gun Electron Scanning Microscopy LEO 1525, metallization with Cr. Elemental composition was determined using Bruker Quantax EDS.).

2.2 Photocatalytic test using powdered nano and micro-TiO$_2$ catalysts

Dyes degradation in water media was performed in a slurry reactor (Fig. 1a) of 0,5 L volume [16]. Irradiation was allowed by the use of an external UV lamp (500W, Jelosil®, HG500, halide lamp), emitting in the range 315-400 nm and with a emitting power evaluated in the middle of the reactor by a radiometer instrument (Delta OHM, model HD2102.2) of 75 W/m$^2$. The reactor was equipped by an internal refrigerating serpentine system.

Figure 1 - a: Continuous stirred slurry reactor. A: refrigerating serpentine system; B: Stirrer; C: UV lamp. b: Cylindrical batch reactor used for photocatalytic experiments. D: UV lamp; E: Orosei Active® tiles; F: Cooling jacket; G: Magnetic stirrer.
Dye adsorption tests have been carried out in the dark using a catalyst amount of 1 g/L at four different dyes solution (concentration ranged between $10^{-6}$-$10^{-4}$M) for six hours.

Photolysis tests have been performed for six hours; the same for photocatalysis performed using fresh 0.1 g/L TiO$_2$ in powder form. Dyes degradation was checked every 60 min. Analytic determination of the dyes concentrations in water solution was performed by a UV-vis spectrophotometer analyzer (T60 UV-vis PG LTD instruments), using water as the reference.

Pure CV has an absorbance maximum at 590 nm, RhB at 555 nm and MB at around 670 nm.

2.3 Photocatalytic test using photoactive TiO$_2$ tiles

A cylindrical batch reactor of 1 L volume was used for dye degradation tests in presence of ten photoactive tiles (0.03 m$^2$ total surface photoactive area) immersed into the liquid solution, as schematically shown in Fig.1b. Refrigeration was allowed by a cooling jacket. Two different lamps directly immersed into the dye solution were used with this setup: a typical germicidal 9 W UV-C lamp (Philips TUV BL-S, model AEPL-7913 mercury vapor low pressure), with a UV-A illuminance at the tiles surface of 1 W/m$^2$ and a 125 W UV-A lamp (Jelosil, mercury vapor low pressure), with an illuminance of 65 W/m$^2$.

The same batch of Orosei Active™ tiles was used for all the tests reported in the present paper; after each test the tiles were simply washed using deionized water and acetone and then left in deionized water all night long.

Adsorption tests were carried out by dipping the tiles into the dyes solutions in dark conditions for six hours. To avoid any alteration of both irradiating conditions and fluid dynamic of the system, photolysis was performed with the tiles still inside the reactor but with the active faces turned towards the dark side of the reactor, thus preventing the photoactivation of the TiO$_2$
catalyst. During photocatalytic tests the TiO$_2$ active faces of the tiles were turned towards the UV light.

The same dyes solution described in the 2.1 section were used in the present setup at a concentration of $1 \times 10^{-5}$ M. Kinetics were monitored by UV-vis spectrophotometric analysis as described in 2.2.

RESULTS AND DISCUSSION

3.1 Powders and tiles characterization

Conventional and HR-TEM investigations indicate that (almost) no ultrafine crystallites are evident for the plain 1077 powder (see Figure 2a, left-hand section): in particular, all particles exhibit well-ordered crystallographic terminations (see Figure 2a, right-hand section), all belonging to the anatase phase (mostly to the (101) family of planes), as also reported in [12], referring to XRD analysis performed on the same sample. HR-SEM images of Orosei® tiles show a homogeneous distribution of TiO$_2$ crystallites in the micro-sized range without ultrafine particles [13].
Figure 2. 2a: TEM images of pure 1077 in powder form. 2b: HR-SEM images of Orosei Active\textsuperscript{TM} tiles refer to 100.00K X.

A further magnification (Fig.2b) reveals the particles dimension that ranges between 100 and 125 nm as already obtained by XRD (Tab.1). By EDX analysis it was possible to determine the quantity of TiO\textsubscript{2} coated on the tiles surface as 1.1 g/m\textsuperscript{2}. Related to the ten tiles used in our tests
with the total photoactive surface of 0.03 m², a quantity of 0.033 g/L of TiO₂ was estimated to work during the photocatalysis tests.

3.2 Photocatalytic degradation of dyes in presence of TiO₂ powders

Experimental dark tests have shown a very low adsorption of all the dyes on both P25 and 1077 catalyst at the spontaneous pH we have in our working conditions. Notwithstanding P25 has specific surface area double than 1077 (25 m²/g and 12 m²/g, respectively) photolysis of CV and MB are almost negligible for both the catalysts (6% for both dyes for P25, 9% and 4% for CV and MB, respectively, for 1077). 12% of dye degradation for simple photolysis (10% for P25) was achieved for RhB.

The dye molecules here considered are all cationic organic-based ones with a several benzene rings and high molecular weight, being thus quite complex systems to be degraded.

Photocatalytic tests show good results in dyes abatement. Nano-sized powder shows the best results for all the considered dyes achieving the complete decolorizing of the water solution in 6 hours in the case of CV (Fig.5SI), but also micro-sized sample are able to degrade the pollutants with a good efficiency (ranging from 48 to 58% depending on the dye in six hours) (Fig.3).
Figure 3. Photocatalysis of dyes performed with powdered micro-TiO$_2$ catalyst (1077):

- □ Crystal Violet; ▲ Methylene Blue; ◊ Rhodamine B.

A study on the reaction rate has been done by elaborating the kinetic constants for both 1077 and P25 samples. Photocatalysis generally follows a Langmuir-Hinshelwood mechanism [17]:

\[ r = k\theta = \frac{kKC}{1 + KC} \]  

(1)

where $r$ is the reaction rate for the oxidation of the reactant, $k$ is the true kinetic constant, including the mass of catalyst and the flux of efficient photons, $\theta$ is the coverage fraction of the material, $C$ is the dye concentration in solution and $K$ is the adsorption equilibrium constant.
Eq. 1 can be approximated to a pseudo-first order kinetic with respect to the negligible adsorption of the dyes by the micrometer catalyst used:

the classical equation can be approximated to a pseudo-first order kinetic with respect to the negligible adsorption of the dyes by the micrometer catalyst used:

\[ r = -\frac{dC}{dt} = k_{app} C \]

where \( k_{app} \) is the apparent first order rate constant and \( t \) is the time. The integral form in function of time of the Eq. 1 can be withdrawn and the slope of the straight line interpolated represents the \( k_{app} \). The rate constants were consequently calculated for both samples and for all the tested dyes and are all in the \( 10^{-3} \) magnitude order. (data in Tab. 2). It is worth noting that both nano- and micro-powders exhibit k values in the same order of magnitude, most likely because the photocatalytic process follows a similar pathway despite the dimensions of the TiO\(_2\) powder.

**Table 2** Rate constant calculated for both 1077 and P25 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RhB rate constant ( *10^{-3} ) (min(^{-1}))</th>
<th>MB constant rate ( *10^{-3} ) (min(^{-1}))</th>
<th>CV constant rate ( *10^{-3} ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1077</td>
<td>1.78</td>
<td>1.78</td>
<td>2.64</td>
</tr>
<tr>
<td>P25</td>
<td>5.0</td>
<td>5.1</td>
<td>8.2</td>
</tr>
</tbody>
</table>
The possibility to recover the powdered catalyst was checked by simply filtering the final degraded solution in a standard Bückner funnel equipped with a filter paper or directly centrifuging it in a laboratory scale equipment working at 10000 rpm.

For 1077 sample the simple centrifugation was sufficient to recover all the used photocatalyst. The powder was washed several times in deionized water and reused in the same dye degradation test (CV discoloration) with no loss of photoactivity. On the other hand, no recovery of P25 was possible neither filtering or centrifuging the solution. The nano-powder passed completely through the filter paper and it was not separated by the solution by centrifugation remaining very well-dispersed in water.

The lower efficiency of 1077 micro-sized TiO$_2$ in the degradation of dyes in water than nano-sized photocatalyst is fully rewarded by the facility to recover the photoactive powder from the solution at the end of the purification reaction and reuse it eventually after a simple washing in water.

### 3.3 Photocatalytic degradation of dyes in presence of TiO$_2$ activated tiles

According to the previous results obtained by the use of micro-sized TiO$_2$ catalyst, the activity of 1077 industrially hot-coated onto porcelain tiles was evaluated in another experimental setup verifying the material efficiency with two different UV lamps immersed inside the dyes solution. Control experiments of photolysis and adsorption of dyes on the tiles were carried out. Dark tests shown a 25% adsorption of CV and MB, while RhB adsorption is on the contrary almost negligible. However, dyes were exclusively fixed in the backside and lateral sides of the ceramic pieces, i.e. in the surfaces uncovered by the photocatalytic layer.
Direct photolysis highlights different results depending on the used lamp: a percentage degradation of 64% for CV, 70% for MB and 14% for RhB was achieved for 9W immersion lamp, a very high result in comparison to the photolysis tests reported in section 2.2. However in this case this was a germicidal lamp and therefore an emission in the UV-C region is present and is probably enhancing the photolysis process.

Lower results were obtained using the 125W UV-A immersion lamp. The absence of UV-C allows to have dyes degradation due to pure photolysis within 30% for CV and MB, 10% for RhB (we have not to forget that tiles are already immersed not to alter the reactor flow dynamic and therefore adsorption process is still present).

Results obtained by photocatalytic tests, carried out by using the coated micro-TiO₂ catalyst onto the tiles surface are showed in Fig. 4 for 9W lamp.
Figure 4. Photocatalysis with Orosei™ Active tiles and UV-light irradiation (9W immersion UV lamp); □ Crystal Violet; ▲ Methylene Blue; ◊ Rhodamine B.

Degradation of dyes is improved by the use of the photoactive tiles; in fact after a six hours reaction, the percentage degradation value obtained is 78% for CV, 88% for MB, and the 30% for RhB, revealing an increase of about 15% of degradation on all dyes in comparison to the simply photolysis tests.

Tests with the 125W UV-A lamp lead to the complete degradation of CV (Fig. 5) and MB in less than three hours and the disappearance of 71% RhB in 6 h.
Figure 5 Attenuation of the 590 nm absorbance peak of CV by OroseiTM Active tiles and UV-light irradiation (125W immersion UV-A lamp)

4. CONCLUSIONS

Main target of the present work was thus to verify the possibility to use micro-sized TiO$_2$, instead of the classical nanopowders, in the degradation of organic molecules in water phase. The obtained results have to be considered with great importance as using micro-sized TiO$_2$ the health risks related to nano-sized particles can be avoided; moreover such a micro-sized powder can be easily filtered and recovered, in order to be immediately reused for further photodegradation reactions, opening the way of a fully industrial use of photocatalysis in environmental remediation.

A further improvement can be achieved coating micro-TiO$_2$ on porcelain tiles surfaces. The photocatalytic materials described here can be reused, just after mere rinsing of the tiles in distilled water, and without affecting the photocatalytic activity. In fact all the tests performed in
the present work were done using the same batch of ten samples obtained from industrially prepared tiles (Orosei Active™), and no loss in their photoactivity was monitored. This indicates that the TiO₂ deposited layers are not deactivated during the reaction either by loss or poisoning of the catalyst, and can be reutilized in subsequent runs. These new industrial ceramic materials are surely an interesting alternative to TiO₂ suspensions, for example in photocatalytic applications avoiding the removal of the particles at the end of the process.

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REFERENCES


