PHOTOCATALYTIC CEMENT: A NEW APPROACH TO ENVIRONMENTAL PROTECTION

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Abstract

The interest for photocatalytic cement pastes to protect environment has here been finalized to abate on degradation PM10 concentration considered as the most dangerous pollutant to citizens of urban centres. The catalytic action of these materials was evaluated on measuring the respiratory capacity of yeast Saccharomyces cerevisiae cells incubated with particulate matter samples treated or untreated with them. The cement contained 3% of TiO2 as photoactive catalyst based for its photocatalytic activity on its semiconducting properties. The experimental time ranged from 24 to 96 hours. The value of abatement was relatively low (about 30%), but it was possible to double it on enriching the cement by addition of TiO2 or by using a cement richer in TiO2 since its preparation step. The catalytic activity is also enhanced by an antimicrobic one.

1. INTRODUCTION

A new and innovative approach contributing to minimize the airborne pollutants in our cities may be the use of suitable photocatalytic cementitious materials containing TiO2. In general heterogeneous photocatalysis can be considered as one of the new “advanced oxidation technologies” used in the recent years as a promising method for the removal of toxic organic and some inorganic contaminants from the air and the water.

Several bibliographical reviews have been recently devoted to this problem [1-8]. When a semiconductor catalyst, such as TiO2, absorbs a photon of energy that is equal to or greater than its band gap (in case of TiO2 amounting to 3.2 eV), an electron (e⁻) may be promoted from the valence band (VB) to the conduction band (CB) thus generating an electron vacancy “hole” (h⁺) and obviously an electronic site. The electron and the hole can migrate to the catalyst surface where they participate in redox reactions with different species adsorbed on catalyst surface. Holes can particularly react with surface-bond H2O or OH⁻ to produce the hydroxyl radical OH⁺, whereas electrons during reaction with oxygen can generate superoxide radical anion O2⁻. The hydroxyl (OH⁺) and superoxide radical anions (O2⁻) are supposed
to be the primary oxidizing species in the photocatalytic oxidation processes. An example of the described mechanism can be resumed as follows:

\[
\begin{align*}
\text{TiO}_2 + h\nu (\text{UV}) & \quad \rightarrow \quad \text{TiO}_2 (e_{CB}^- + h_{VB}^+) \quad (1) \\
\text{TiO}_2 (h_{VB}^+) + H_2O & \quad \rightarrow \quad \text{TiO}_2 + H^+ + OH^- \quad (2) \\
\text{TiO}_2 (e_{CB}^-) + O_2 & \quad \rightarrow \quad \text{TiO}_2 + O_2^- \quad (3) \\
O_2^- + H^+ & \quad \rightarrow \quad HO_2^- \quad (4) \\
\text{Organic compounds} + OH^- & \quad \rightarrow \quad \text{degradation products} \quad (5)
\end{align*}
\]

At the end of the process, most organic compounds can be oxidized to carbon dioxide and water. In a recent patent of Italcementi, also the cementitious materials opportune prepared containing titanium dioxide, mainly in the form of anatase, show photocatalytic activity when irradiated with adequate wavelength light. Therefore, these materials containing a non-toxic semiconductor catalyst such as titanium dioxide might be a good help and a new way to abate the airborne pollutants (i.e. particulate matter PM containing many different organic chemical species adsorbed on it). In the present work, the main objective was aiming to evaluate action of photocatalytic cementitious materials on PM10 (airborne particulate matter with aerodynamic diameter less than 10 μm) in a possible decrease of the concentration of this dangerous environmental pollutant. This evaluation has been realized by suitable respirometric tests on S. Cerevisiae cells. It’s well known that, in the cellular respiration, using glucose as a nutrient, the aerobic cells consume oxygen as schematically described in the following reaction:

\[
\begin{align*}
\text{yeast cells} \quad C_6H_{12}O_6 + 6O_2 & \quad \rightarrow \quad 6CO_2 + 6H_2O + \text{Energy} \quad (6)
\end{align*}
\]

However, in the presence of any chemical perturbation (i.e. PM10 containing many toxic substances for one or more of the metabolic processes in the cell respiration), it’s possible to observe a variation of oxygen consumed by the yeast cells. As larger is this variation, as higher has to be considered the concentration of toxic substances to which yeast cells have been exposed. Therefore, the toxicity can be expressed as inhibition percentage of yeast cells respiration and estimated by appropriate respirometric curves consisting in the measure of the oxygen consumed by the yeasts with the time. From the experimental point of view, the catalytic action of photocatalytic cementitious materials has been realized using two halves of each PM10 filter sample (PM10 fibre glass filters exposed to urban air were provided by ISS in Rome - Italy) to estimate the PM10 toxicity itself with the first half and with the second one the toxicity of photoexposed PM10 to UV light in presence of an Italcementi photocatalytic material for 48, 72, and 96 hours. The photoexposure has been performed in controlled conditions by a veterometer photodegradator QUV Weathering Tester and Italcementi photocatalytic cementitious paint containing 3% of titanium dioxide was used as catalyst. In particular two half filters sampling treated-untreated PM 10 were incubated with the yeasts and toxicity tests were subsequently carried out. In conclusion, the comparison
between the obtained results has permitted to evaluate the photocatalytic cementitious material action on the toxicity abatement of treated PM10 samples. Some other preliminary tests indicated that the photocatalytic materials richer (up to 7%) in TiO₂ than those containing 3% of dioxide titanium might be more active in PM10 abatement.

2. EXPERIMENTAL

2.1 Materials and instruments

The following reagents and materials were used: D-glucose for microbiology, a buffer solution prepared at pH about 5.6 by suitable phosphate salts, as catalyst material it has been used a photocatalytic cementitious paint containing 3% of TiO₂ made available by Italcementi. The cells used in the toxicity tests belonged to a wild diploid strain of Saccharomyces cerevisiae. Such tests will be described in a next paragraph. The following apparatus was used: veterometer, photodegradator QUV Weathering Tester-Model QUV/spray Q-Panel LAB-Products for the photoexposures (UV - λ = 310 nm, irradiance 0.6 W/m², humidity 58%) of the PM10 samples in presence of photocatalytic cementitious paint; Amel Instruments, Dissolved oxygen meter, model 360 and amperometric oxygen gas diffusion sensor (Clark electrode). A computer was used to record as function of time the oxygen consumed by the yeast cells in respiration.

2.2 Samples

The PM 10 samples have been provided by the I.S.S. in Rome – Italy. Such samples of PM 10 have been collected on fibre glass filters (Schleicher & Schuell, d= 47 mm) in urban area of Rome.

2.3 Preparation of samples

At the beginning of the preparation of PM10 samples, each filter has been divided in two identical halves and three petri dishes have been prepared. Subsequently in the first dish we have exactly injected 1500 μl of a Saccharomyces cerevisiae yeast solution (this was previously prepared by hydration of yeasts in distilled water) and 10 ml of phosphate buffer solution (pH = 5.6). In the second petri dish containing the same quantity of yeast cells and buffer solution, the first half of PM10 filter has been added. In the last petri dish we have exactly added 1500 μl of the Saccharomyces cerevisiae yeast solution, the another half of PM10 filter previously exposed to UV light with photocatalytic paint, and 10 ml (final volume) of buffer solution which had been used in the photocatalysis. The three petri dishes (respectively, blank/control, untreated PM10 sample, treated PM10 sample) containing the yeasts have been subjected to incubation time of 24 hours under magnetic stirring. After incubation period, the content of the three petri dishes has been poured off one by one in three suitable tubes to which their washing water was also added. Then such tubes have been centrifugated to 3000 rpm for 20 min. At the end, the pellet of yeast in the bottom of each tubes was recovered without the solution which was above. The pellets of yeast were again suspended in each tube by 1500 μl of distilled water. The solutions of yeast in the three tubes have been later used for respirometric tests. The photoexposures of PM10 half filters have been carried out in vetterometer by opened dishes to which it was applied the photocatalytic paint. In each modified dish there was the PM10 sample and 5 ml of the buffer solution.
At the end of photoexposures (48, 72, 96 hours), the treated PM10 samples have been used as said above, that is evaluated for their respirometric toxicity.

2.4 Method
The principle of method consists in measuring with oxygen electrode the change in O$_2$ concentration which is due to yeast cellular respiratory activity (DppmO$_2$) [9].

In particular the measurement is performed comparing, for each measure, the obtained value of DppmO$_2$ (2-3) from the cells exposed to PM 10 (treated or untreated with UV light in presence of photocatalitic paint) with the DppmO$_2$ (1) one deriving from cells (blank) that have been subjected to same incubation time and same experimental protocol in absence of exposure to PM10. The inhibition percentage of respirometric activity has been related as to toxicity. It can be calculed as follows:

\[
\text{Toxicity \%} = \frac{\left| \text{DppmO}_2 (1) - \text{DppmO}_2 (2-3) \right|}{\text{DppmO}_2 (1)} \times 100
\]

(a)

From the experimental point of view, for the measurement of dissolved oxygen, the electrode has been immersed in a glass beaker containing a standard glucose solution, concentration 1 M, under constant magnetic stirring. After stabilisation of the signal, 1000 µl of yeast solution contained in one of the tubes (see paragraph 2.3) were added to the glucose solution. The variation of dissolved oxygen concentration, caused by yeast cells in respiration, has been recorded as function of time. In this way we obtained the “respirometric curves” and from these it has been possible to calculate the toxicity of the coupled half filters of treated-untreated PM10.

3. RESULTS AND CONCLUSION
The respirometric tests data on the treated PM10 half filters for 48, 72 and 96 hours by photocatalytic paint under UV light are shown in fig. 1, 2 and 3. In these graphics also the data of respirometric tests of the blanks and untreated PM10 half filters are plotted.

**FIG. 1 - Respirometric tests data (treated PM10 for 48h by UV light and photocatalytic cementitious paint containing TiO$_2$ 3%)**
FIG. 2 - Respirometric tests data (treated PM10 for 72h by UV light and photocatalytic cementitious paint)

FIG. 3 - Respirometric tests data (treated PM10 for 96h by UV light and photocatalytic cementitious paint)

In Tab.1 we have summarized the obtained results on treated-untreated PM10 samples:

<table>
<thead>
<tr>
<th>Treatment time of PM10 by UV and photocatalytic paint (hours)</th>
<th>Toxicity % of treated PM10</th>
<th>Toxicity % of untreated PM10</th>
<th>Toxicity reduction</th>
<th>Toxicity reduction (absolute value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>(9 ± 2)</td>
<td>(15 ± 2)</td>
<td>(34 ± 12)</td>
<td>(6 ± 4)</td>
</tr>
<tr>
<td>72</td>
<td>(9 ± 3)</td>
<td>(19 ± 5)</td>
<td>(44 ± 20)</td>
<td>(10 ± 4)</td>
</tr>
<tr>
<td>96</td>
<td>(12 ± 2)</td>
<td>(20 ± 3)</td>
<td>(39 ± 13)</td>
<td>(8 ± 3)</td>
</tr>
</tbody>
</table>
The confidential intervals shown in tab. 1 have been calculated with 80% probability level by following mathematic equation:

\[ X = \bar{X} \pm t \times \frac{\text{ST. DEV.}}{\sqrt{N}} \]

- \( \bar{X} \) mean
- \( N = 10 \) number of tests
- \( t = 1.38 \) for (N-1) freedom degrees and 80% confidence level

In details after exposing PM10 samples to UV (48, 72, 96 hours) with Italcementi photocatalytic paint, the toxicity values of PM10 decreased respectively from (15 ± 2)\% to (9 ± 2)\%, from (19 ± 5)\% to (9 ± 3)\%, and from (20 ± 3)\% to (12 ± 2)\%. It’s also necessary to consider that the wide variability of obtained data reflects the variegated composition of the PM10. In regard to the results of toxicity reduction percentage the following mean values were respectively obtained (34 ± 12)\%, (44 ± 20)\%, and (39 ± 13)\% for exposure time of 48, 72, 96 hours. As the toxicity abatement value was relatively low, we have supposed that photocatalytic cementitious materials containing a larger concentration of TiO2 may be more active than those ones containing 3% TiO2. For this reason two screening measures were carried out in abating PM10 toxicity by photocatalytic cementitious materials enriched in TiO2 concentration (7%). The results are shown in tab. 2

<table>
<thead>
<tr>
<th>Treatment time of PM10 by UV and photocatalytic cementitious material (hours)</th>
<th>Photocatalytic cementitious material containing TiO2 - 7%</th>
<th>Toxicity % of treated PM10</th>
<th>Toxicity % of untreated PM10</th>
<th>Toxicity reduction %</th>
<th>Toxicity reduction (absolute value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>blank paint</td>
<td>32</td>
<td>50</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td>24</td>
<td>blank cement</td>
<td>28</td>
<td>71</td>
<td>61</td>
<td>43</td>
</tr>
</tbody>
</table>

Last data show that the photocatalytic cementitious materials enriched in TiO2 have a higher action in abating PM10 toxicity than others containing 3% in TiO2. However, further measures will be necessary to confirm such results. Some results on the antimicrobial activity of photocatalytic cementitious materials show that during the first 130 minutes of photoexposure they have more active than ones not containing photocatalyst (tab. 3).
### Tab. 3

<table>
<thead>
<tr>
<th>Treatment time (min.)</th>
<th>DA (ppmO₂)</th>
<th>DB (ppmO₂)</th>
<th>DC (ppmO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>oxygen consumption from the respiration of yeasts after their treatment in dark in presence of blank cement containing TiO₂</td>
<td>oxygen consumption from the respiration of yeasts after their treatment by artificial solar light in presence simply of blank cement</td>
<td>oxygen consumption from the respiration of yeasts after their treatment by artificial solar light in presence of blank cement containing TiO₂</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>30</td>
<td>1.7</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>60</td>
<td>1.8</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>90</td>
<td>2.0</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>130</td>
<td>1.7</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In conclusion the tested photocatalytic cementitious materials behave as abating toxicity of PM even if at relatively low rate. But on the basis of our results their performances can be improved on increasing TiO₂ concentration at higher value than 3%.

## REFERENCES


