Photocatalytic degradation of phenol in aqueous phase with TiO$_2$ immobilized on three different supports with a simple method

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Abstract

Photocatalytic treatment of water and wastewater is a process which has been introduced since at least a couple of decades ago. But, in spite of its high capabilities, it has not yet reached its real niche among the other treatment methods. Immobilization of TiO$_2$ nano-particles seems to be the key to the industrialization of this process. In this research, an attempt was made to step toward this goal, by immobilizing the successful Degussa P-25 photocatalyst using a very simple and inexpensive method. The selected supports were glass plates, perlite granules, and steel fiber. Perlite granules have a porosity of more than 95%, which allows them to stay afloat on water surface. This gives the medium a unique characteristic from the processing point of view, which enables it to get wetted with the polluted solution without requiring any pumping and simultaneously be exposed to the radiation source when coated with the photocatalyst.

XRD analyses did not reveal any sensible changes in the structure of P-25 as a consequence of the applied immobilization process. HPLC analyses of the photocatalytic treatment experiments of waters synthetically polluted with phenol showed a fairly good performance for the three immobilized catalysts. But, the ones immobilized on perlite and steel fiber underwent some catalyst washout, which shows that the immobilization method used must be worked out more.

Keywords: Photocatalytic water treatment; Phenol; Titanium dioxide (TiO$_2$) immobilization; Perlite; Steel Fiber; Glass plates.

1. Introduction

Photocatalytic oxidation has been proposed since the 1980s as a solution to the problem of toxic water pollutants [1-2]. The key to the problem of industrializing the technology seems to be immobilization of TiO$_2$ nano-particles, as the most successful photocatalyst used in researches [3-4], on solid media suitable for the treatment process without lowering its photocatalytic efficiency. This study is based on this idea.

Many techniques have been developed for immobilizing TiO$_2$ catalysts onto a solid substrate, for example, dip coating from suspension, spray coating, sputtering, solgel-related methods, and electrophoretic deposition and different types of substrates have also been tested, for example glass beads, glass tubes, fiberglass, woven mesh, steel mesh, quartz, stainless steel, aluminum, metal fibers, and many types of plastics and ceramics such as alumina, silicon carbide, silica, etc. [5, 2].

The method used in this research was a very simple and inexpensive method, the very characteristics which are ideal for industrialization, originally developed by scientists at ECN (Netherlands Energy Research Foundation) for deposition of TiO$_2$ on quartz slides to prepare solar cells. We applied the method with minor changes for preparing coatings of TiO$_2$ on glass plates, steel fibers and perlite granules to use them as photocatalysts.

For glass-supported TiO$_2$ catalysts, it has been reported that oxygen bridges are formed between OH groups bound to the TiO$_2$ catalyst surface and the supporting glass plate during thermal treatment, and these strengthen the adherence of the catalysts to the glass plate [5]. Therefore, a mechanically stable coating should be expected from a properly coated TiO$_2$ layer on glass plates.

Perlite is a volcanic glass able to expand 4-20 times of its original volume upon heating resulting in flakes with a porosity greater than 95% [6]. This gives a unique characteristic to perlite: Pieces of this material can easily
float on water surface due to its extremely low density, even after being coated with TiO$_2$ particles, without being precipitated or suspended. This means that when TiO$_2$ coated pieces of perlite, usually available in the form of granules, are used as photocatalysts floating on top of the polluted water solution, they can be in direct contact with the polluted solution and the radiation source simultaneously, and the radiation source need not be immersed in the solution and it can be located above the solution. This also eliminates the need to use pumping to put the catalyst into contact with the solution, and no filtration is required either, because the granules can be easily managed to stay in the reactor without much effort, even in a continuous process with a reasonably low flowrate.

The main elements of perlite have been reported to be SiO$_2$ (~67 mol%), Al$_2$O$_3$ (~13 mol%), Na$_2$O (~6 mol%), K$_2$O (~5 mol%), CaO (> 1 mol%), and others (< 1 mol%) [6].

2. Experimental

2.1 Preparation of coating samples

The immobilization technique applied in this research was as follows:

1. In a beaker, 1.5 mL of very dilute nitric acid solution (pH = 3.5) and 4.5 mL of ethanol and 0.5 g of Degussa P-25 TiO$_2$ powder, a material widely studied as a standard of photocatalytic reactivity [11, 12], were added while stirring.

2. After a minute of stirring, a lump free paste was obtained, which was then sonicated for 5 minutes in ultrasound bath. It was then allowed to equilibrate.

3. The support sample was then coated with the TiO$_2$ suspension as uniform as possible.

4. The coated sample was then annealed for 30 minutes at 450°C.

Exceptions to the above procedure were: (1) For the samples coated on glass plates and steel fibers, a lower temperature (350°C) yielded similar results. (2) For the perlite samples, a much more dilute TiO$_2$ suspension was required. Therefore, the amount of ethanol used was quadrupled. Also, perlite granules were coated by the suspension during sonication.

2.2 Structural characterization

The quality of the coatings from the structural point of view, i.e. whether or not the P-25 crystals have undergone noticeable changes in structural properties such as rutile to anatase phase ratio and crystallite size during the immobilization process (esp. while heating), was assessed by analyzing the X-Ray Diffraction (XRD) patterns of the coating samples obtained using a Bruker D4 XRD analyzer with a Cu Kα X-Ray source. The main grain size ($L$) can also be estimated from XRD data by applying the Scherrer’s formula [5, 7].

2.3 Photocatalytic experiments

In order to assess the photocatalytic efficiency of the prepared catalysts, different reactor setups was constructed as follows:

1. A falling film micro-reactor for the catalysts supported on glass plates, consisting of an inclined surface with an angle of 10°, on which the glass plates where put and the solution was pumped from a vessel located beneath the inclined surface and poured onto the catalysts with a flowrate of ~15 ml·min$^{-1}$. The contacted solution slides down back to the vessel by gravity, where it was aerated at a rate of ~2.25 l·min$^{-1}$ to provide it with the dissolved oxygen required for the reactions, and to provide some agitation. The UV radiation source was located 12 cm above the catalysts. Two glass plates 100 x 50 mm in size each with a total amount of ~80 mg of P-25 powder coated on them was used in these experiments (Fig. 1).

2. A falling-film micro-reactor for the catalyst samples supported on steel fibers in which the piece of coated catalyst was hung over the solution vessel, from where the solution was pumped onto the catalyst with a flowrate of ~100 ml·min$^{-1}$ and dropped back to the vessel, where it was aerated at the same rate as in the previous setup. The UV light source was located 12 cm in front of the catalyst. Approximately 22 g of the catalyst ~1000 mg of which was the P-25 coating was used in these experiments. (Fig. 2)

3. For the catalysts immobilized on perlite granules, the catalyst was directly poured onto the contaminated solution surface in the Pyrex vessel. The solution was aerated from the bottom and the UV source was located 12 cm above the vessel. The amount of catalyst for each run was 11 g·l$^{-1}$ which is identical to 1000 mg·l$^{-1}$ of P-25.

4. The P-25 powders where directly used as the photocatalyst in a way quite similar to the coated perlite granules, except that it formed a slurry solution. Therefore, the samples taken from these experiments...
had to be filtered with 0.2 μm Millipore cellulose filters prior to analysis.

In all experiments, 200 ml of 1 mM phenol solution in ultra-pure deionized water was processed.

The UV illumination sources used for the experiments were two mercury lamps (Osram), one 125 W and the other 80 W, whose bulbs had been removed to avoid transformation of the UV light to visible light. Radiation spectra of both of the lamps were measured using an EPP 2000 Stellar Net spectrometer and both showed good radiation in the UV region with a peak at a wavelength of 254 nm (data not shown).

The photocatalytic runs were analyzed using Waters 2478 HPLC set with a two-channel UV-Visible light absorption detector set at 270 nm absorbance for phenol detection. A Novapack 150 mm x 39 mm ID C18 column was used, and the applied mobile phase was 1 ml·min\(^{-1}\) of gradient chromatography grade acetonitril (Merck) and deionized water (0.055 μS) at a ratio of 70:30.

### 3. Results and discussion

#### 3.1 XRD Analysis results

The resulting graphs of the XRD analysis are shown in Fig. 3. Also, the results of the calculations of the structural parameters as described in section 2.2 have been summarized in table 1. The following conclusions can be made from these data:

**Table 1. Structural analysis of the catalysts based on XRD data.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anatase Content (%)</th>
<th>Crystallite size</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-25 plain powder</td>
<td>89.2</td>
<td>24.5</td>
</tr>
<tr>
<td>Coating on glass plates</td>
<td>83.2</td>
<td>30.0</td>
</tr>
<tr>
<td>Coating on perlite</td>
<td>67.3</td>
<td>14.5</td>
</tr>
<tr>
<td>Coating on steel fibers</td>
<td>86.0</td>
<td>24.9</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of the reactor setup designated for the photocatalytic assessment of the catalyst supported on glass plates.

Fig. 2. Schematic diagram of the reactor setup designated for the photocatalytic assessment of the catalyst supported on steel fibers.

Fig. 3. XRD patterns of Degussa P-25 (a) plain powder, (b) coated on glass plates, (c) coated on perlite granules, and (d) on steel fiber.

1. In the XRD pattern obtained for the sample coated on perlite a disorder in the form of an arc-shaped base line can be observed which shows that some of the material present in the sample is amorphous. Remembering that this sample was ground without separating the perlite support itself, the amorphous portion of the sample can be attributed to the perlite. This makes the calculations of this sample harder and less accurate. In spite of this, still a rather high anatase to rutile content ratio and a much smaller crystallite size is obtained from the calculations. The authors, therefore concluded that the P-25 material has not undergone significant changes due to the coating process, and the differences observed in the calculation results is due to the disturbance of the XRD test introduced by the presence of perlite.
2. No noticeable impurities can be distinguished in the graphs. This is especially important about the steel fiber coating, since iron impurities resulting from heating the steel could have a negative effect on the photocatalytic efficiency of the catalyst. Fe$^{3+}$ ions have been reported to be present in TiO$_2$ coated steel plates heated at 600°C and more, but not at lower temperatures [5]. Therefore, the obtained result was already expected.

3. Some differences in the calculation results for the coated samples with those of plain P-25 can be observed, but these differences can be attributed to the differences in the physical conditions of the samples that affect the XRD test. Therefore, it was concluded that, overall, the coating process has not brought significant changes to the P-25 material used in the coatings and a good photocatalytic efficiency must be expected from the catalyst samples used.

3.2 Results of photocatalytic experiments

The data of the final degradation results after 4 hours of UV illumination has also been summarized in Table 2. Overall, all the catalysts used showed a rather good photocatalytic activity.

Please notice that, although the operational conditions of the reactions had been tried to be as near as possible, an accurate comparison among these catalysts cannot be quite logical, because the reactor setups used had differences that had been dictated by the shapes and physical characteristics of the catalysts. But, in terms of overall results, if for example one wants to select one of the catalysts for a specific treatment process, they should also include the operating conditions that are required for using that catalyst into the efficacy to make a comparison. This means that, for instance, 22 g/L of steel fiber catalyst that contains ~1000 mg of P-25 coating with a recycle rate of ~100 ml·min$^{-1}$ for processing 200 ml of 1 mM phenol solution is somewhat less efficient than 100 cm$^2$ of glass plate catalyst that contains ~80 mg of P-25 coating. Of course, in selecting a catalyst for an industrial-scale treatment process the easier and less expensive operating conditions, like that of the perlite catalyst, should also be taken into account.

The catalyst coating on the glass plates showed very good mechanical stability too, but some catalyst washout was observed in the case of perlite and steel fiber supports, which means that the coating process needs more practice. Perlite, because of its unique and outstanding characteristics mentioned earlier that enables it to be a very good candidate to act as catalyst support for photocatalytic reactions, is sure worth of more research and our team is continuing the work on this valuable medium.

3.3 Kinetics of the reactions

The kinetics of photocatalytic reactions has been proposed to follow the Langmuir–Hinshelwood model when the concentration is in milimolar range [8]; for TiO$_2$ [9]; the initial degradation rates [10].

Fig. 4 shows the plots of the results of the photocatalytic experiments on logarithmic scales. The linear trend observed in these plots proves that the photocatalytic degradation of phenol at the conditions of the reactions follows a pseudo-first-order kinetics. The pseudo-first-order reaction rate constants hence calculated (slopes of the lines) are shown in Table 2 and Table 3.

<table>
<thead>
<tr>
<th>Table 2. Photocatalytic degradation of phenol (% removal after 4hr)</th>
</tr>
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<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>P-25 plain powder</td>
</tr>
<tr>
<td>Coating on glass plates</td>
</tr>
<tr>
<td>Coating on perlite</td>
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<td>Coating on steel fibers</td>
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Table 3. Results of kinetic apparent reaction rate constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>125 W UV lamp</th>
<th>80 W UV lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-25 plain powder</td>
<td>0.0151</td>
<td>0.0036</td>
</tr>
<tr>
<td>Coating on glass plates</td>
<td>0.0105</td>
<td>0.0031</td>
</tr>
<tr>
<td>Coating on perlite</td>
<td>0.0072</td>
<td>0.0023</td>
</tr>
<tr>
<td>Coating on steel fibers</td>
<td>0.0057</td>
<td>0.0020</td>
</tr>
</tbody>
</table>

4. Conclusions

The standard photocatalyst Degussa P-25 was coated on three different supports. It was concluded from the XRD analysis of the coatings that no sensible changes in the structure of P-25 has occurred due to the coating process. The photocatalytic tests of phenol degradation as the model pollutant also show a good photocatalytic activity for the catalysts, and the pseudo-first-order kinetics model was confirmed to satisfy these reactions.

Some catalyst washout was observed in the case of perlite and steel-fiber coated catalysts which shows a need for more practice on the coating method used for these media. Perlite due to its very outstanding characteristics seems to be an ideal support for the immobilization of photocatalysts and our research on this medium continues.

References