Reusability of photocatalytic TiO$_2$ and ZnO nanoparticles immobilized in poly(vinylidene difluoride)-co-trifluoroethylene

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**ABSTRACT**

Pollutants present in water are increasingly becoming an important public health issue. After their transportation across the sewer network they can pass through the wastewater treatment plants (WWTPs) mostly unchanged because WWTPs are not designed to remove pollutants present at trace levels. Conventional treatments are therefore ineffective. Immobilized photocatalytic systems are thus an advantage for the treatment of contaminated water, because they are eco-friendly, cost-effective and allow reusability. This work reports on TiO$_2$ and ZnO commercial nanoparticles immobilized in poly(vinylidene difluoride)-co-trifluoroethylene (P(VDF-TrFE)). Nanocomposites of P(VDF-TrFE) with different concentrations of TiO$_2$ nanoparticles (5, 10, and 15 wt.%) and ZnO nanoparticles (15 wt.%) were produced by solvent casting and tested on the degradation of methylene blue, a model organic dye. Each nanocomposite was tested three times to assess its reusability. It is shown that increasing the photocatalyst concentration results in higher photocatalytic efficiencies; the degradation rates of 15% of TiO$_2$ and ZnO are similar; and the photoactivity decreases 6%, 16%, 13%, and 11% after three utilizations, for TiO$_2$ 5%, TiO$_2$ 10%, TiO$_2$ 15%, and ZnO 15%, respectively. Thus, the low decrease in the photocatalytic activity after three uses makes the nanocomposites suitable for applications in which reusability is an important key factor.

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1. Introduction

The presence of pollutants in water has become an increasing concern because of the adverse consequences for human health and wildlife, arising from their release into the environment [1,2]. They may enter the environment via several different sources, like waste, effluents of sewage treatment plants, landfill effluent or veterinary usage [3,4], acting as slant persistent pollutants [1,5].

Conventional wastewater treatment plants are ineffective in removing pollutants present at trace levels [6–9]. Thus, photocatalysis may become an alternative to promote the degradation of contaminants in the aquatic environment since it allows their rapid and efficient removal from water, transforming them into by-products with lower toxicity [3,10,11].

Among several semiconductor materials, titanium dioxide (TiO$_2$) and zinc oxide (ZnO) are suitable photocatalysts for the degradation of organic pollutants because of their unique optical properties, low cost and availability [12,13].

These catalysts can be employed either in a colloidal or in an immobilized form. Whenever the particles are dispersed in the aqueous phase the depth of penetration of radiation is limited due to absorption or scattering by the dissolved organic species and the catalyst particles [14]. The main aim of using the immobilized form is that the costly and extra final filtration process can be avoided which is especially important for water decontamination [15–18]. The supports of the catalyst have to be inert, erosion and corrosion resistant and to show large surface area with the capability to keep the catalyst immobilized, so that the catalyst particles do not get unattached from the support and act as suspended catalysts.

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2. Materials and methods

2.1. Polymer nanocomposite

Poly(vinylidene difluoride)-co-trifluoroethylene, P(VDF-TrFE) (Piezotec) composite membranes with 5, 10, and 15 wt.% titanium dioxide P25 (Evonik) and 15 wt.% zinc oxide (IOLITEC Ionic Liquids Technologies GmbH) were prepared by solvent casting. The nanoparticles were added to 9.5 mL of N,N-dimethylformamide (DMF, Merck), and aiming to achieve good dispersion of the particles, the solution was placed in an ultrasound bath (Elma) for 4 h. Afterwards, 1 g of the P(VDF-TrFE) co-polymer was added to the solution, achieving a concentration of 10 wt.% polymer, and kept under magnetic stirring until complete dissolution. Finally, the solution was placed in a glass Petri dish and the DMF solvent evaporated at room temperature.

2.2. Characterization of the photocatalyst nanoparticles and the nanocomposite

The specific surface area of the photocatalyst nanoparticles was determined by the Brunauer-Emmett-Teller (BET) method. This property was analyzed at −176 °C by nitrogen adsorption-desorption in a Micromeritics TriStar analyzer (Micromeritics). Before performing adsorption experiments, samples (0.5 g) were outgassed at 26.7 Pa and 350 °C for 6 h. Nanoparticles were characterized by X-ray diffraction using a Phillips PW 1710 diffractometer, with an incident radiation of Cu Kα (40 kV e 30 mA) and a wavelength of 1.54 Å. The obtained diffractograms were analyzed in Match 1.10 (Crystal Impact) software. The UV–vis diffuse reflectance spectra were obtained by using a Shimadzu UV–vis spectrophotometer 2101PC, in the range of 250–700 nm, equipped with a diffuse reflectance attachment, using BaSO4 as reference. The morphology of both photocatalysts and nanocomposite membranes was analyzed with a scanning electron microscope (SEM) operated at 10 kV and 25 kV. Prior to the SEM analysis, the nanocomposite membranes were coated with carbon. Also the microstructure of the nanocomposites was studied by SEM, and the chemical structure assessed by attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR). The size distribution of nanoparticles measured in the micrographs, as well as the pore size distributions, were performed by using Image J software.

2.3. Photocatalytic activity

The photocatalytic activity of ZnO or TiO2/P(VDF-TrFE) nanocomposite membranes, under UV irradiation, with different concentrations of photocatalyst (ZnO or TiO2) was assessed by their photocatalytic decomposition of a methylene blue (MB) solution.

A 4 x 4 cm membrane sample was fixed in the wall of a borosilicate-glass beaker and immersed with 50 mL of MB aqueous solution (17.6 μM) under UVA radiation and constant stirring. Water was obtained from a Millipore Milli-Q.

Prior to the degradation experiments, the MB solution and the nanocomposite membranes were stirred in the dark for 30 min to achieve an adsorption–desorption equilibrium of the dye on the surface of the nanocomposite. Afterwards, the samples were exposed under continuous stirring to UVA-radiation. The peak wavelength of the lamp was 365 nm (6 Philips 8W mercurial fluorescent lamps – UMEX). The beakers were placed at 15 cm from the illuminating device. The UV intensity ranged from 1.6 to 1.7 mW cm−2 and was determined by a UV34 Lux Meter (PCE). To analyze the degradation of MB, samples were taken at certain time intervals. The photodegradation of MB was determined by analyzing the decrease of the absorption peak ranging from 662 to 665 nm using a Varian CARY-100 UV–vis spectrophotometer. A control (a P(VDF-TrFE) membrane without TiO2 or ZnO exposed to UV) and a dark control (a ZnO and TiO2/P(VDF-TrFE) nanocomposite membrane kept in the dark) were also tested. To test the reusability of the nanocomposite membranes, the photodegradation experiments were carried out in triplicate under the same conditions. For that, after each use, the membranes were placed in a beaker with milipore water for one hour and were then used two more times in photodegradation assays, in the aforementioned conditions.

3. Results and discussion

3.1. Nanoparticles characterization

For TiO2 P25 nanoparticles, it was obtained a specific surface area of 56 m² g⁻¹ by the BET method and 5.23 m² g⁻¹ for the ZnO nanoparticles. Both values are in accordance with the data of the manufacturer. This difference can also be observed in the SEM images (Fig. 1). The TiO2 particles are smaller than the ZnO particles. TiO2 is present as monodisperse nanospheres while ZnO have polydisperse rectangular-like structures.

To assess the crystalline structures and impurities, the X-ray diffraction (XRD) patterns of ZnO and TiO2 nanoparticles were examined (Fig. 2). Regarding TiO2 nanoparticles, XRD patterns
exhibited strong diffraction peaks at $27^\circ$, $36^\circ$, and $55^\circ$ indicating TiO$_2$ in the rutile phase. The XRD pattern also exhibits strong diffraction peaks at $25^\circ$ and $48^\circ$ indicating TiO$_2$ in the anatase phase. All peaks are in good agreement with the standard spectrum (JCPDS nos.: 88-1175 and 84-1286) [36]. Anatase, brookite, and rutile, the three main phases of TiO$_2$, present different photocatalytic activities, being anatase the most photocatalytic active [37]. Concerning ZnO nanoparticles, diffraction peaks with 2θ values located at $32^\circ$, $34^\circ$, $36^\circ$, $47^\circ$, $57^\circ$, and $63^\circ$ have been associated to the hexagonal wurtzite phase and correspond to the crystal planes of (100), (002), (101), (102), (110), and (013) respectively. Additionally, these results are also well related with previous works [38,39] and with the manufacturer results. The squares in Fig. 2 correspond to the standard XRD pattern of wurtzite ZnO (JCPDS no.: 36-1451).

The UV–vis diffuse reflectance spectra of ZnO and TiO$_2$ are included in Fig. 3, where also the emission spectra of the radiation lamp is plotted.

It can be observed that ZnO absorbs more radiation in the range of approximately 330–380 nm compared to TiO$_2$. The stronger absorption in this range corresponds to the intensity peak of the lamp source. Therefore, this increased absorption in the UV for ZnO increases the absorption intensity resulting in a probable higher photocatalytic activity.

3.2. Characterization of the nanocomposites

A porous polymeric structure is of main importance for photocatalysis, as the efficiency depends on the interaction between the pollutant and the catalytic surface. Additionally, porous support materials favor the dispersion of the nano photocatalysts and the percolation of water [40]. The formation of porous structure was achieved by solvent evaporation at room temperature from a homogeneous solution in DMF [32]. SEM micrographs, Fig. 4, for the P(VDF-TrFE) nanocomposite membranes with 15 wt.% of the TiO$_2$ and ZnO show a good nanoparticles dispersion, nanoparticles aggregates are not visible. Using Image J software, average pore sizes of $21.3 \pm 8.1 \mu m$ and $28.4 \pm 7.5 \mu m$ were estimated for 15 wt.% of the TiO$_2$ and ZnO nanocomposites, respectively. These
results indicate that regardless of the used nanoparticles, there is no significant difference in the pore size of the nanocomposites. For the other produced nanocomposites, with different amounts of nanoparticles, a similar porous structure was observed (data not shown).

To determine the polymer phase content and the chemical interaction between the photocatalytic nanoparticles and the polymer matrix we performed Infrared Spectroscopy (FTIR) tests. The FTIR spectra of nanocomposite membranes show that P(VDF-TrFE) crystallization induces the formation of β-phase (Fig. 5) due to the presence of absorption bands at 840 and 1290 cm\(^{-1}\), independently of the type or content of the nanoparticles used. No evidence of non-polar α-phase (855, 795 and 766 cm\(^{-1}\)) or of γ-phase (833, 812 and 766 cm\(^{-1}\)) was observed.
776 cm\(^{-1}\)) was found [41]. Thus, filler content or type do not change the crystallization phase of the polymer, which crystallizes in the all-trans \(\beta\)-phase, and no chemical bonds were detected between the polymer and the incorporated nanoparticles.

### 3.3. Degradation efficiency

Photocatalytic activity was tested by degrading MB in an aqueous solution under UV radiation. MB shows a maximum absorption peak at about 665 nm. The absorption peak was gradually diminished upon exposition to UVA irradiation, illustrating the degradation of MB. It fits to a pseudo-first-order reaction, Langmuir–Hinshelwood model, which can be expressed by Yu et al. [42]:

\[
\ln \left( \frac{C}{C_0} \right) = -kt
\]

Where \(C\) represents the concentration of the dye at the time \(t\) and \(k\) is the pseudo first-order rate constant of the reaction. The economy of the photocatalytic process depends upon how many times a photocatalyst can be reused without decreasing its efficiency. Also it is important to study the effect of the photocatalyst’s concen-
Table 1
Reaction rates for the different nanocomposites.

<table>
<thead>
<tr>
<th>Uses</th>
<th>Reaction rate (h⁻¹)</th>
<th>5% TiO₂</th>
<th>10% TiO₂</th>
<th>15% TiO₂</th>
<th>15% ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td></td>
<td>0.12</td>
<td>0.18</td>
<td>0.30</td>
<td>0.42</td>
</tr>
<tr>
<td>2nd</td>
<td></td>
<td>0.024</td>
<td>0.18</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>3rd</td>
<td></td>
<td>0.06</td>
<td>0.12</td>
<td>0.24</td>
<td>0.30</td>
</tr>
</tbody>
</table>

![Graph showing degradation percentage](image)

**Fig. 7.** Comparison of the degradation percentage of methylene blue according to the reusability of the photocatalytic nanocomposites for three utilization, after 5h of exposition to UV.

It is observed that P(VDF-TrFE) nanocomposite with 5 wt.% of TiO₂ shows the lowest degradation profile. The first and the third use show a relatively small loss of photocatalytic activity although its second use show a higher loss of photocatalytic activity. This behavior might be due to the presence of organic contaminants on its surface in the second use which will compete for the active sites of the photocatalyst. For the P(VDF-TrFE) nanocomposite with 10 wt.% of TiO₂ the loss of efficiency between the first and the second use can be neglected, although it increases in the third use more likely due to the loss of the photocatalyst particles from the polymeric matrix. The same trend occurs for the samples of ZnO 15 wt.%, although the loss of efficiency to the third use is lower. The sample with 15 wt.% of TiO₂ shows a different behavior from the previous samples. The second use shows slightly higher photocatalytic activity most likely due to the presence of organic contaminants on its surface in the first use that were washed out before the second use.

**Fig. 7** summarizes the previous results regarding the degradation of MB according to the photocatalyst and use.

As expected, the photocatalytic activity of the nanocomposites showed superior degradation of MB when the concentration of the catalyst increased. In the range of low concentrations, an increase in the photocatalyst concentration produces an increase of the active sites resulting in higher photocatalytic efficiencies [43]. However, after a certain concentration, further increase of filler concentration limits the photocatalytic activity of the composite membrane due to both filler agglomeration (decrease of surface active area) and detachment from the polymeric matrix.

The degradation profile of 15 wt.% of TiO₂ and ZnO are similar. The photoactivity decreased 6%, 16%, 13%, and 11% after three utilizations, for TiO₂ 5 wt.%, TiO₂ 10 wt.%, TiO₂ 15 wt.%, and ZnO wt. 15%, respectively, after 5 h of exposition to UV, indicating that the photocatalytic activity slightly decreases after three uses and therefore these nanocomposites have suitable reusability. The loss of activity for higher concentrations of the photocatalyst suggests a higher detachment of the particles from the matrix. This is an expected behavior since increasing the filler content will increase the amount of nanoparticles on the membrane’s surface. These nanoparticles weakly bonded to the matrix, are exposed to the solution and may be easily washed out during their use during degradation assays. Table 1 summarizes the reaction rates for the different nanocomposites according to their use and concentration. The reaction rates decreased with the number of uses from 0.003 min⁻¹ to 0.002 min⁻¹ for 10 wt.% TiO₂, and from 0.007 min⁻¹ to 0.005 min⁻¹ for 15 wt.% ZnO. For TiO₂ 5 wt.% and TiO₂ 15 wt.%, the second use presented higher reaction rates for the reasons aforementioned. The reaction rates changed from 0.002 min⁻¹ for the first use to 0.0004 min⁻¹ for the second use and to 0.001 min⁻¹ for its third use for 5 wt.% TiO₂ and 0.005 min⁻¹ for the first use to 0.006 min⁻¹ for the second use to 0.004 min⁻¹ for its third use for 15 wt.% TiO₂. Additionally, nanocomposites with ZnO wt. 15% presented higher reaction rates when compared to TiO₂ wt. 15%, which is consistent with the reflectance spectra results (Fig. 3), indicating higher ability of ZnO nanoparticles than TiO₂ nanoparticles to absorb UV radiation, especially at the lamp emission peak (365 nm).

The reusability of immobilized TiO₂ nanoparticles has been previously reported. The photocatalytic oxidation of phenol for 4 h under UV illumination was assessed using three support materials (steel fiber, glass, and perlite) coated with TiO₂ nanoparticles [23]. About 5% of the original weight of TiO₂ was washed out when perlite and steel fiber coated catalysts were used, which might explain the better performance by using glass. This work did not examine the reutilization of the immobilized system, however, within a single use, after 4 h approximately 40% of phenol was degraded. Hanel et al. [44] immobilized TiO₂ on glass beads and tested three times its re-use on the degradation of a phenol solution for 5 h under a xenon lamp. Although the loss of photoactivity was 8% after three uses, the degradation of phenol was ca. 20% [44]. In both works the depletion of nanoparticles due to inefficient attachment/imobilization is singled out as a possible reason to the photocatalytic activity loss after the first use. These findings are consistent with our results, which also indicates that similar events may cause the loss of efficiency during use. Joy and Tayade [45] immobilized 1 g L⁻¹ of TiO₂ on a mosquito net and tested the photocatalytic activity on the degradation of 15.6 μM of MB. The total decolorization took nearly 8 h [45].

The sample with the nanocomposite without photocatalyst exposed to UV radiation presented only small changes in the concentration of MB due to a slight adsorption on its surface (Fig. 6 a). A similar behavior was observed in the photocatalytic nanocomposite controls in the dark (results not shown). This effect is due to adsorption until the adsorption-desorption equilibrium is reached. These control results certify that both UV radiation and photo-
catalytic nanoparticles are necessary to induce the degradation process. As mentioned, efficiency loss in the degradation of MB may be caused by the loss of catalytic nanoparticles during the use of the nanocomposites. This is in good agreement with the loss of efficiency of just 5% from the first (34%) to the third (29%) use, regarding the nanocomposite with TiO₂ wt. 5%, and with a higher efficiency loss of ~16% and ~13%, for TiO₂ wt. 10% and 15% nanocomposites, respectively. Such results indicate that by increasing the photocatalyst concentrations in the nanocomposites, a higher amount of nanoparticles remain exposed and detaches from its surface.

4. Conclusions

Imobilized photocatalytic systems are an advantage for water decontamination. Although the immobilization of the photocatalyst is recommended, the stability of the immobilized photocatalyst is typically weak due to the low attachment of the catalyst onto the supporting material. In this work, P(VDF-TrFE) was chosen to immobilize the photocatalyst because of its good chemical stability, nontoxicity, and facile synthesis. Results showed that increasing the photocatalyst concentration provided higher photocatalytic efficiencies. The degradation rates of 15 wt.% of TiO₂ and ZnO are similar. It can be seen that the photocatalytic increases 16%, 12.8%, and 11% after three utilizations, for TiO₂ 10 wt.%, TiO₂ 15 wt.%, and ZnO wt. 15%, respectively, after 5 h of exposition to UV, indicating that the photocatalytic activity slightly decreases after three utilizations and therefore these nanocomposites have suitable reusability. The loss of the photocatalytic particles to the water or/and the accumulation of intermediates with a poisoning effect on the surface of the nanocomposites, might have contributed to the lower performance of photocatalytic activity during its reusability. The process herein described is ecofriendly, cost-effective, and reusable for the treatment of contaminated water. More importantly, the produced photocatalytic nanocomposites showed suitable reusability due to its excellent performance which is advantageous for a scaling-up of these green photocatalyst systems.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apusc.2016.05.073.

References


