A composite of clay, cement, and wood as natural support material for the immobilization of commercial titania (P25, P90, PC500, C-TiO2) towards photocatalytic phenol degradation

L. Morjène, M. Tasbihi, M. Schwarze, R. Schomäcker, F. Aloulou and M. Seffen

ABSTRACT

Different types of commercial titania (P25, P90, PC500, and C-TiO2) were immobilized as single or mixed photocatalyst onto the surface of a natural support material made of cement, clay, and wood fibers. The successful immobilization was studied by different techniques showing a composite material with the mechanical properties of the support material and the photocatalytic behavior of the immobilized titania. The supported photocatalyst showed high mechanical stability and was applied to the photocatalytic degradation of phenol as a model pollutant under UV light irradiation. As the most active photocatalytic material, a mixture PC500 and P90 (comp-PC500/P90) was identified with an apparent pseudo first-order kinetic rate constant ($k_{app}$) of 0.010 min$^{-1}$ at a degradation efficiency of 100%. The catalyst was used several times and showed minor loss in activity during four runs due to degradation intermediates adsorbed to the surface, shown by a color change from white to yellow.

Key words | composite, composite-TiO$_2$/TiO$_2$, phenol, photodegradation, supported TiO$_2$ photocatalysts, UV-C light

HIGHLIGHTS

● The new composite material used is a natural support made of cement, clay and wood fibers.
● The mixture of two types of commercial titania (PC500 and P90) was immobilized on the surface of a composite material.
● The physico-chemical properties of as-prepared photocatalyst were identified by different techniques.
● The degradation of phenol reaches 100% in the presence of comp-PC500/P90 photocatalyst.
● The catalyst shows minor lost of its activity during four reaction runs.

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INTRODUCTION

Currently, there is a big interest in the evaluation of various semiconductors as photocatalysts in a wide range of applications (Mousli et al. 2019). Especially in the field of environmental engineering, organic compounds like industrial dyes represent a source of environmental contamination, since they are mostly toxic and non-biodegradable (Dessie Sintayehu et al. 2011). Phenol, which is toxic and very harmful to the environment (Hayati et al. 2012), is also one of the organic contaminants. The maximum approved concentration of phenolic compounds in drinking water is 0.5 mg L$^{-1}$ (European Union regulation no. 80/778/EC). Therefore, wastewater treatment is required to remove organic pollutants and contaminants. Several treatment techniques were developed; for example, coagulation, flocculation, adsorption (Eniola et al. 2019; Rehman et al. 2019), biological treatment, and photocatalysis (Helali 2015). Especially the latter has become a new approach in modern research for removing pollutants and purifying waters in the presence of light (Truppi et al. 2017). In recent studies, different kinds of semiconductors such as ZnO, MgO, SiO$_2$, and Fe$_2$O$_3$ were used as photocatalysts. Titanium dioxide (TiO$_2$) (Sboui et al. 2017) is an n-type semiconductor and a popular photocatalyst material used by researchers to mineralize toxic organic molecules. It has been used for self-cleaning surfaces and photocatalytic applications (Fatimah & Sopia 2017). It is the most widely used oxide in photocatalytic processes due to its properties; for example, less toxicity (Grabowska et al. 2012), good chemical/mechanical stability, minimum cost, and high photocatalytic efficiency. However, pure TiO$_2$ has some limitations. One limitation is its large band-gap energy, because it absorbs only photons of wavelengths in the UV spectrum. Another limiting problem associated with TiO$_2$ photocatalyst is its aspect of agglomeration into larger particles (Janus et al. 2015). To solve this issue, many researchers study new ways to use the technology for immobilization of particles (Hayati et al. 2018; Ashouri et al. 2019) on different supports such as cement, activated carbon, clay, graphene oxide (Fattahi et al. 2015), and silica sheets (García-Muñoz et al. 2014; Shahbazi et al. 2018; El-Mekkawi et al. 2019). Immobilizing TiO$_2$ on the surface of co-catalysts has been proposed to reduce the recombination rate of the electron–hole pairs, to depose nanoparticles of TiO$_2$ as a support for treatment water, to enhance the photocatalytic activity of TiO$_2$ (Folli et al. 2010), and to improve the percentage of removal of organic pollutants. Bel Hadjltaief et al. (2019) have synthesized SnO$_2$-TiO$_2$-clay and ZnO-TiO$_2$-clay, which were prepared by immobilization of SnO$_2$-TiO$_2$ oxides onto the surface of the clay using a sol-gel method (Nachit et al. 2016; Marien et al. 2017). In comparison to clay and pure TiO$_2$, these materials have demonstrated higher photocatalytic activity for the photodegradation of phenol and methyl orange (Akbal & Onar 2003; Jamali et al. 2015). Additionally, the immobilization of TiO$_2$ using different solid supports has been studied by Hosseini et al. (2007) to test the degradation of phenol on the surface of perlite, and showed that after 240 min of irradiation the photocatalytic conversion was about 39.7%. Different kinds of materials such as cement, clay, quartz, and glass were widely used as supports to increase the degradation efficiency (Folli et al. 2010; Xing et al. 2018). Currently, TiO$_2$ photocatalysts have shown a double role in a wide range of applications, in the field of construction and building (Fatimah 2012), and also in the environmental field (Lee et al. 2013; Steiner 2017), for the cleaning effect, used on the surface, and to change some properties of the base materials, such as glass, ceramics,
polymers, plastic or metal, silica, and aluminum (García-Muñoz et al. 2014). In our previous work, the elaborated composite (cement, wood fiber, and clay) used in the construction of buildings (Aloulou & Alila 2018) showed the best mechanical performance and a homogeneous microstructure without cracks. It shows good qualities, validity and also aesthetic qualities due to high mechanical stability and less thermal conductivity (Aloulou et al. 2019a, 2019b).

In this paper, four commercial titania semi-conductors, namely P25, P90, PC500, and C-TiO2, were immobilized onto the surface of a natural support material by the ‘blending with bruch’ method. A composite made from cement, clay, and wood fibers was used as the natural support. The immobilized TiO2 photocatalyst materials were characterized by X-ray diffraction (XRD), N2 adsorption-desorption measurement (BET), scanning electronic microscopy (SEM), energy dispersive X-ray (EDX) analysis, Fourier transform infrared spectroscopy (FTIR), and UV-vis reflectance spectroscopy (DRS). Single TiO2 photocatalysts and mixtures of two types of TiO2 were immobilized as well as investigated. To find the best conditions for phenol degradation, a series of operating parameters; for example, phenol concentration, amount of catalyst, and type of light source, was investigated for the most active immobilized TiO2 photocatalyst material. Additionally, the pseudo first-order kinetic was applied to determine the apparent reaction rate constant ($k_{app}$).

**MATERIALS AND METHODS**

**Chemicals**

Four types of titanium oxide (TiO2) were used as photocatalysts: P25 (99.5% purity, Evonik), P90 (99.5% purity, Evonik), PC500 (99.9% purity, Millennium/Cristal ACTiv™), and C-TiO2 (87.8% purity, KRONOClean). As support for TiO2 immobilization, a composite of clay, cement, and wood fibers was used. The clay was natural Kaolinite clay from the Tunisia deposit in Jemmel (Monastir). Before its use, the Kaolinite clay was washed with distilled water and dried at 80 °C for 24 h. The paste was shaped into plates with a dimension of 3.3 cm × 3.3 cm and dried at air temperature. The second step is the dispersion of 50 mg of TiO2 in 1.5 mL of water. The third step is the coating of the support material prepared in step one with the suspension prepared in step two using a brush. In addition, the prepared composite materials were cured for 24 h in air. By following the same procedure, two types of titania were deposited onto the composite surface. After the synthesis, the catalyst was ready for use. The final supported TiO2 photocatalysts were named comp-P25, comp-P25/P90, comp-P25/PC500, comp-C-TiO2/P25, comp-C-TiO2/P90, comp-C-TiO2/PC500, and comp-PC500/P90.

**Preparation of supported catalysts (comp-TiO2)**

The preparation of the supported catalysts consists of three steps. The first step is the preparation of the support material by simple mixing of the ingredients in 5 mL of water, resulting in a composition of 97 wt.% of cement, 1 wt.% of clay, and 2 wt.% of wood fibers. Before its use, the Kaolinite clay was washed with distilled water and dried at 80 °C for 24 h. The paste was shaped into plates with a dimension of 3.3 cm × 3.3 cm and dried at air temperature. The second step is the dispersion of 50 mg of TiO2 in 1.5 mL of water. The third step is the coating of the support material prepared in step one with the suspension prepared in step two using a brush. In addition, the prepared composite materials were cured for 24 h in air. By following the same procedure, two types of titania were deposited onto the composite surface. After the synthesis, the catalyst was ready for use. The final supported TiO2 photocatalysts were named comp-P25, comp-P25/P90, comp-P25/PC500, comp-C-TiO2/P25, comp-C-TiO2/P90, comp-C-TiO2/PC500, and comp-PC500/P90.

**Characterization of supported TiO2 photocatalysts**

The photocatalysts were examined by XRD in the 2θ range between 20 and 80°, using CuKa ($\gamma=1.54060$ Å) radiation. Diffraction peaks were compared with reference JCPDS powder diffraction files (anatase: 21-1272, rutile: 21-1276). The surface morphology of the prepared photocatalysts was examined by SEM (Hitachi SEM type SU8030 microscope operated at an acceleration voltage of 10 kV and a probe current of 15 pA). The functional groups of supported photocatalysts were investigated by FTIR using a Perkin Elmer Instrument (Spectrum Two, from 2011). Samples were measured at room temperature and a resolution of 4 cm$^{-1}$. All FTIR measurements were done in transmittance mode after baseline correction. The Brunauer-Emmett-Teller (BET) specific surface area, the pore volume, pore size of the powder specimen of the composites were determined from nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics-ASAP 2020 chemisorption system.

**Table 1 | Characteristic data of different types of titanium dioxide and Kaolinite clay**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P25</th>
<th>P90</th>
<th>PC500</th>
<th>C-TiO2</th>
<th>Kaolinite clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase phase (%)</td>
<td>82</td>
<td>87</td>
<td>100</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>Rutile phase (%)</td>
<td>18</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>Band-gap energy (eV)</td>
<td>3.2</td>
<td>3.3</td>
<td>3.5</td>
<td>3.3</td>
<td>–</td>
</tr>
<tr>
<td>Specific surface area (m$^2$ g$^{-1}$)</td>
<td>56</td>
<td>102</td>
<td>286</td>
<td>298</td>
<td>47.6</td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>18.1</td>
<td>12.6</td>
<td>8.8</td>
<td>7.6</td>
<td>16.4</td>
</tr>
</tbody>
</table>

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The diffuse reflectance UV-vis absorption spectra was measured using a UV-vis spectrophotometer equipped with an integrating sphere (LAMBDA 650 UV-vis with 150 mm integrating sphere, Perkin Elmer, USA). Indirect band-gap energies were determined by plotting the Kubelka–Munk transformation of the original diffuse reflectance spectra vs. photon energy (Tauc plot):

\[ F(R) = \left(\frac{1 - R_\infty}{2R_\infty}\right)^2 \]

where \( R_\infty \) is the measured reflectance (\( R_\infty = R_{\text{sample}}/R_{\text{standard}} \)).

**Photocatalytic degradation tests**

The photocatalytic performance of supported TiO_2 photocatalysts was investigated for phenol degradation. A plate of the composite (5.3 cm × 5.3 cm) was placed together with a stirring bar on the ground of a beaker. 50 mL of the phenol solution was added to the beaker. It was placed on a magnetic stirrer under slow stirring speed to avoid damage to the plate. The 8 W Hg UV light source (with a maximum intensity at 254 nm wavelength, Ultra-Violet Products Ltd) was mounted at a distance of 12 cm on top of the beaker. A scheme of the setup is shown in Figure 1.

Before turning the light source on, the comp-TiO_2 was kept in the dark for 30 min to achieve adsorption-desorption equilibrium. After starting the UV lamp, liquid samples were taken every 15 min for the first hour and then every 30 min until a total irradiation time of 180 min was reached. The samples were named \( c_t \), with \( t \) being the time of irradiation. Additionally, samples of the prepared feed solution (\( c_0 \)) and after adsorption-desorption equilibrium (\( c_{t,0} \)) were taken. For comparison, experiments with suspended photocatalysts have been done. For this, 50 mg was dispersed into 50 mL of phenol solution (50 ppm) and the procedure was similar to that described above for the immobilized photocatalyst.

The liquid samples were analyzed by high-performance liquid chromatography (HPLC). The HPLC equipment consists of an Agilent Technologies 1,200 Series chromatograph coupled with a UV-vis detector. A Multospher 120 RP 18 column (Ziemer Chromatographic, 250 mm × 4 mm, 5 μm) was used for the separation and a 70:30 mixture of acetonitrile and distilled water was used as the eluent. The eluent flow rate was 1.0 mL min\(^{-1}\) and the injection volume was 10 μL. The elution of the compounds was monitored by a UV/vis detector at 225 nm.

**RESULTS AND DISCUSSION**

**Preparation and characterization of supported TiO_2 photocatalysts**

Supported TiO_2 photocatalysts were prepared as described in the experimental details. The support material has a gray color (see Figure S1 in the Supporting Information). After the immobilization of TiO_2, the color changes to white. Besides the visual change in color, we used different techniques to (a) verify the successful immobilization of TiO_2 and (b) study the characteristics of the supported photocatalysts; for example, N\(_2\) adsorption, SEM, EDX, FTIR, and XRD.

**XRD**

XRD pattern of the support material and comp-PC500/P90 are shown in Figure 2. Further XRD spectra of the single TiO_2 powders and the support material compounds are shown in Figure S2 and Figure S3 of the Supporting Information.

Figure 1 | Scheme of the setup for the photocatalytic degradation of phenol using supported TiO_2 photocatalysts.

Figure 2 | XRD pattern of (a) comp-PC500/P90 and (b) support material.
Information, respectively. This supported photocatalyst was exemplarily selected to demonstrate the successful immobilization of TiO₂ because it shows the best photocatalytic performance in phenol degradation. In addition, new anatase peaks appeared, which is attributed to the good adhesion of TiO₂(PC500/P90) on the surface of the supported materials. Comp-PC500/P90 was a favourable candidate as support to TiO₂ due to its mechanical properties as construction and building materials.

After the immobilization of TiO₂, further peaks in the 2θ range from 20° to 32° are obtained. These peaks can be attributed to the crystalline phase of TiO₂, as demonstrated by many researches (Djellabi et al. 2014; Fatimah et al. 2018). The 2θ peaks at 25.28° (101), 48°, 53°, 62° and 74° for the (comp-PC500/P90) indicate the anatase phase, whereby the rutile (110) peaks do not appear in the spectra, maybe due to the low amount of TiO₂ inside the supported photocatalysts. The presence of peaks between 40° and 45° might be due to some impurities present in the support material (refer to the clay). Therefore, it was concluded from the XRD spectra that the immobilization of TiO₂ was successful.

N₂ adsorption-desorption

To get more information about the porous nature of the materials, N₂ adsorption-desorption isotherms were measured. The individual adsorption isotherms of the support material and selected supported TiO₂ photocatalysts are shown in Figure S4 of the Supporting Information. The results of N₂ adsorption-desorption are summarized in Table 2.

Although the surface areas of the single TiO₂ photocatalyst are large and show high values (>100 m² g⁻¹), the supported photocatalyst (pore diameter about 2 nm) has a low surface area of about 4–5 m² g⁻¹. The reason is the low amount of TiO₂ used for the synthesis of the supported photocatalyst. Only 50 mg of TiO₂ was used, whereby the mass of support material was about 3.3 g. So the overall physical properties of the supported photocatalyst are dominated by the support material. However, the surface properties; for example, the photocatalytic activity, are governed by the TiO₂ layer. The physical properties of the supported photocatalyst allow us to use it in different fields, such as photocatalytic wastewater treatment without the drawback of TiO₂ agglomeration in aqueous solution under UV-C light, as material for solar energy conversion, and as a high-performance construction and building material with self-cleaning abilities.

SEM and EDX

After structural analysis by XRD, the successful preparation of the supported photocatalysts from clay, cement, and wood fibers was evaluated via EDX spectroscopy. Figure 3 shows the SEM images and EDX spectra of the support material (Figure 3(a)) and the supported photocatalyst before (Figure 3(b)) and after (Figure 3(c)) phenol degradation.

The main peaks for the clay (Al, Si), the cement (Ca), and the wood fibers (C, O) appear in the EDX spectrum of the support material showing the formation of a composite material (Figure 3(a)). After immobilization of the photocatalyst, Ti peaks appear showing the successful formation of a supported TiO₂ photocatalyst (Figure 3(b)). In the SEM image of the supported photocatalyst (Figure 3(b)), it seems that the cement particles with a small amount of wood powder are well attached to the clay layers, whereby most of the surface is covered by cement. The EDX confirms this distribution of the cement. After the degradation test, we concluded that the supported TiO₂ photocatalyst shows no change in the surface morphology (Figure 3(c)). Figure 3(c) shows the elemental composition after phenol degradation, which is comparable to before.

FTIR

The spectra of the support material and supported photocatalyst are shown in Figure 4. FTIR was used as a further method to analyse the surface of the supported catalyst. In contrast to other methods, FTIR is able to determine the composition of thin layers on surfaces; here, TiO₂ on top of the composite material.

In the spectrum of the support material (Figure 4(a)), a peak for Si-O stretching (1090 cm⁻¹) has been assigned to Fe-O-Si asymmetric vibration. The bands centered at
1400–1471 cm\(^{-1}\) are due to the presence of the carbonate in the clay and the band present at 857 cm\(^{-1}\) is attributed to polysaccharides (Kankılıç et al. 2016). The spectrum of the comp-PC500/P90 (Figure 4(b)) shows an important band around 642 cm\(^{-1}\) that is attributed to the vibration of Ti–O–Ti in the range of 400–800 cm\(^{-1}\). Similar spectra and analysis were reported in the literature (Kibanova et al. 2009; Fatimah 2012). The peaks of the wood fibers cannot be seen because of the low content used in the preparation. The FTIR spectrum of the pure wood fibers is shown in Figure S5 of the Supporting Information.

**DRS**

Diffuse reflectance UV/vis absorption spectrum of comp-PC500/P90 was measured to determine the band gap of the supported photocatalyst and to check if the photocatalytic properties of TiO\(_2\) are influenced by the support material. The band-gap energy is obtained from the Tauc plot (Figure 5).
The band-gap of comp-PC500/P90 is about 3.3 eV (387 nm), which is close to the values of P90 (3.3 eV) and PC500 (3.5 eV) (Oblak et al. 2018). This indicates that TiO₂ is on top of the support material and still possesses its photocatalytic properties. Similar results were published by Oblak et al. 2018 for titania pillared clay and also immobilized TiO₂-ZnO on montmorillonite (Fatimah 2012). As this band-gap energy is high, UV light is required for the photocatalytic reaction.

Photolysis and phenol adsorption

To prove whether lower phenol concentrations are a result of phenol photolysis, phenol adsorption (as support material or supported TiO₂ catalyst) or photodegradation, preliminary experiments (Figure 6) have been done. These experiments show no significant change in the phenol concentration in the absence of the photocatalyst or under dark conditions. Only in the presence of both light and the supported TiO₂ photocatalyst is significant phenol degradation observed. For the best catalyst from our investigations, comp-PC500/P90, full degradation is shown within 3 hrs of UV irradiation.

Phenol degradation with suspended TiO₂ photocatalyst

Before the experiments with immobilized TiO₂ photocatalysts, suspensions of TiO₂ have been investigated for phenol degradation. The degradation profiles of four types of TiO₂ for a degradation time of 3 h are shown in Figure 7.

The degradation efficiency for an initial phenol concentration of 50 mg/L was found to be in the following order: P90 (69%) > P25 (49%) > C-TiO₂ (44%) > PC500 (28%). To enhance the efficiency of phenol degradation, in the next step, the four catalysts were immobilized on the surface of the composite material.

Phenol degradation with comp-TiO₂

After investigating the TiO₂ powders for the degradation of phenol, supported TiO₂ photocatalysts were prepared and investigated for phenol degradation. This was done because of two reasons: (a) to allow for better reusability of TiO₂ in technical applications and (b) to have a construction material with self-cleaning properties. As support material, a composite made from wood, clay, and cement was used. As shown in Figure 8, the phenol degradation efficiency for the comp-TiO₂ photocatalyst is in the following order: comp-C-TiO₂ (86%) ≈ comp-P90 (81%) > comp-PC500 (64%) > comp-P25 (55%).

From the comparison of Figure 7 (suspended TiO₂) and Figure 8 (comp-TiO₂), we can conclude that the immobilization of TiO₂ enhances the photocatalytic activity. The comp-TiO₂ photocatalyst is more efficient for phenol degradation, which is surprising, as in most cases, the activity of the immobilized catalyst is lower.

To investigate if the efficiency of comp-TiO₂ for phenol degradation can be further improved, two types of TiO₂ were immobilized. One type was P90 because comp-P90 showed the best performance, and the other type was P25, PC500, or C-TiO₂. The degradation of phenol is shown in Figure 9.
A very good result with a degradation efficiency of 100% after 180 min under UV light exposure was obtained for the comp-PC500/P90 photocatalyst, whereby the efficiency for the other combinations was only about 85%. Also, with the degradation of phenol, a color change from white to yellow was obtained (see Figure S6 of the Supporting Information). The phenol solution is colorless, but in the middle of the reaction, the color changed to yellow. The change of the color may be explained by the compilation of phenol degradation intermediates with cement. This effect is already reported by other groups (Tasbihi et al. 2018; Tchinda et al. 2018). A comparison of the different catalysts coated onto the support material showed a very good mechanical stability, good removal of phenol, and the mixture of PC500 and P90 as photocatalyst improved the total degradation (see Table S1 in the Supporting Information).

**Investigation of operational parameter**

As comp-PC500/P90 showed the best results, it was used for the following experiments to study the impact of different operational parameters.

**Effect of the initial phenol concentration**

In the photocatalytic reaction, the concentration of phenol plays an important role. The influence of the initial phenol concentration on the photocatalytic efficiency was investigated (Figure 10), and it was observed that the degradation efficiency decreases with increasing phenol concentration.

Until a phenol concentration of 50 ppm, the degradation efficiency is 100% for the comp-PC500/P90 photocatalyst. When the phenol concentration is further increased, the degradation efficiency significantly decreases to 47% (75 ppm) and 36% (100 ppm). The decrease in the activity of phenol degradation can be attributed to the higher concentration of phenol. Higher phenol concentrations need a longer irradiation time for attaining the same efficiency of degradation. The light might be screened by the phenol solution.

**Effect of the TiO₂ amount in comp-PC500/P90**

The effect of mₜio₂ with the same ratio of P90 to PC500 (1:1) on the phenol degradation was investigated (Figure 11). The
curves show that the photocatalytic efficiency for phenol degradation increases when the mass of TiO_2 is increased to 50 mg and thereafter decreases. The total degradation efficiency and divided by the mass of photocatalyst is summarized in Table 3.

When immobilizing TiO_2 onto a support material, with increasing catalyst concentration the irradiation area will be constant, but the thickness of the coated layer will increase. As photocatalysis happens only at the surface of the photocatalyst, more catalyst is wasted when the layer becomes too thick.

Effect of light source

The effect of the light source on the photocatalytic degradation of phenol was examined with comp-PC500/P90. Three light sources with different fractions of UV light were used: UV-C lamp (254 nm), UV-A lamp (365 nm), and a 300 W Xe lamp. The light sources were varied to get information about the transfer of laboratory scale experiments with artificial light sources to experiments with real sunlight. Besides, a sunlight simulator was used. The phenol concentration profiles are shown in Figure 12.

It is shown that the degradation of phenol after 180 min is more effective and faster with UV-C light (100%), followed by the 300 W Xe lamp (40%). Based on the band-gap energy of 3.3 eV, UV light is required to obtain electron-hole pairs for the photocatalytic reaction. The UV-A light shows only slight degradation (6%) of phenol because the wavelength is only 269 nm. However, using the sunlight simulator shows about 20% degradation. As the sunlight simulator consists of UV and visible light, the result is expected, and in addition, a proof for the utilization of the comp-PC500/P90 under real conditions (e.g. water treatment, self-cleaning, etc.).

Recycling test

Studying the photocatalytic activity and reusability of the photocatalyst is an important aspect of their utilization. After the first batch run, the comp-PC500/P90 was reused in three consecutive runs under the same operating conditions. After each run, the comp-PC500/P90 photocatalyst was washed with distilled water several times. The results for the degradation efficiency are shown in Figure 13.

The photocatalyst is still active after four runs. However, a loss in the activity of about 35% is seen, whereby the highest decline was between the first and second run. The lower degradation activity can be explained by different aspects, but a loss in the material during the runs can be neglected as supported catalysts were used. Also, after four runs, an intensive yellow color of the comp-PC500/P90 surface was obtained (see Figure S7 of the Supporting Information). The single phenol concentration profiles are shown in Figure S8 of the Supporting Information.

### Table 3 | Degradation efficiency for different catalyst concentrations

<table>
<thead>
<tr>
<th>m_100 (mg)</th>
<th>Degradation (%)</th>
<th>Degradation/m_100 (%) mg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>59</td>
<td>2.3</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>2.0</td>
</tr>
<tr>
<td>75</td>
<td>48</td>
<td>0.64</td>
</tr>
<tr>
<td>100</td>
<td>66</td>
<td>0.66</td>
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</tbody>
</table>
Kinetics of phenol degradation

The photocatalytic degradation of phenol proceeds over adsorbed molecules at the catalyst surface. In principle, a model considering the impact of adsorption is needed to describe the photocatalytic reaction. The Langmuir-Hinshelwood (L.-H) model (1) considers the impact of adsorption by the adsorption constant $K_A$, but it is often simplified to a pseudo first-order kinetic model (2) when $K_A C_A < 1$. In the majority of cases, the kinetics of photodegradation of several organic molecules are evaluated as a pseudo first-order reaction (Hosseini et al. 2007; Ritz et al. 2010). The apparent first-order kinetic constant ($k_{app}$) allows for a general comparison of catalyst activity and can be obtained from the linear plot $\ln(c/c_{t,0})$ vs. $t$, with $c_{t,0}$ being the concentration after adsorption-desorption equilibrium and $c_t$ the concentration at any time of irradiation. All parameters of the degradation study are summarized in Table 4, and the linear plots are shown in Figures S9–S12 of the Supporting Information.

$$r = -\frac{dC_A}{dt} = \frac{k_{app}C_A}{1 + K_A C_A}$$

$$r = -\frac{dC_A}{dt} \approx k_{app}C_A$$

$$\ln \left( \frac{c_t}{c_{t,0}} \right) = k_{app}t$$

All plots of $\ln(c/c_{t,0})$ vs. time show a linear behavior with correlation coefficients $R^2 > 0.97$. The $k_{app}$ values for the suspended TiO$_2$ photocatalyst are in the range of $1 \cdot 10^{-3}$ min$^{-1}$–$11 \cdot 10^{-3}$ min$^{-1}$, whereby the $k_{app}$ values follow the trend observed for the degradation efficiency. The highest $k_{app}$ value of about $11 \cdot 10^{-3}$ min$^{-1}$ is obtained for P90. After immobilization, the $k_{app}$ values differ as expected. Interestingly, for the low surface area types of TiO$_2$ (P25, P90) the $k_{app}$ value is the same or decreases. A decreased $k_{app}$ value is often observed after immobilization on different substrates. But for the high surface types of TiO$_2$ (PC 500, C-TiO$_2$), the $k_{app}$ value is higher as for the powders. This could be a result of less agglomeration of the TiO$_2$ particles after immobilization. After mixing PC500 and P90 (1:1 ratio), and its immobilization onto the support material, the $k_{app}$ value for comp-PC500/P90 is about $10 \cdot 10^{-3}$ min$^{-1}$ and comparable to P90, but at a higher degree of phenol degradation.

CONCLUSIONS

In this contribution, different commercial TiO$_2$ photocatalyst powders were successfully immobilized onto a support material consisting of cement, clay, and wood fibers. The immobilized photocatalyst showed high mechanical stability and good photocatalytic activity for phenol degradation. After 3 hrs of UV irradiation, the degradation efficiency for the most active TiO$_2$ powders, P90 and comp-C-TiO$_2$, was 81% and 86%, respectively. By using a mixture of P90 and PC500 as the photocatalyst, the degradation efficiency was increased to 100%. Several operating conditions were varied and for efficient phenol degradation, the best conditions are mass of immobilized TiO$_2$ about 25–50 mg (1:1 ratio of P90 and PC500), phenol concentration below $\text{ppm}$, and UV wavelength $\lambda = 254 \text{ nm}$.
50 ppm, and UV light. The immobilized PC500/P90 photocatalyst was reused up to three times with minor loss of its activity due to adsorbed intermediates. Kinetic investigation showed pseudo first-order reaction for phenol degradation with \( k_{\text{app}} \) values up to 10·10^{-2} \( \text{min}^{-1} \) and 11·10^{-3} \( \text{min}^{-1} \) for suspended P90 and a mixture of PC500/P90 immobilized onto the natural support material. The good results obtained for comp-PC500/P90 in this study make this supported photocatalyst an interesting candidate for continuous wastewater treatment or as a building block with self-cleaning properties.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIAL

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