Enhancement of photocatalytic degradation of furfural and acetophenone in water media using nano-TiO$_2$-SiO$_2$ deposited on cementitious materials

Sahar Soltan, Hoda Jafari, Shahrara Afshar and Omid Zabihi

ABSTRACT

In the present study, silicon dioxide (SiO$_2$) nanoparticles were loaded to titanium dioxide (TiO$_2$) nanoparticles by sol-gel method to make a high porosity photocatalyst nano-hybrid. These photocatalysts were synthesized using titanium tetrachloride and tetraethyl orthosilicate as titanium and silicon sources, respectively, and characterized by X-ray powder diffraction (XRD) and scanning electron microscope methods. Subsequently, the optimizations of the component and operation conditions were investigated. Then, nano-sized TiO$_2$ and TiO$_2$-SiO$_2$ were supported on concrete bricks by the dip coating process. The photocatalytic activity of nano photocatalysts under UV irradiation was examined by studying the decomposition of aqueous solutions of furfural and acetophenone (10 mg/L) as model of organic pollutants to CO$_2$ and H$_2$O at room temperature. A decrease in the concentration of these pollutants was assayed by using UV-visible absorption, gas chromatography technique, and chemical oxygen demand. The removal of these pollutants from water using the concrete-supported photocatalysts under UV irradiation was performed with a greater efficiency, which does not require an additional separation stage to recover the catalyst. Therefore, it would be applicable to use in industrial wastewater treatment at room temperature and atmospheric pressure within the optimized pH range.

Key words | concrete, nano-TiO$_2$-SiO$_2$, organic pollutant, photocatalysts

INTRODUCTION

Photodegradation is an advance process to breaking up the organic molecules to smaller species by irradiation of various light wavelengths. This phenomenon is in a physical correlation with solid catalyst efficiency and light wavelengths in order to degrade pollutants from water (Hoffmann et al. 1995). In this process, target molecules were partially or completely oxidized by the semiconductor catalysts possessing certain band-gap energy. Among the metal oxide semiconductors suitable for photocatalytic processes, titanium dioxide (TiO$_2$) in anatase phase is most broadly used because of very clear properties, availability, non-toxicity (Qourzal et al. 2009), low cost (Makhdoomi et al. 2015), and stability against corrosion (Liao et al. 2004). In contrast, its activity is not high enough to be utilized in true commercial applications (Liao et al. 2004). A proper photocatalyst should possess a large specific surface area, and high pore volume, and high active-sites available for the adsorption and decomposition of the organic pollutants (Nakata & Fujishima 2012). A simple method to enhance the activity of TiO$_2$ is the use of a support matrix such as stainless steel (Evans & Sheel 2007), Pyrex (Mellott et al. 2006), paper (Park et al. 2007), and monolith and building materials (Yuranova et al. 2007) or additionally a second semiconductor, such as silica, having large surface area and high porosity. Thus, the new catalytic active sites formed on the surface because of interaction between TiO$_2$ and silicon dioxide (SiO$_2$), which improve the photocatalytic activity and the hydrophilicity of the composite (Anderson & Bard 1997; Yamazaki et al. 2001; Sakai et al. 2012). Moreover, to avoid filtration which leads to lower the risk of losing nanoparticles by abrasion or washing, the most efficient technique to benefit from full-potential catalytic activity is by applying TiO$_2$ as a thin layer on the surface of cementitious materials. Besides, the hybridization of TiO$_2$ with transition metals such as iron (III) has been also recommended for enhancement of catalytic activity (Liao et al. 2004).
In photodegradation process of pollutants by semiconductors, a photon having higher energy rather than the band-gap energy of the semiconductor (ca. 3.2 eV to TiO$_2$) causes the generation of an electron-hole pair through photonic excitation of an electron from valence band (VB) to conduction band (CB), which is schematically illustrated in Figure 1. The presence of scavenger species, e.g. H$_2$O and organic molecules, results in trapping the electron/hole and subsequent redox reaction in which VB holes (h$^+$) act as oxidants and CB electrons act as reducing agents. In the photodegradation solution of aromatic compounds, the hydroxylate radicals, which formed either through interacting water molecules with holes or through the O$_2$ that interacts with the host electrons, are the key active species (Al-Ekabi et al. 1993; Turchi & Ollis 1993) and during the oxidation and aromatic ring opening convert to aldehyde and carboxylic acid, eventually formed CO$_2$ (Amereh & Afshar 2013).

In this work, the enhanced photocatalytic efficiency of nano-TiO$_2$-SiO$_2$ over a concrete support was investigated. Unlike the common sol-gel method which uses organic precursor (such as titanium tetraisopropoxide, titanium butoxide (Ti(OBu)$_4$) and titanium ethoxide (Ti(OEt)$_4$) (Venkatachalam et al. 2007; Macwan et al. 2011), an inorganic precursor such as titanium tetrachloride (TiCl$_4$) has been used to synthesize nano-TiO$_2$. The use of inorganic precursors rather than organic precursors because of reducing the charge of synthesis and avoiding the use of organic solvents which could cause pollution have more justification in environmental issues (Jafari et al. 2015). The porous solid of silica, which has moderate hydrophobicity, was selected as a unique support since it has been widely used in industry and does not possess a charged framework. In addition, concrete support was used as a fixing substrate and the source of metallic cations, e.g. iron. Then, the efficiency of immobilized nano-TiO$_2$-SiO$_2$ on the concrete brick surface was investigated for the removal of organic pollutants at moderate concentrations.

### METHODS

#### Materials and reagents

The titanium tetrachloride solution (TiCl$_4$) as a titania source, tetraethyl orthosilicate (TEOS) as a silicon source, sodium hydroxide (NaOH), nitric acid (HNO$_3$), ammonia (NH$_3$), acetophenone, and furfural were purchased from Merck Co. Also, Portland concrete Type 1 was commercially available in Iran.

#### Preparation of nano-TiO$_2$-SiO$_2$

The TiO$_2$ was produced by a sol-gel method detailed in our previous works (Ahmadi et al. 2008; Jahromi et al. 2009; Amereh & Afshar 2010; Afshar et al. 2011; Jafari et al. 2015; Jafari & Afshar 2016). Typically, a 2.5% NH$_3$ solution was dropped into TiCl$_4$ solution and the white precipitate was obtained at pH = 7 at room temperature. The resulting precipitate was washed with deionized water until the complete removal of Cl$^-$/C0 and NH$_4^+$ ions; then a certain amount of deionized water was added to the suspension. Under a strong stirring, the exact amount of HNO$_3$ solution (0.5M) was added in 500 mL of suspension containing 10.7 mmol titanium until pH reaches 1.5 and the total solution was kept at 343 K for 24 h to create a stable TiO$_2$ sol. Subsequently, the 2.4, 1.07 and 0.46 mL TEOS were slowly dropped into 50 mL of TiO$_2$ sol to achieve 30:70, 50:50 and 70:30 molar portion of titania to silica, respectively. Afterwards, the resulting mixtures were heated at 343 K for 1 h under strong stirring and then cooled to room temperature.

#### Loading of photocatalyst on concrete bricks by dip-coating process

Portland cement concrete bricks were first produced by mixing cement, sand, and water with the sand/cement weight ratio of 3:1. The resulting paste was molded into (1 × 1 × 1 cm$^3$) and dried at room temperature overnight. Then for the loading of TiO$_2$ and TiO$_2$-SiO$_2$, the Portland cement concrete bricks were immersed in TiO$_2$ and TiO$_2$-SiO$_2$ solutions three times, taking 10 min each time. Subsequently, the coated samples were dried at room temperature for 1 h, and then dried in an oven at 339 K and 343 K for 20 and 30 min, respectively. Finally, the bricks were calcined in a programmable furnace at 673 K and 723 K for 3 h for TiO$_2$/concrete bricks and TiO$_2$-SiO$_2$/concrete bricks, respectively.

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*Figure 1* | The photonic excitation process in TiO$_2$ photocatalyst particles (E: excitation, R: relaxation, D: diffusion).
The calcination process leads to strong adhesion of the nanoparticles to the pore walls of the concrete bricks (Jafari & Afshar 2016). The amount of photocatalyst deposited on the concrete bricks is calculated by the difference of weights before and after the deposition using dip-coating processes which are approximately 1 g in 50 mL of pollutant solution (10 mg.L⁻¹).

**Photoreactivity experiment**

The photocatalytic activity evaluation of nano-TiO₂-SiO₂/concrete bricks was conducted using degradation analysis of organic compounds under UV irradiation at room temperature. The air was bubbled into the solutions inside of the batch photo reactor during irradiation and then the coated samples were immersed in 50 mL of pollutant solution (10 mg.L⁻¹). Prior to irradiation, the initial concentration of pollutant solution was measured without illumination, and then the mixture was only aerated and magnetically stirred in the dark for 1 h to ensure the establishment of absorption-desorption equilibrium. During the photocatalytic process, the mixtures were irradiated by a UV lamp (125 W, UVA, λmax = 365 nm) and the distance between UV lamp and pollutant solutions was kept within 20 cm. At certain times (60, 90, 120 min), 2 mL aliquot was taken from the solution, and if needed, centrifuged to remove the catalyst. A decrease in the concentration of these pollutants was measured by using UV-visible absorption for furfural, gas chromatography (GC) technique for acetophenone, and chemical oxygen demand (COD) for both. The degradation ratio of dye i.e. C/Co (concentration/initial concentration of dye) can be simply calculated from the ratio A/A₀ where A₀ is the solution absorbance at time zero, and A is the solution absorbance at time t after irradiation. For comparison, the nano-TiO₂ powder, nano-TiO₂-SiO₂ powder (30–70), TiO₂/concrete bricks, and concrete bricks were also observed as a control group.

**Characterizations**

Morphologies of the deposited surfaces were investigated by a Cambridge S-360 scanning electron microscope (SEM). UV-visible spectra were obtained by diffuse reflectance spectroscopy by using a UV-2550 PC spectrometer (Shimadzu-2550, Japan). Elemental analysis of the samples was performed using energy-dispersive X-ray (EDX) analysis. Photodegradation probes were analyzed by a GC instrument (Shimadzu-2010, Japan). For noting the mineralization of the organic compounds, the COD of the pollutant solutions before and after the irradiation was measured with Check It Direct photometer systems in the measuring range of 0–1,500 mg.L⁻¹.

**RESULTS AND DISCUSSION**

**Photocatalytic decomposition of furfural**

The UV-visible spectrum of the 10 ppm of furfural solution of at pH = 7.5 is shown in Figure 2. The absorbance band at 276 and 229 nm is attributed to the π → π* transition in the aromatic rings. According to the proposed mechanism (Parkash 1994), hydroxyl radicals can lead to decomposition of furfural by a ring opening process that destroys C = C bonds, which causes the disappearance of π → π* electronic transition related to the C = C bonds at 279 nm. Figure 2(a) shows that the concrete support can increase the activity of TiO₂
photocatalyst. Decomposition of furfural to CO₂ and H₂O is an oxygen-consuming reaction. Measurement of the COD confirms enlargement of oxygen depletion during the degradation by coated concrete bricks and nanoparticles. Photometric measurements show that COD of the furfural solution after 120 min UV irradiation decreases from 168 mg L⁻¹ to 68, 39, 35, and 15 mg L⁻¹ due to photocatalytic degradation using TiO₂, TiO₂-SiO₂, TiO₂/concrete bricks and TiO₂-SiO₂/concrete bricks (30/70), respectively.

Furthermore, photodegradation of the furfural was examined under identical conditions, e.g. absence and presence of the nanophotocatalysts which coated on concrete bricks and bare concrete bricks. The results showed that degradation of furfural significantly occurs only under UV irradiation. After 120 min irradiation, the photodegradation percentage reaches to ~26, ~44, ~50, ~55, and ~70% for bare concrete bricks, TiO₂, TiO₂-SiO₂, TiO₂/concrete bricks, and TiO₂-SiO₂/concrete bricks (30–70), respectively Figure 2(b). While in the of absence of coated samples, the degradation percentage of furfural solution is only ~10% under UV light.

**Effect of SiO₂**

TiO₂-SiO₂ nanocomposite shows a better photocatalytic activity in comparison with TiO₂, especially in the loaded form on the concrete bricks. The difference between their activities can be originated from the size of the catalyst particles (surface to volume ratio) as well as the strength of adsorption bond and distribution of adsorbing sites on the catalyst surface (Xu et al. 1999). The optimized composition of TiO₂-SiO₂ ratio was achieved at TiO₂-SiO₂ (30/70) so that degradation in this ratio reaches its maximum and COD reaches its minimum, as presented in Figure 3.

Photocatalytic activity of TiO₂ by mixing with SiO₂ nano-sized particle is improved when compared with TiO₂ without SiO₂ particles.

The absorption spectrum of the degradation of furfural by TiO₂-SiO₂/concrete bricks and TiO₂-SiO₂ powder in the optimized ratio of TiO₂:SiO₂ (30:70) is shown in Figure 4.

Moreover, SiO₂ can act as cohesion factor and firmly attach TiO₂ particles on the support substrate. In the addition, incorporation of SiO₂ into TiO₂ particle reduced the crystallinity by inhibiting the growth of the titania particle. As is shown in Table 1, the minimum particle size calculated by Scherrer equation belongs to TiO₂-SiO₂ (30/70) (Bastakoti et al. 2015). It is also proved that the titania-silica nanocomposite has high thermal stability, making possible to calcine these particles at higher temperatures without forming the rutile phase (Hong et al. 2003; Bahadur et al. 2012). Lewis acidic sites on the surface are formed due to the interaction between SiO₂ and TiO₂ particles; as a result, more adsorption sites are generated which can promote higher hydroxide ions adsorption on total composition. Furthermore, the -OH groups on silica particles can assist the adsorption of organic pollutants on the

**Table 1**

<table>
<thead>
<tr>
<th>Ti:Si</th>
<th>70:30</th>
<th>50:50</th>
<th>30:70</th>
</tr>
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<tbody>
<tr>
<td>Crystallite size (nm)</td>
<td>26</td>
<td>17</td>
<td>7</td>
</tr>
<tr>
<td>Content of anatase phase %</td>
<td>63.11</td>
<td>78.63</td>
<td>100</td>
</tr>
</tbody>
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**Figure 3** | Photocatalytic activity of different ratios of TiO₂-SiO₂ in TiO₂-SiO₂/concrete: (1) 30:70, (2) 50:50, (3) 70:30 and (4) 100:0 after 120 min irradiation of UV light.

**Figure 4** | Absorption spectra of 10 ppm furfural solution degraded by nano-TiO₂-SiO₂ (30/70) in the powder form and coated on the concrete bricks.
photocatalyst surface because they can operate as the holes trap which prevent electron–hole recombination and oxidize adsorbed molecules (Ohno et al. 2009; Li et al. 2014).

**Effect of pH**

Table 2 presents the extent of the furfural degradation and COD test using optimized composition of TiO$_2$-SiO$_2$/concrete (30–70) in pH = 3, 7.5, 9, 11 after 120 min of UV illumination. As is clear, pH = 7.5 shows a higher percentage of degradation of furfural, which is in accordance with the degradation mechanism (Gilbert & Baggot 1991). Beyond the zero-point pH of silica-supported TiO$_2$ (pHzc $\approx$ 4), the surface of nano-SiO$_2$-TiO$_2$ has been negatively charged. Moreover, more hydroxyl radicals (OH$^-$) form by the reaction between hydroxide ions and photo-induced holes on the TiO$_2$ surface. These radicals are considered as the main species at neutral or high pH levels. Therefore, the production of the hydroxyl radicals, and consequently, furfural degradation is facilitated at weak basic pHs. However, the strong basic pHs lead to recombination of electron-holes due to higher concentration of hydroxyl radicals due to repulsion between the negatively charged surface of photocatalyst and OH$^-$. Moreover, due to preventing the penetration of UV light to reach the surface of the catalyst, the degradation rate is significantly reduced (Qamar et al. 2006). Consequently, adsorption and photocatalytic reactions on the catalyst could particularly occur at

<table>
<thead>
<tr>
<th>pH</th>
<th>Photodegradation (%)</th>
<th>COD (mg.L$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>65</td>
<td>36</td>
</tr>
<tr>
<td>7.5</td>
<td>82</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>78</td>
<td>18</td>
</tr>
<tr>
<td>11</td>
<td>70</td>
<td>32</td>
</tr>
</tbody>
</table>

**Table 2** | Photodegradation percentage and COD test of furfural after 120 min UV illumination at various pHs

![Figure 5](https://example.com/fig5.png)

**Figure 5** | (a) and (c) SEM with different magnifications and (b) EDX analysis of TiO$_2$/concrete bricks.

![Figure 6](https://example.com/fig6.png)

**Figure 6** | (a) and (c) SEM with different magnifications and (b) EDX analysis of TiO$_2$-SiO$_2$/concrete photocatalyst (formation of silica substrate over concrete is shown schematically in the figure).
weak basic medium so that the pH = 7.5 was achieved as the optimized pH value.

**Concrete supports**

As shown in Figures 3 and 4, the concrete support can increase the efficiency of the photodegradation. Higher specific surface in loaded photocatalysts due to the porous structure of the concrete support, on the one hand, and other elements as impurities (especially iron) in the concrete materials on the other hand, improve the photocatalytic activity of concrete-supported catalysts. Figures 5 and 6 show SEM and EDX analysis of TiO$_2$ and TiO$_2$-SiO$_2$ on the concrete support. As a consequence of the high penetration depth of the electron beam in EDX analysis, this result is related to both substrates and thin layers (nano-TiO$_2$ and TiO$_2$-SiO$_2$), demonstrating the existence of impurities of concrete bricks. As it is shown in EDX patterns, the main elements were Ti, Ca, Si, and Fe among which came from the TiO$_2$ and SiO$_2$ in concrete and TiO$_2$-SiO$_2$ nanocomposite distributed on the concrete bricks' surface is approximately 11 nm and 7 nm, respectively, obtained by Scherrer equation and titania nanoparticle distribution, is considerably improved upon the addition of silica (Gilbert & Baggot 1991). According to the mapping analysis shown in Figure 7, the distribution of the titania particles over the concrete bricks, as well as the iron and aluminium elements...
on the concrete bricks, are homogeneous. The presence of the silica can facilitate this uniform distribution of photocatalyst and increase its efficiency.

**Photocatalytic decomposition of acetophenone**

Photodegradation of aromatic compounds by TiO$_2$–SiO$_2$/concrete bricks leads to hydroxylated-aromatic compounds due to the mechanism consisting of OH$^-$ radicals (Brigden et al. 2009). Probable products of photodegradation of acetophenone in partial oxidation are hydroxyl-acetophenone, phenol, and diacetyl-biphenyl (DABP). The formation of DABP is due to the interaction of a hole ($h^+$) and adsorbed molecular acetophenone on a TiO$_2$ surface (Nur 2006b; Brigden et al. 2009).

The GC technique is commonly used for detection of produced compounds during the photodegradation (Brigden et al. 2009). The photodegradation is an oxidation reaction; therefore, COD technique can be used as complementary evidence. The results show that in the absence of coated samples, the degradation percentage of acetophenone solution is only $\sim$12%, whereas for concrete, nano-TiO$_2$ powder, nano-TiO$_2$-SiO$_2$ powder, TiO$_2$/concrete bricks, and TiO$_2$-SiO$_2$/concrete bricks reach to $\sim$44, $\sim$40, $\sim$50, $\sim$74, and $\sim$82%, respectively, at pH = 3 under UV light.

As is obvious in Figures 8 and 9, similar to the furfural photodegradation, the concrete support improves the photodegradation of acetophenone. The COD analysis shows that COD of the solution containing acetophenone decreases from 220 mg.L$^{-1}$ to 70 mg.L$^{-1}$ due to the photodegradation of acetophenone in 120 min over the TiO$_2$/concrete bricks.

**Effect of SiO$_2$**

There is an accumulating effect of silica on the homogeneous distribution of TiO$_2$ particles on concrete bricks (see Figure 6); and as the presence of SiO$_2$ inhibits the size growth of nano-TiO$_2$, it leads to form more anatase phase having better photocatalytic activity in comparison to rutile phase of TiO$_2$ (Zenkovets et al. 2009). As shown in Table 1, the anatase phase is more stable when particle size is smaller than 14 nm, and the phase transition of anatase to rutile is significantly reduced. The -HO groups on the silica facilitate the adsorption of organic pollutants on the photocatalyst surface. Disposal and participation of hydroxyl radicals for decomposition of organic contaminants are more favorable for the absorbed species than the free species, due to the short lifetime of the radicals which are close to the catalyst surface. The most privilege of the concrete support in this process is the abundance of the metallic oxides in its composition. Metallic oxides and silica can produce an alkaline pH in the solution, facilitating the hydroxyl formation upon the photocatalyst. Our results demonstrate that the photodegradation rate of acetophenone enhance with increasing the silica content in nano-TiO$_2$-SiO$_2$ and it reaches to the maximum degradation rate of 95% in nano-TiO$_2$-SiO$_2$ with molar ratio 30:70 (Figure 10).

**Effect of pH**

Irradiation time of light and pH was optimized similar to furfural decomposition. The results reveal that photodegradation of acetophenone occurs optimally at pH = 3. At acidic pHs, which is under its pH$_{ZPC}$, the surface charge is
positive, based on titania charge, and the adsorbed amount of the acetophenone upon the photocatalyst surface reaches the maximum amount. More than 95% of photodegradation of acetophenone is achieved after 120 min irradiation of the light, and more times cannot significantly reduce the amount of the acetophenone. The COD test shows that the concentration of oxygen decreases from 220 mg L\(^{-1}\) to 5 mg L\(^{-1}\) within 150 min irradiation of UV light, which is almost the same amount with COD of the solution of acetophenone after 120 min irradiation. Thus, the optimum time for irradiation of UV light to the target solution is achieved to be 120 min.

**CONCLUSION**

In summary, the photodegradation of furfural and acetophenone as organic pollutants was performed using TiO\(_2\)-SiO\(_2\)/concrete bricks under UV illumination. Our analysis shows that silica substrate improves photocatalytic activity of TiO\(_2\), which is because of enhancement of the anatase phase versus rutile phase in TiO\(_2\). The EDX analysis shows that various cations in the concrete composition can facilitate the photocatalytic activity of titania. Our results implied that the presence of the SiO\(_2\) causes the limitation of TiO\(_2\) particles size and increases its activity. In the case of furfural degradation using TiO\(_2\)-SiO\(_2\)/concrete bricks under UV light irradiation, maximum yield was achieved at pH = 7.5 with optimum component of 30:70 ratio in TiO\(_2\)-SiO\(_2\), which was confirmed with COD and UV-vis spectrometry techniques. In the case of acetophenone, the maximum yield of photodegradation with an optimal component of TiO\(_2\)-SiO\(_2\)/concrete (50:70 in TiO\(_2\)-SiO\(_2\)) is achieved at pH = 3, which was confirmed by COD and GC techniques. The silica/concrete-supported TiO\(_2\) shows a more efficient photoactivity in comparison to its powder form. According to this work, utilization of TiO\(_2\)-SiO\(_2\)/concrete system in treatment of industrial wastewater containing these organic pollutants is not only economical, but also due to immobilized form it does not require the filtration or separation stage to recover the catalyst.

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