Photodegradation of organic matter in fresh garbage leachate using immobilized nano-sized TiO$_2$ as catalysts
C. Chen, Q. Xie, B. Q. Hu and X. L. Zhao

ABSTRACT
Two immobilized nano-sized TiO$_2$ catalysts, TiO$_2$/activated carbon (TiO$_2$/AC) and TiO$_2$/silica gel (SG) (TiO$_2$/SG), were prepared by the sol–gel method, and their use in the photocatalytic degradation of organic matter in fresh garbage leachate under UV irradiation was investigated. The influences of the catalyst dosage, the initial solution pH, H$_2$O$_2$ addition and the reuse of the catalysts were evaluated. The degradation of organic matter was assessed based on the decrease of the chemical oxygen demand (COD) in the leachate. The results indicated that the degradation of the COD obeyed first-order kinetics in the presence of both photocatalysts. The degradation rate of COD was found to increase with increasing catalyst dosage up to 9 g/L for TiO$_2$/AC and 6 g/L for TiO$_2$/SG, above which the degradation began to attenuate. Furthermore, the degradation rate first increased and then decreased as the solution pH increased from 2 to 14, and the degradation rate increased as the amount of H$_2$O$_2$ increased to 2.93 mM, after which it remained constant. No obvious decrease in the rate of COD degradation was observed during the first four repeated uses of the photocatalysts, indicating that the catalysts could be recovered and reused. Compared with TiO$_2$/AC, TiO$_2$/SG exhibited higher efficiency in photocatalyzing the degradation of COD in garbage leachate.

Key words | COD, garbage leachate, immobilized nano-sized TiO$_2$ photocatalysts

INTRODUCTION
Garbage leachate is known as a high strength wastewater that is difficult to treat by biological, physical or chemical methods due to its highly variable compositions and the presence of highly recalcitrant organic compounds, ammonia and heavy metals (Meeroff et al. 2002). In recent years, UV-TiO$_2$/solar-TiO$_2$ assisted photocatalytic degradation has been used in the treatment of landfill leachates (Cho et al. 2002; Mansouri et al. 2007; Jia et al. 2011; Meeroff et al. 2012). The photocatalytic activity generally increases as the particle size decreases (Metzler et al. 2011). Thus, nano-scale TiO$_2$ is expected to have higher photocatalytic activity than their bulk particles (Sohrabnezhad et al. 2009). Nevertheless, the post-separation, recovery and reuse of nano-sized TiO$_2$ particles remain the major obstacles to their use in industrial applications (Chong et al. 2010). Currently, studies have focused on the immobilization of TiO$_2$ particles on different substrates, such as activated carbon (AC), mesoporous clays, films and fibers (Chong et al. 2010). The influences of the initial pH, the catalyst loading, the UV irradiation sources and the hydrogen peroxide concentrations on the photocatalytic performance of the photocatalysts have also been investigated (Achilleos et al. 2010; Chong et al. 2010).

Of these immobilized nano-sized TiO$_2$, the granular activated-carbon immobilized TiO$_2$ (TiO$_2$/AC) are receiving increasing attention for use in the degradation of humic and phenolic compounds, pesticides, chlorinated compounds and dyes (Kitsiou et al. 2009; Xue et al. 2011). However, little experimental information is available concerning the treatment of garbage leachate. The aim of the present study was to investigate the effects of various operational conditions on the photodegradation of organic matter in fresh leachate collected from a municipal solid waste incineration plant catalyzed by the nano-sized TiO$_2$/AC synthesized by the sol–gel process, which is an attractive method for obtaining more effective TiO$_2$ as a photocatalyst (Seck et al. 2012). To explore new carriers for supporting the nano-sized TiO$_2$, the feasibility of applying
the nano-sized TiO$_2$ immobilized onto silica gel (TiO$_2$/SG) in leachate treatment was also investigated. The degradation of organic matter in leachate was evaluated by the measurement of the chemical oxygen demand (COD).

**MATERIALS AND METHODS**

**Pretreatment of garbage leachate**

Fresh leachate was collected from the Tongxing Garbage Incineration Plant located in Chongqing, China. The properties of the leachate were as follows: turbidity 1,500–1,600 FTU, COD 20,000–22,000 mg/L, NH$_3$-N 800–1,000 mg/L, and pH 6.9–7.4. The leachate was pretreated by the coagulation method to create a clarified environment for the photocatalytic oxidation process. To accomplish this, 100 mL of leachate was added to a 250 mL beaker and 6 mL of 10% (w/w) poly aluminum chloride solution (PAC, as a flocculant) and 5 mL of 1‰ (w/w) polyacrylamide (PAM, as a coagulant aid) were added. The leachate was then stirred using a six-joint electric blender for 40 min, after which it was allowed to stand for another 40 min. The supernatant was used for the photocatalytic degradation experiment. A water quality analysis indicated that the pH value, turbidity and COD concentration in the pretreated leachate solution ranged from 5.8 to 6.5, 105.25 to 135.18 FTU and 13,000 to 15,000 mg/L, respectively.

**Preparation and characterization of immobilized nano-sized TiO$_2$ photocatalysts**

Commercial AC and SG were used as carriers to immobilize TiO$_2$ particles. Briefly, the carriers were washed with deionized water until the solution clarified, after which they were dried at 80°C for 2 h and then used to prepare the immobilized nano-sized TiO$_2$ photocatalysts through the sol–gel method, as described by Xie & Zhao (2011). A portion of the 100 mL of tetrabutyl titanate was dissolved in 35 mL of ethanol, after which the pretreated carrier was added. After vigorously stirring the mixture solution with a magnetic stirrer for 3.5 h, several drops of nitric acid (as the inhibitor) and 1 mL of deionized water were added. The resultant solution was then aged in a confined space for 48 h to form a gel. The obtained gel was washed with ethanol and deionized water until the upper solution became optically clear, after which it was dried at 80°C for 2 h. Next, the gel was calcined at 400°C in a muffle furnace for 4 h, which yielded the immobilized nano-sized TiO$_2$ photocatalysts.

The phase compositions of the photocatalysts were identified using a RAX-10 X-ray diffraction (XRD) analyzer operated with a Cu-$K_{\alpha}$ source at 20 kV. The surface morphology of the photocatalysts was observed using a scanning electron microscope (SEM, JEM-200CX, Japan).

**Photocatalytic degradation experiments**

A series of experiments were devised to investigate the optimal conditions for the photodegradation of organic matter in garbage leachate catalyzed by the immobilized nano-sized TiO$_2$ particles. 100 mL of pretreated leachate and the immobilized nano-sized TiO$_2$ with a given rate were added to a beaker. The mixture in the beaker was then magnetically stirred for 15 min in the dark until the adsorption equilibrium was reached, after which it was irradiated by the UV lamp. During UV irradiation, air was bubbled continuously through the solution, and 5 mL samples were taken every 15 min to determine the COD concentration. The COD concentration in each sample was determined by the potassium dichromate method. In addition, the influence of each of the factors of catalyst dosage, initial pH of the garbage leachate and H$_2$O$_2$ dosage on the photocatalytic activity of the immobilized nano-sized TiO$_2$ was systematically investigated.

**Data processing**

The COD degradation rate was calculated from the differences of the initial and final COD concentrations in the leachate according to the following equation:

$$y(\%) = \frac{C_0 - C}{C_0} \times 100$$  \hspace{1cm} (1)

where $y$ is the COD degradation rate, and $C_0$ and $C$ are the initial and final COD concentrations (mg/L), respectively.

The variation of COD degradation with time was fitted to the following linear first-order kinetic model (Mahmoodi et al. 2006):

$$\ln(C/C_0) = -kt$$  \hspace{1cm} (2)

where $k$ is the reaction rate constant (min$^{-1}$), and $t$ is the reaction time (min).
RESULTS AND DISCUSSION

Characteristics of the immobilized nano-sized TiO2 photocatalysts

TiO2 has three main crystal structures: anatase, rutile and brookite. The anatase phase of TiO2 has higher photocatalytic activity than the other types of TiO2 because of its appropriate band-gap energy upon UV irradiation. The XRD pattern peaks at 25°, 37°, 48°, 55°, 56°, 62°, 71° and 75° correspond to anatase titania, while those at 28° (major), 36°, 42° and 57° indicate the rutile phase (Panpranot et al. 2009). Figure 1 presents the XRD spectra of TiO2/AC and TiO2/SG prepared by the sol–gel method for 2θ ranging from 20° to 55°.

Peaks characteristic of anatase with a minor amount of rutile phases were detected. The maximum diffraction peaks appeared at 2θ = 25.3° in both patterns, and three primary peaks were found at 2θ = 25.3°, 37.8° and 48.0°, which could be vested in diffraction from the (101), (004) and (200) planes of anatase, respectively (Xu & Meng 2009). These results indicated that anatase was the dominant phase of TiO2 immobilized on both AC and SG.

Figure 2 shows the SEM images of the prepared TiO2/AC and TiO2/SG. Upon introduction of TiO2 and after calcination, parts of the pores on the surface were filled with TiO2, and the immobilized TiO2 particles were serried and uniformly distributed on the surface of AC (Figure 2(a)) and SG (Figure 2(b)), indicating the immobilization of TiO2 particles. Further magnification of the images indicated that the particle sizes of TiO2 on AC and SG ranged from 70 to 100 nm and from 60 to 100 nm, respectively. These results indicated that the immobilized nano-sized TiO2/AC and TiO2/SG photocatalysts had been successfully prepared by the sol–gel method. The weight differences of the carriers before and after TiO2 immobilization indicated that the rates of TiO2 deposited onto AC and SG were 8.9 ± 0.8% and 17.1 ± 1.1%, respectively.

Figure 1 | XRD patterns of TiO2/AC (a) and TiO2/SG (b).

Figure 2 | SEM images of TiO2/AC (a) and TiO2/SG (b).
Effect of the operational conditions on the degradation of COD in leachate

Effect of the immobilized catalyst dosage

TiO2 dosage is a significant factor that can affect the degradation of organic pollutants in wastewater (Achilleos et al. 2010). The dosages of the TiO2/AC and TiO2/SG in the present study ranged from 3 to 11 g/L and from 3 to 7 g/L, respectively. The degradation rates of the COD from the pretreated leachate at different reaction times are presented in Figure 3. The degradation rate increased dramatically during the first 60 min, after which it increased slowly or remained nearly constant. The experimental data were fitted to the linear first-order kinetic model (Equation (2)), with the results listed in Table 1. The variation of the degradation rate with reaction time is well described by the first-order kinetic model, with correlation coefficients greater than 0.90 \( r_{0.05} = 0.811 \). The degradation rate after 120 min of UV irradiation was 28.6% for the TiO2/AC catalyzed system and 43.4% for the TiO2/SG catalyzed system. These results indicated the feasibility of removing organic matter from the actual garbage leachates through photodegradation catalyzed by immobilized nano-sized TiO2 particles.

The effect of catalyst dosages on the COD photodegradation rate in the pretreated leachate are also shown in Figure 3 and Table 1. As expected, the degradation rate increased with increasing dosage of photocatalysts, but the extents of the increase differed among the two photocatalytic systems. The degradation rate increased as the photocatalytic dosage increased from 3 to 9 g/L for the TiO2/AC catalyzed system and 3 to 6 g/L for the TiO2/GS catalyzed system but decreased as the photocatalytic dosage increased further for both systems. The maximal COD degradation rates were observed at the dosage of 9 g/L for TiO2/AC and at 6 g/L for TiO2/SG. Regarding the reaction rate constant \( k \), in the TiO2/AC catalyzed system, it increased from 0.0015 to 0.0032 min\(^{-1}\) as the photocatalytic dosage increased from 3 to 7 g/L, but remained constant as the catalytic dosage increased from 7 to 11 g/L. Similarly, in the TiO2/SG catalyzed system, the reaction rate constant increased from 0.0029 to 0.0053 min\(^{-1}\) as the catalyst dosage increased from 3 to 6 g/L, but decreased to 0.0043 min\(^{-1}\) as the dosage increased to 7 g/L. This phenomenon indicated that, as the amount of catalyst increased, it provided ample photocatalysis activity that could sufficiently utilize the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( k ) min(^{-1})</th>
<th>( r )</th>
<th>Catalyst</th>
<th>( k ) min(^{-1})</th>
<th>( r )</th>
</tr>
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<tbody>
<tr>
<td>TiO2/AC</td>
<td>3 g</td>
<td>0.0015</td>
<td>0.9278**</td>
<td>3 g</td>
<td>0.0029</td>
</tr>
<tr>
<td></td>
<td>5 g</td>
<td>0.0019</td>
<td>0.9527**</td>
<td>4 g</td>
<td>0.0036</td>
</tr>
<tr>
<td></td>
<td>7 g</td>
<td>0.0032</td>
<td>0.9669**</td>
<td>5 g</td>
<td>0.0047</td>
</tr>
<tr>
<td></td>
<td>9 g</td>
<td>0.0032</td>
<td>0.9567**</td>
<td>6 g</td>
<td>0.0053</td>
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<tr>
<td></td>
<td>11 g</td>
<td>0.0032</td>
<td>0.9530**</td>
<td>7 g</td>
<td>0.0043</td>
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\( C_0 = 13,080 \text{ mg/L, reaction time} = 120 \text{ min.} \)

\( r_{0.05} = 0.811; r_{0.01} = 0.917. \)

Figure 3 | Effect of the photocatalyst dosage of TiO2/AC (a) and TiO2/SG (b) on the COD degradation rate.
absorbed photon energy to degrade the organic matter adsorbed onto the catalyst. However, as the catalyst dosage increased further, the excess immobilized TiO₂ particles had masked part of the photosensitive surface, thereby hindering light penetration or even reflecting the light (Kaniou et al. 2005), resulting in the observed stagnation stage. Considering the facts that the COD degradation rate and the reaction constant did not obviously change as the catalyst dosage increased from 7 to 9 g/L in the TiO₂/AC system, and both the maximum COD degradation rate and reaction constant were obtained at the dosage of 6 g/L in the TiO₂/SG system, the dosages of 7 g/L for TiO₂/AC and 6 g/L for TiO₂/SG were chosen for the subsequent photocatalytic degradation experiments.

Figure 3 also shows that the COD degradation rates from the TiO₂/SG photocatalyzed system are much higher than those from the TiO₂/AC photocatalytic system, indicating that TiO₂/SG displayed greater photocatalytic activities than did TiO₂/AC. This difference could be explained by increased TiO₂ loading on SG than on AC. In addition, the more uniform distribution of TiO₂ on SG than on AC may contribute to the improved photocatalytic efficiency (shown in Figure 2).

Effects of the initial pH

Initial pH is a major factor determining the efficiency of photocatalysis (Jia et al. 2011). Numerous works have been published dealing with the effect of pH on the photocatalytic degradation of various organic compounds (Canle et al. 2005; Pekakis et al. 2006; Jia et al. 2011). The initial pH values of the pretreated leachate were adjusted from 2.0 to 12.0 using diluted H₂SO₄ and NaOH solutions. The COD degradation rate decreased as the solution pH increased to 8.0, above which it increased with the increase in solution pH (Figure 4). The COD degradation rates were the highest under pH 2.0 and pH 4.0, followed by the rates under pH 6.0 and pH 12.0, and the rates were the lowest at pH 10.0 and pH 8.0. These result indicated that both of the immobilized nano-sized TiO₂ types exhibited a higher photocatalytic activity under acidic conditions than under neutral and/or weak alkaline conditions, which was consistent with the behaviors of TiO₂ (Pekakis et al. 2006; Jia et al. 2011). This phenomenon could be explained by the influence of electrical charges and hence the adsorption of organic pollutants on TiO₂ (Cho et al. 2002). The point of zero charge (pHpzc) reported in literature for TiO₂ ranged from 6.3 to 6.8 (Alaton et al. 2002; Canle et al. 2005; Pekakis et al. 2006). Therefore, alkaline pH values are favorable for the photocatalytic degradation of the pollutant molecules present in their cationic forms, while negatively charged molecules are more readily degraded at low pH values, where the photocatalyst surface is positively charged (Alaton et al. 2002). The phenomenon can also be attributed to the fact that under acidic conditions, the positively charged catalyst surface is conducive to the transferring process of photogenerated electrons to the surface of catalyst, which contributes to the generation of active radicals, such as O₂⁻ and HO⁻ in the presence of oxygen in aqueous medium, while avoiding the recombination of photogenerated electrons and holes (Xue et al. 2011). The increase of the COD degradation rates with solution pH value above

Figure 4 | Effect of the initial pH on the COD photodegradation at 120 min. (a) TiO₂/AC; (b) TiO₂/SG.
8.0 would likely be attributed to the negative surface of the TiO2 with HO\(^{-}\) ions at higher alkaline pH acting as an efficient trap for the photogenerated holes, resulting in the production of hydroxyl radicals according to the following reactions: HO\(_{\text{surface}}\) + h\(_{vb}\) ↔ HO\(_{\text{surface}}^*\) (Ghaly et al. 2011).

**Effects of the H\(_2\)O\(_2\) dosage**

H\(_2\)O\(_2\) is generally expected to influence photodegradation reactions because it functions as both a powerful oxidant and an electron acceptor. There are two contradictory results about the effect of H\(_2\)O\(_2\) on the photocatalytic degradation of organic contaminations in TiO2 suspensions. H\(_2\)O\(_2\) is expected to promote degradation because it may react with conduction band electrons and superoxide radical anion to yield hydroxyl radicals and anions (shown in Equations (3) and (4)), which is the dominant oxidizing species contributing to the mineralization process due to the TiO2 photocatalyst (Pekakis et al. 2006; Chu et al. 2007; Achilleos et al. 2010).

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{HO}^- + \text{HO}• \\
\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{HO}^- + \text{HO}• + \text{O}_2
\]  
Equations (3) and (4)

Therefore, H\(_2\)O\(_2\) can also act as an electron scavenger, thereby suppressing the electron–hole recombination, which is a major cause of low TiO2 photocatalytic quantum yield (Pekakis et al. 2006). However, Lu et al. (1995) has reported that some organic contaminants, such as trinitrotoluene, dichlorvos and trinitrobenzene, have shown negative effects on the use of hydrogen-peroxide assisted photocatalytic degradation. Seck et al. (2012) also observed that as the H\(_2\)O\(_2\) concentration increased from 0 to 10 mM, the apparent rate constant of bentazon photocatalytic degradation over ECT-1023 and Degussa P25 suspension decreased from 0.143 to 0.034 min\(^{-1}\) and 0.083 to 0.041 min\(^{-1}\), respectively. Therefore, the influences of H\(_2\)O\(_2\) on the photocatalytic degradation of organic contaminations depend on the reaction conditions and the nature of the reductants.

As shown in Figure 5, in the TiO\(_2\)/AC and TiO\(_2\)/SG suspensions, the COD degradation rate increased with the increase of H\(_2\)O\(_2\) concentration up to 2.93 mM. These results demonstrated the beneficial effect of the H\(_2\)O\(_2\) addition on the photocatalytic reaction for organic matter degradation. However, when the H\(_2\)O\(_2\) concentration exceeded 2.93 mM, the COD degradation rate decreased with the increase of the H\(_2\)O\(_2\) concentration, indicating the negative effect of excessive H\(_2\)O\(_2\) addition on the photocatalytic degradation of organic pollutants in leachate. This behavior can be explained by the fact that excessive H\(_2\)O\(_2\) may act as an electron and radical scavenger (Equations (5)–(7)), resulting in a decreased degradation of the COD (Poulos et al. 2003; Mahmoudi et al. 2006). Meanwhile, the radical–radical recombination must be considered as a competitive reaction. Furthermore, H\(_2\)O\(_2\) can be adsorbed onto the TiO\(_2\) particles, which modify the TiO\(_2\) surfaces and subsequently decrease their catalytic activity (Ghaly et al. 2011).

\[
\text{H}_2\text{O}_2, 2h_{vb}^+ \rightarrow \text{O}_2, 2\text{H}^+
\]  
Equation (5)

![Figure 5](https://iwaponline.com/wst/article-pdf/69/6/1219/472303/1219.pdf)

Figure 5 | Effect of the H\(_2\)O\(_2\) dosage on the photodegradation of COD. (a) TiO\(_2\)/AC; (b) TiO\(_2\)/SG.
\[
\begin{align*}
H_2O_2 + HO\cdot &\rightarrow HO_2\cdot + H_2O \quad (6) \\
HO_2\cdot + HO\cdot &\rightarrow H_2O + O_2 \quad (7)
\end{align*}
\]

The above results illustrated that the optimum H2O2 concentration in the present study was 2.93 mM. Under these conditions, the reaction kinetics were similar to those observed without H2O2 addition, but the COD degradation rate at 120 min and the reaction rate constant increased by 13.9 and 54.05%, respectively, for the TiO2/AC system, and the COD degradation rate at 120 min and the reaction rate constant increased by 10.1 and 39.2%, respectively, for the TiO2/SG system.

**Effects of catalyst reuse**

The possibility of catalyst recovery and reuse has drawn considerable attention due to its potential to reduce the cost of photocatalytic reaction systems (Pekakis et al. 2006). The TiO2/AC and TiO2/SG were recovered and reused several times in the present study. As shown in Figure 6, the degradation rates declined slightly after the photocatalysts were reused four times. The reaction rate constant \(k\) for the TiO2/AC system and TiO2/SG system decreased from 0.006 to 0.0055 min\(^{-1}\) and from 0.0075 to 0.0069 min\(^{-1}\), respectively, demonstrating the sufficiently high photocatalytic efficiency. The reuse of TiO2 in catalyzing photodegradation of organic matter has also been reported by other studies. Fernández-Ibáñeza et al. (2003) found the Degussa P25 TiO2 did not lose efficiency after several photocatalytic processes. Meeroff et al. (2012) reported that there was little difference in COD removal from leachate after Degussa P25 TiO2 was reused three times. The present results indicated that the two immobilized nano-sized TiO2 types exhibited a good recovery and stable photocatalytic activity. Nevertheless, with the continuous reuse of catalysts, the photocatalytic efficiency obviously decreased. The decreased photocatalytic efficiency caused by repeat use of photocatalysts such as TiO2 might be explained by the accumulation of chloride and compounds containing N onto the surface of catalysts because landfill leachates are rich in those compounds, which can act as catalyst poisons in photocatalysis (Cho et al. 2002; Fernández-Ibáñeza et al. 2003). An additional explanation is the transformation of some TiO2 particles from active form (anatase) to the rutile form upon irradiation (Pekakis et al. 2006). In addition, the elimination of some particles from the catalyst surface during use may contribute to the decreased photocatalytic efficiency. Rao et al. (2004) have observed the phenomenon that some TiO2 supported on pumice stone and organic fibers could be removed from the catalyst surface after long time use.

**CONCLUSIONS**

The photodegradation of COD in fresh garbage leachate using immobilized nano-sized TiO2/AC and TiO2/SG as catalysts is well described by first-order kinetics. The photodegradation rate was influenced by factors that include the catalyst dosage, initial pH and H2O2 addition. The photodegradation rate was the highest at the dosages of 7 g/L for TiO2/AC and...
of 6 g/L for TiO2/SG when the initial pH was 2.0 and 2.93 mM of H2O2 was added, as indicated by the COD degradation rates of 51 and 55% for TiO2/AC and TiO2/SG, respectively. Therefore, the two immobilized nano-sized TiO2 were efficient at photocatalyzing the degradation of organic matter in fresh garbage leachate. In addition, the two immobilized nano-sized TiO2 photocatalysts had a good recovery and stability of photocatalytic activity and could be recovered and reused four times with similar performance during the treatment of garbage leachate.

REFERENCES


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