Effect of W doping level on TiO$_2$ on the photocatalytic degradation of Diuron

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ABSTRACT

In the present study, three compositions of W-doped titania nano-photocatalyst are synthesized via the sol–gel method. The powders obtained were characterized by X-ray diffraction, Raman spectroscopy and UV–visible diffuse reflectance spectroscopy. The photocatalytic performances of the different photocatalysts are tested with respect to the degradation of Diuron in water solutions under simulated solar light and visible light irradiation. The W$_{0.03}$Ti$_{0.97}$O$_2$ catalyst exhibits better photoactivity than the pure TiO$_2$ even under simulated solar light and visible light. This improvement in activity was attributed to photoelectron/hole separation efficiency.

INTRODUCTION

Industrial development and human activities produce a very large quantity of chemical pollutants (dyes, intermediaries of synthesis, plant health products, drugs, for example). Among them, pesticides have a very important place because they are deliberately introduced into the environment. The diffusion of the pesticides in nature generates a pollution of the various compartments of the biosphere (water, ground and atmosphere) and can induce acute toxic effects on the living being and food web (Celis et al. 2008). The presence of pesticides such as Diuron was detected in streams and urban surface water, sometimes with concentrations of several micrograms per liter. Among these various types of pesticides, Diuron, as a herbicide, is one of the most commonly used substances to control a wide variety of grassy weeds in intensive agriculture (Giacomazzi & Cochet 2007). Given the potential toxicity of these pollutants and their by-products, their elimination from natural water and the human environment proves to be a real need.

The pollution problem generated by the Diuron contamination of water resources has led to increasing interest in good technologies for its elimination. This can be reached by classical physico-chemical methods, such as adsorption onto activated carbon (López-Ramón et al. 2007) and membrane filtration (Musbah et al. 2015). A disadvantage of activated carbon adsorption, however, is the difficulty of reactivating or eliminating the activated carbon loaded with pesticide. Membrane filtration is a relatively expensive process.

During the last 20 years, the studies showed that practically all the organic molecules, including some of the most refractory ones such as pesticides, can be degraded until their complete mineralization by photocatalysis, which is one of the advanced oxidation processes (Mills & Lehunte 1997).

Titanium dioxide and especially its anatase crystalline form is the most popular semi-conductor, due to its low cost, low toxicity, photo-stability and chemical inertness (Anderson et al. 2002; Li et al. 2008). However, it has several defects: TiO$_2$ can only be excited by UV light ($\lambda < 380$ nm) due to its large band gap of 3.2 eV, which means that it absorbs a small fraction of visible light (less than 5% of the solar spectrum) (Riboni et al. 2015). The rapid recombination of photogenerated electrons and holes at the TiO$_2$ surface significantly diminishes the photocatalytic efficiency (Yu et al. 2008).

There are several solutions to extend the optical absorption of TiO$_2$ into the visible light region, including doping metal ions such as iron, copper, vanadium and cobalt into the TiO$_2$ lattice (Woo et al. 2007), adsorption of monolayer organic dye at the TiO$_2$ surface (Alex et al. 2005) and coupling TiO$_2$ with another appropriate semi-conductor such as ZnO, V$_2$O$_5$, CdS and WO$_3$ (Robert 2007). As
mentioned by an author of this paper (Robert 2007), most other research work has centered on techniques for improving the process by the introduction into the TiO₂ of either anions (such as N³⁻, S²⁻ or C⁴⁺; these species substitute the oxygen lattice on TiO₂ and lead to a band gap narrowing, resulting in high visible absorption) (Sakthivel & Kisch 2003; Gole et al. 2004; Zhao et al. 2005) or cations (such as vanadium, iron (Yamashita et al. 2002)) and electron or hole scavengers adsorbed on the surface (H₂O₂, O₂, S₂O₈²⁻, etc.) (Bamwenda et al. 2001; Mills & Valenzuela 2004). The process induces a change in the concentration of the hole or electron, thus increasing the charge carrier concentration and improving the conductivity of the materials. Another possibility is to use light-emitting diodes as an alternative artificial light source for photoreactors in the absence of solar irradiation with N-doped TiO₂ for the elimination of contaminants (Subagio et al. 2010; Jo & Kang 2012; Vaiano et al. 2015).

Doping with tungsten (W) transition metal ions can help to delay the recombination of photogenerated electrons and holes, which thus increases the lifetime of charge carriers. Moreover, additions of tungsten can extend the spectral response of TiO₂ into the visible region through a positive shift in the conduction band. In 2013, Khan et al. reported that the substitutional W doping at Ti sites reduced the electron transition energy from valence to conduction band by about 0.12 eV, assigned to the creation of W 5d states just below the conduction band minimum (Khan et al. 2013). In another work, the authors have prepared successfully a W-doped TiO₂ using both sol–gel and surface impregnation methods. The obtained photocatalyst showed a visible light photocatalytic activity that was three times higher than pure TiO₂ for the degradation of phenol in water solution (Grabowska et al. 2012). Finally, in another recent study, Oseghe and co-authors showed the effect of the W dopant on the crystal size (Oseghe et al. 2015). The composite with a lower crystal size exhibited the best photocatalytic performance in MCPA (4-chloro-2-methylphenoxycetic acid) degradation, which is attributed to the synergistic effect of its characteristics. These characteristics include relatively small crystal size, lowest oxygen vacancy, least band gap, and least electron-hole recombination rate.

In this study, we focused on the modification of TiO₂ by W and thus a series of catalysts, WₓTi₁₋ₓO₂ with three different amounts of W (x = 3, 20, 40% wt.), were synthesized by the sol–gel method. TiO₂ and WO₃ were also prepared for comparative purposes. Photocatalytic efficiency of the catalysts has been evaluated for the degradation of Diuron under visible (λ > 420 nm) and simulated solar light.

**MATERIALS AND METHODS**

**Materials**

All reagents used to prepare the semi-conductor powders were of analytical reagent grade. Titanium tetraisopropoxide (TIP), tungsten(VI) oxychloride WOCl₄ and isopropanol were used as received and without further purification. They were purchased from Aldrich Chemical. Diuron (chemical formula, C₉H₁₀Cl₂N₂O; molecular weight = 233.095 g/mol) was used as the model pollutant and obtained from Aldrich. The chemical structure of Diuron is shown in Figure 1. It has a maximum absorbance at a wavelength of 248 nm. Solutions were prepared by dissolving appropriate amount of the pesticide in double distilled water.

**Methods**

**Photocatalyst preparation**

WₓTi₁₋ₓO₂ nanoparticles were synthesized using a sol–gel template technique with the following procedure: firstly, WOCl₄ was dissolved in isopropanol for 3 h under stirring at ambient temperature. Subsequently, TIP was added to this solution. The mixture was kept under vigorous stirring for 16 h at 25°C, and then a required volume of water at 0°C was dropwise added to hydrolyze the TIP to WₓTi₁₋ₓO₂. Finally, after evaporation of the solvent, the produced sample was vacuum-dried at 70°C for 48 h and calcined, under air or nitrogen, at 450°C for 1 h. The different volumes of the chemical precursors were adjusted according to the desired Ti/W ratio.

For comparison purposes, pure TiO₂ and WO₃ were also prepared using the same procedure described above.

**Photocatalyst characterization**

The crystalline phases of the prepared samples were determined by X-ray diffraction (XRD) measurements (Siemens...
D500) with a D8 Advance Bruker diffractometer, in a q/2q mode and using the Kα radiation of Cu at 1.5406 Å at room temperature. Diffraction patterns were recorded in the angular range of 10°–90°. The Scherrer formula (Equation (1)) was used to estimate the average crystallite size of the synthesized particles:

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]  

(1)

where D is the crystallite size, \( \lambda \) is the X-ray wavelength, \( \beta \) is the full-width at half maximum of the (1 0 1) diffraction peak of anatase TiO\(_2\), and \( \theta \) = Bragg diffraction angle.

The Raman spectra of the samples were recorded using a LabRam HR micro-Raman instrument coupled to a micro Olympus BX41 HORIBA Jobin Yvon at room temperature.

The optical absorption of the photocatalysts was measured with a Varian Cary 4000 UV–visible (UV–vis) spectrophotometer equipped with DRA900 integrated sphere. The values of the band gap energy (Eg) were calculated using Equation (2).

\[ (ahv)^{1/2} = A (hv - Eg) \]  

(2)

where \( a \), \( v \), Eg, and A are the absorption coefficient, frequency of vibration, band gap and proportional constant, respectively.

Photocatalytic activity

The photocatalytic performance of the photocatalysts was evaluated in the degradation of Diuron under simulated solar light and visible irradiation. The photocatalytic reactions were conducted in an open photoreactor at ambient temperature, Figure 2. The light source was a vapor xenon lamp (500 < \( \lambda \) < 800 nm, 1,500 W air-cooled xenon lamp). For visible light measurements, all the experimental parameters were the same except for the fact that the UV part of the light was cut by means of a 3 mm thick GG420 filter (Schott) placed on the photoreactor. The distance between the lamp and the reactor was 18 cm. The synthesized W-doped TiO\(_2\) catalyst (C = 0.5 g/L) was suspended in 300 mL of Diuron (C\(_{\text{Diuron}}\) = 10 mg/L) aqueous solution under a reaction container (volume: 400 mL). Before the photoreaction, the suspension was stirred in the dark for 30 min in order to reach the adsorption equilibrium. During the irradiation procedure 3 mL of the solution was taken from the reactor at regular intervals and filtered (Whatman, 0.45 μm) to remove the photocatalyst. The concentration of the remaining liquid was analyzed with a LIBRA S12 UV–vis spectrophotometer at \( \lambda_{\text{max}} \) (248 nm).

The degradation activity can be calculated using Equation (3) (Matos et al. 1998).

\[ \text{degradation efficiency (\%)} = 100\% \times \frac{(C_0 - C_t)}{C_0} \]  

(3)

where \( C_0 \) is the initial concentration of Diuron before simulated solar light or visible light irradiation, and \( C_t \) is the concentration of Diuron remaining in the solution at certain reaction time ‘t’ (min).

It is possible to measure also the by-products that absorb at 248 nm in addition to Diuron with UV spectrophotometry, but in unpublished work, we verified by high-performance liquid chromatography that these by-products are negligible (at 248 nm).

RESULTS AND DISCUSSION

Photocatalyst characterization

XDR diffraction

The XRD patterns of prepared samples are shown in Figure 3. It may be noted from these results that the anatase phase, which is the desired phase for photocatalytic applications, is predominant in all samples. The sample without and with low W-content equal to 3 wt% show a peak at 2θ = 31° indicating the presence of brookite crystalline phase and it disappears at high concentration of W equal to 20 and 40 wt%. This result supports the theory which stipulated that tungsten inhibited the transformation of anatase phase (Riboni et al. 2015). Otherwise, no additional WO\(_3\) phase is observed, which suggests that W is incorporated into the TiO\(_2\) matrix. The broad diffraction peaks of the anatase
phase indicate that the crystallite had small sizes. Fitting to the Scherrer equation of the widths of the (101) reflections at $2\theta = 25–26^\circ$ resulted in 7–11 nm for the crystallite size.

Raman spectra

The Raman spectra shown in Figure 4 confirmed the phase identification by XRD. Four Raman bands appear at 144, 399, 510 and 643 cm$^{-1}$, corresponding respectively to peaks of anatase modes related to Eg, B1g, A1g and Eg (Yang et al. 2005). For $W_xTi_{1-x}O_2$ samples with W loading of 5 and 20 wt%, no new Raman band appears except for those characteristic peaks of anatase. This indicates that the tungsten species are highly dispersed into the titania crystal lattice matrix. When, the W loading increases to 40 wt%, a band appears in the Raman spectrum at 810 cm$^{-1}$, which is assigned to the stretching vibration mode of W–O bonds and deformation vibration mode of W–O–W bonds (Figure 4(b)) (Lethy et al. 2008).

To better see the brookite phase, as found by XRD, we selected the range between 200 and 400 cm$^{-1}$, characteristic of brookite (Figure 4(c)). Indeed, for samples corresponding to the uncharged TiO$_2$ and TiO$_2$ loaded at 3 wt%, there is the presence of three peaks at 247, 323 and 366 cm$^{-1}$,
which correspond to modes A1 g, B1 g and B2 g of brookite (Tompsett et al. 1995). Then, these peaks disappear for higher contents than 3%, which confirms that the presence of W inhibits the formation of brookite.

**Optical properties**

The UV–vis diffuse reflectance spectra of the synthesized TiO$_2$ and W$_x$Ti$_{1-x}$ O$_2$ are shown in Figure 5.

According to UV–vis spectral data, it can be seen that W$_x$Ti$_{1-x}$O$_2$ composites absorb more in the visible light region than that does TiO$_2$ sol–gel. The incorporation of W extended the capacity of TiO$_2$ to respond to higher wavelengths. Regarding the Eg values, there was a visible-shift in the absorption edge for W$_{0.03}$Ti$_{0.97}$O$_2$ (Eg = 2.95 eV), W$_{0.2}$Ti$_{0.8}$O$_2$ (Eg = 2.82 eV) and W$_{0.4}$Ti$_{0.6}$O$_2$ (Eg = 2.73 eV) compared to the TiO$_2$ (Eg = 3.12 eV). The obtained results are in accordance with those obtained by some other authors (Kwon et al. 2000; Iliev et al. 2010) showing that the shift in the absorption of the W$_x$Ti$_{1-x}$O$_2$ systems depends on the preparation method of the photocatalyst composites, the composition of the precursors, and the conditions of the thermal treatment of the samples (Tompsett et al. 1995), and when we introduced the W in TiO$_2$, the creation of defect energy levels within the forbidden band gap of WO$_3$ and TiO$_2$ decreased the total band gap of the W$_x$Ti$_{1-x}$O$_2$ catalyst during the calcination process (Yang et al. 2013).

**Photocatalytic activity**

The photocatalyst samples were evaluated for the degradation of Diuron in aqueous solution under simulated solar light and visible light ($\lambda > 420$ nm) irradiation at room temperature.

Figure 6 shows better activity for the degradation of Diuron under both visible and simulated solar light for the catalyst with 3 wt%. Under simulated solar light, this catalyst has a degradation of almost 100% after 60 min of irradiation while the composites with W contents of 20 and 40 wt% shows up to 85 and 70% photocatalytic degradation. When tungsten is introduced into anatase, once optical excitation takes place, the photogenerated electrons are transferred to the lower conduction band of tungsten, while the positive holes move toward the valence band of titania, with a consequent increase of charge separation efficiency and, therefore, an improved photocatalytic activity (Bayati et al. 2011). During the same time, the W$_x$Ti$_{1-x}$O$_3$ photocatalyst shows red-shift in the absorption wavelength range compared to pure TiO$_2$. There is an optimum load in tungsten after this optimum; we observe a decrease of
photocatalytic efficiency. High tungsten content leads to abundant defects as trapping centers in the oxide structure, so that photogenerated charge carriers recombine more easily. By increasing the amount of W to 20.0 wt% and higher, the adsorption of Diuron increases so that it perhaps makes certain oxidation sites deactivate, or target molecules could be retarded with too much WO₃ coupling (Tennakone et al. 1992; Tada et al. 2004). These results agree well with those obtained previously using sol–gel prepared powders (Yang et al. 2002). The W₀.₀₃Ti₀.₉₇O₂ showed far superior activity as compared to pure TiO₂ due to the presence of doped W(VI) and efficient charge separation.

**Kinetic studies of photocatalytic degradation**

The photodegradation reaction kinetics of organic pollutants can be described by a classical Langmuir–Hinshelwood model. The photocatalytic reaction is simply described by Equation (4):

\[
\ln\left(\frac{C_0}{C_t}\right) = K_{app}t
\]

where C is the remaining concentration of Diuron in the solution at irradiation time ‘t’ and C₀ is the initial concentration at t = 0; k_{app} denotes the degradation rate constant. Figure 7 shows ln(\(C_0/C\)) as a function of irradiation times.

The reaction follows a first order kinetic because the graph of the relation ln(\(C_0/C\)) = f(t) is linear. The calculated apparent rate constant k_{app} values for TiO₂ and different catalysts in visible and simulated solar light are given in Table 1. The pseudo first order apparent rate constant (k_{app}) determined in our experiments is higher for the catalyst at 3 wt% W under simulated solar light and visible light. However under simulated solar light, TiO₂ charged with W at 20 and 40 wt% degrades more slowly than uncharged TiO₂, whereas under visible light, the TiO₂ photocatalyst is less active.

For comparison, it is clear that the rate constants for W₀.₀₃Ti₀.₉₇O₂ are higher than for TiO₂, by a factor of 2 under simulated solar light and up to 10 times higher under visible light. This result shows that the Diuron herbicide is quickly degraded in the presence of W₀.₀₃Ti₀.₉₇O₂.

**Table 1 | Apparent rate constant values for the degradation of Diuron over different catalysts in visible and simulated solar light**

<table>
<thead>
<tr>
<th>Photocatalyst samples</th>
<th>R² simulated solar light</th>
<th>k_{app} (min⁻¹) simulated solar light degradation</th>
<th>R² visible</th>
<th>k_{app} (min⁻¹) visible degradation</th>
<th>k_{vis}/k_{ssl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.980</td>
<td>0.0219</td>
<td>0.993</td>
<td>0.0012</td>
<td>0.055</td>
</tr>
<tr>
<td>W₀.₀₃Ti₀.₉₇O₂</td>
<td>0.968</td>
<td>0.0436</td>
<td>0.995</td>
<td>0.0119</td>
<td>0.273</td>
</tr>
<tr>
<td>W₀.₂Ti₀.₈O₂</td>
<td>0.986</td>
<td>0.0112</td>
<td>0.985</td>
<td>0.0059</td>
<td>0.527</td>
</tr>
<tr>
<td>W₀.₄Ti₀.₆O₂</td>
<td>0.985</td>
<td>0.0072</td>
<td>0.988</td>
<td>0.0041</td>
<td>0.057</td>
</tr>
</tbody>
</table>

Figure 7 | Kinetics of the photocatalytic degradation of Diuron over pure TiO₂ and different WₓTi₁₋ₓO₂ composites: (a) simulated solar light and (b) visible light–irradiation: pH (7), C 10 mg/L, T 25°C.
Recyclability studies

For an industrial application of photocatalysis for sustainable wastewater treatment process, the recycling of spent catalyst after reaction is a necessary condition. The results for re-use of photocatalyst are shown in Figure 8. After degradation of pollutants, the solid phase was separated from water, washed thoroughly with distilled water, dried and re-used for photodegradation of a fresh Diuron solution under the same conditions. The removal efficiency was determined after 90 min under simulated solar light and 4 h under visible light for each experiment. The degradation efficiency in simulated solar light and visible light of the W$_{0.03}$Ti$_{0.97}$O$_2$ catalyst for four consecutive cycles was in the range 92–99% and 83–92%, respectively. The sample of W$_{0.03}$Ti$_{0.97}$O$_2$ showed no significant change in these conditions. This shows that the catalyst has a good stability during the photocatalytic decomposition of Diuron. Hence, the photocatalytic degradation using W$_{0.03}$Ti$_{0.97}$O$_2$ in simulated solar light and visible light is a good alternative method for treating water containing pesticides pollutants.

CONCLUSIONS

W$_x$Ti$_{1-x}$O$_2$ catalysts with different W loading contents have been successfully synthesized via the sol–gel method. Photocatalytic activities of these composites were evaluated using Diuron pesticide as a model contaminant. The W species were completely dispersed into the titania matrix, and the crystalline WO$_3$ phase was not detected with the XRD and Raman spectroscopy even for the W loading as high as 20 wt%. These experiments showed that optimizing the addition of tungsten into titania can inhibit the formation of the others phases as brookite. W-loaded TiO$_2$ can shift the light absorption band from near UV to the visible region. The TiO$_2$ loaded with 3% of W exhibited better photoactivity as compared to pure TiO$_2$ in the degradation of Diuron in simulated solar light and visible light. However, excess content of W in TiO$_2$ (20 and 40 wt%), lowered the separation efficiency of electrons and holes, reducing the photocatalytic reactivity and the destruction efficiency against the pesticide molecule. W$_{0.03}$Ti$_{0.97}$O$_2$ photocatalyst also showed good stability against the photodegradation and it could be recycled at least four times without significant loss of its activity.

REFERENCES


Khan, M., Cao, W., Chen, N., Usman, Z., Khan, D. F., Toufiq, A. M. & Khaskheli, M. A. 2013 Influence of tungsten doping


