Photocatalytic degradation of rhodamine B, paracetamol and diclofenac sodium by supported titania-based catalysts from petrochemical residue: effect of doping with magnesium

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ABSTRACT

Three different lots of a residual Ziegler-Natta catalyst slurry (bearing Ti and Mg) obtained from an industrial petrochemical plant were employed as sources for the photocatalyst supported on silica. The effect of additional magnesium (1.0–25.0 wt% Mg/SiO₂) on the photocatalytic properties of the doped materials was investigated. Doping the titania-based photocatalyst with Mg results in a shift in the absorption threshold toward the visible spectrum. The optical band gap energy of the bare supported photocatalyst was in the range of 2.5 eV and shifted to 1.72 eV after 25 wt% Mg doping. The systems were evaluated for the photodegradation of one dye (rhodamine B (RhB)) and two drugs (paracetamol and diclofenac sodium) either under ultraviolet (UV) (365 nm – UVA) or visible radiation, separately. Among the evaluated systems, doping with 25 wt% Mg afforded the highest degradation values for the target molecules under UV and visible radiation (i.e. 87%, 60% and 55% of the RhB, paracetamol and diclofenac under UV, respectively, and 82%, 48.3% and 48% under visible irradiation, respectively).

Key words | drugs, dyes, industrial residue, magnesium doping, photocatalyst

INTRODUCTION

Industrial discharge of organic contaminants plays an important role in river pollution. Many industrial organic contaminants continue to be discharged undetected and uncontrolled. The variety of organic compounds that are industrially synthesized is enormous (Dzikowitzky et al. 2013). The number of byproducts, educts and intermediates, which might be performed during the synthesis of these regularly used chemicals, is unknown. The industrial wastewater constituents are discharged into aquatic systems and may pose a threat to aquatic organisms (Rovani et al. 2014; Trujillo-Reyes et al. 2014). In general, two strategies are employed for waste minimization including source reduction and recycling. Using recycling as an approach to reduce the effect of the disposal of catalytic residues, some alternative methods have been studied to minimize this problem including the incorporation of petrochemical residue in cement (Trujillo-Reyes et al. 2014) and the potential use of catalytic residue to provide better properties for cement (i.e. better resistance to corrosion) (Payá et al. 2009). Additional attempts to find alternative uses for industrial wastes have been reported in the literature and include silica materials recovered from photonic industrial waste (Lin et al. 2011), supported photocatalysts prepared from agroindustrial and industrial wastes (Da Silva et al. 2014; Da Silva et al. 2016) and sorbents prepared from industrial waste materials (Bhatnagar & Silanpää 2010; Bilal et al. 2015).

Advanced oxidation processes (AOPs) have received much interest in recent years as complementary methods to the conventional water treatment approach or as alternative treatment strategies for industrial wastewater (Yang et al. 2010; Xekoukoulaki et al. 2011). One of the AOP methods that can be useful for organic pollutant oxidation is heterogeneous photocatalysis. This method employs the
photoinduced charge separation of electrons and holes, which can react with water or oxygen to form reactive oxygen species (i.e. predominantly hydroxyl radicals). The high oxidizing potential of hydroxyl radicals allows mineralization of most of the low molecular weight organic molecules. Such a method has been applied in the degradation of dyes and pharmaceuticals, such as paracetamol (Moctezuma et al. 2012; Da Silva et al. 2015), diclofenac sodium (Ratola et al. 2012; Deng et al. 2013; Bagal & Gogate 2014; Tiwari 2015) and rhodamine B (RhB) (Da Silva et al. 2014; Ji et al. 2015; Li et al. 2015).

The ideal photocatalyst for heterogeneous photocatalysis should have unique electronic and optical properties with high physical and chemical stability and be inexpensive and non-toxic (Wu et al. 2012). However, some drawbacks of photocatalysts, such as a wide band gap energy and high rate of electron–hole recombination, restricts their practical applications to use with ultraviolet (UV) irradiation (Xu et al. 2010; Liu et al. 2015). Therefore, many studies have focused on extending the optical absorption edge of photocatalysts from the UV region to the visible light region and decreasing the electron–hole recombination rate. A prominent approach to overcome these limitations involves altering the band gap energy via doping with metals (e.g. Cu, Fe, Zn, Co, Mg and Al) and non-metals (e.g. N and Cl) (Doong et al. 2009; García-Serrano et al. 2009; Long et al. 2009; Wu et al. 2010; Han et al. 2011; Lin et al. 2011a, 2011b; Liu et al. 2011a, 2011b; Zhang et al. 2012; Abed et al. 2015).

Magnesium possesses some interesting features, such as being non-toxic, cheaper than many other metals and recyclable, and its metallurgy is simple. Therefore, Mg-based materials have received considerable attention (Vadivel & Rajarajan 2015). Among these materials, Mg-doped n-type semiconducting oxide materials are particularly interesting because they have the potential for applications in nanoscale electronics, optoelectronics, biochemical sensing and photocatalysis. Moreover, the ionic radius of Mg (approximately 160 pm) is comparable to that of Ti (approximately 140 pm). Therefore, Mg doping can be predictably substituted into the Ti host lattice, which results in a decrease in the band gap energy. This property can be expected to increase the photocatalytic performance (Chen et al. 2015a, 2015b; Vadivel & Rajarajan 2015). In the current study, we prepared photocatalysts doped with Mg from a catalyst prepared from petrochemical residue (rich in Ti and Mg, residues of a supported polymerization Ziegler-Natta catalyst) and investigated the role of the Mg dopant in the photocatalytic degradation of two drugs (paracetamol and diclofenac sodium) and one dye (RhB) in aqueous solutions.

EXPERIMENTAL

Materials

Three lots of a residual Ziegler-Natta catalyst slurry (Ti-based polymerization catalyst obtained after their disposal) from a petrochemical plant were employed as the source of the photocatalyst. Fumed silica (Wacker HDKN20) was used as the support (agglomerate particle size d50 mean >50 μm, surface area 272 m2/g, pore diameter 20.1 nm, pore volume 1.50 cm3/g). RhB (Prótón Química), diclofenac sodium (Multilab®) and paracetamol (Multilab®) were used in the photocatalytic tests. Double distilled deionized water was used for preparation of the solutions used in the catalytic tests. MgCl2 (Synth) was used for preparation of the doped photocatalysts.

Synthesis and characterization of photocatalysts

Three millilitres of the industrial residue were added to 1.0 g of silica and stirred for 90 min. Then, the solution was placed in a muffle furnace for 4 h for calcination (450 °C). Three different lots were used from the petrochemical plant for the preparation of the supported photocatalysts: SiTi, SiTi® and SiTi®®.

Four photocatalysts doped with magnesium chloride were prepared according to a previously published procedure with modification (Chen et al. 2015a, 2015b). For the doping of Mg, aqueous solutions were prepared by mixing the photocatalyst with magnesium at concentrations of 1 wt%, 2 wt%, 10 wt%, and 25 wt% relative to Mg/SiO2. The prepared Mg-doped SiTi photocatalysts are referred to as x Mg-SiTi, where x refers to the weight percentage of Mg.

The specific surface area, pore diameter and pore volume of the samples were calculated from nitrogen measurements performed on Micromeritics Gemini 2375 equipment. Zeta potential (ZP) was determined on equipment brand Malvern Zetasizer® nanoZS-style. The analyses were performed at the small angle X-ray scattering (SAXS) line D11A at the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil) using the routine evaluation Irena (Ilavsky & Jemian 2009) implemented in Igor Pro (WaveMetrics, Portland, USA) software (Kline 2006). A multi-level unified fit was used to describe one or two levels of structural organization from the scattering
data (Beaucage 1996; Beaucage et al. 2004; Kammler et al. 2005). UV-Vis spectra were recorded by using a Varian Cary 100 Scan Spectrophotometer with an accessory DRA-CA 301 (Labsphere) in the diffuse reflectance mode to determine the energy band gap by means of the Kubelka-Munk function. X-ray photoelectron spectroscopy (XPS) measurements were undertaken using a KRATOS XSAM 800 equipped with an energy analyser. The X-ray source employed was an Al Ka X-ray source (hν 1,486 eV) generated from an aluminum anode operating at an emission voltage of 15 keV and 5 mA. All spectra were referenced by setting the hydrocarbon C 1s peak to 285.0 eV to compensate for residual charging effects. X-ray diffraction (XRD) analyses were performed on a Rigaku DMAX 2200 diffractometer equipped with a Cu tube and secondary monochromator, theta-theta Ultima goniometer and scintillation [NaI(Tl)] detector.

Photocatalytic degradation of RhB, diclofenac sodium and paracetamol

For the photocatalyst tests, the solutions containing the target molecule were prepared by dissolving the powder in distilled water. All solutions were prepared at a concentration of 20 mg L\(^{-1}\). The photocatalytic activity tests were performed in a 50 mL reactor that was immersed in a water bath at 30 °C. The visible light source was a mercury vapor lamp (125 W). A similar UV lamp was employed but with a different bulb. For the tests, a catalyst concentration of 0.7 g L\(^{-1}\) was added to 25 mL of the target molecule (20 mg L\(^{-1}\)) at the natural pH (ca. 4.3) of the reaction medium. The concentrations of the solutions were determined on a Varian Cary 100 spectrophotometer at the wavelength of maximum absorbance of the target molecule (i.e. 553 nm for RhB, 276 nm for diclofenac and 243 nm for paracetamol). The radiation was adjusted to 202 W m\(^{-2}\) for visible radiation (Pyranometer Type SL 100, Skilltech Instruments) and 30 W m\(^{-2}\) (Radiometer Series 9811, Cole-Parmer Instrument) for UV radiation. The suspension was initially maintained in the dark to reach adsorption equilibrium (ca. 60 min). Then, the suspension was exposed to radiation for 1 h with visible light. A polycarbonate filter was used to spread the radiation below 385 nm.

The calibration curves (\(N = 7\)) were obtained by dilution of a stock solution of each tested organic molecule. The reproducibility was verified by repeating the measurements at least twice, and the relative standard deviation was within 5%.

Photodegradation kinetics

Kinetics interpretations were conducted as a function of the remaining concentration of phenol in solution over time. Data were fitted as a kinetic model of Langmuir-Hinshelwood (Konstantinou & Albanis 2004; Gogate & Pandit 2004; Herrmann 2005), according to Equation (1):

\[
- r_t = \frac{dC_i}{dt} = \kappa_s \cdot K \cdot C_i (1)
\]

where \(\kappa_s\) is the true photodegradation rate of the organic compound, \(C_i\) is the concentration of the compound, \(t\) is the illumination time, and \(K\) is the adsorption coefficient of the compound to be degraded. \(\kappa_s\) is related to several parameters such as mass of catalyst, efficient photon flow and layer of oxygen. The L–H model can be simplified to a pseudo-first-order kinetic equation and \(\kappa\) is the apparent rate of the pseudo-first-order reaction, according to Equations (2) and (3) (Konstantinou & Albanis 2004):

\[
\ln \left( \frac{C_{io}}{C_t} \right) = \kappa_s \cdot K \cdot t = \kappa \cdot t \quad \text{or} \quad C_t = C_{io} \cdot e^{-\kappa t} (3)
\]

The pseudo-first-order reaction rate constant was determined from the slope of the linear regression of \(\ln(C_{io}/C_t)\) versus time.

RESULTS AND DISCUSSION

Catalyst characterization

The elemental analysis of the three resulting supported photocatalysts was carried out using XPS, and the results are shown Table 1. This technique provides the composition of the external surface of the catalyst grain. Because photocatalyst degradation involves interactions on the surface of the catalyst, we chose this technique because it provides elemental analysis of the surface but not the catalyst bulk, which can be achieved by other atomic spectroscopic techniques, such as atomic absorption spectroscopy or inductively coupled plasma optical emission spectroscopy, after acid digestion of the samples. As shown in Table 1, the peaks mainly consist of Ti 2p, Si 2p and Mg 1s. Figure 1 shows a typical high resolution XPS spectrum in the Ti 2p
According to Table 1, the SiTi, SiTi* and SiTi** samples had a Ti/Mg atomic ratio of 0.3, 0.25 and 0.27, respectively. The average Ti/Mg was 0.27 ± 0.03, indicating that there is little variation among the three residue lots. Moreover, the Ti 2p3/2 and 2p1/2 spin-orbital splitting photoelectrons for TiO2 are located at binding energies of 459.1 and 464.9 eV, respectively. This result indicates that the Ti elements primarily existed as Ti4⁺ (Erdem et al. 2001), and the 1,303.98 eV Mg 1s peak results from Mg-O bonding, indicating that the Mg element may replace the Ti site in the SiO2 lattice (Li et al. 2003). Moreover, the commercial catalyst (TiO2) exhibited a Ti 2p3/2 peak, which was assigned to an oxidation state +4 for Ti (Yu et al. 2001; Liu et al. 2002). The observed positive shift of 0.81, 1.31 and 1.03 eV in the binding energy of Ti 2p3/2 for SiTi (from 459.71 to 458.90 eV), SiTi* (from 460.21 to 458.90 eV) and SiTi** (from 459.93 to 458.90 eV), compared to TiO2 may be due to titania (Ti4⁺) and/or magnesium (Mg2+) incorporation into the SiO2 lattice (Grigorova et al. 2013; Sui et al. 2015). These results indicate that Ti moieties are more cationic than those of commercial Ti. Moreover, the full width at half maximum (FWHM) of the prepared supported photocatalysts are larger than that of commercial TiO2, suggesting an increased heterogeneity of the generated supported species.

The catalytic activity of the particle samples is also proportional to their specific surface area because this arrangement requires the adsorption of reactants and the transfer of photoexcited electrons into the adsorbed molecules (Bayal & Jeevanandam 2013). Among the essential properties of a photocatalyst, the electronic (band gap

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### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak designation</th>
<th>Binding energy (eV) Ti/Si</th>
<th>Ti/Mg</th>
<th>Mg/Si</th>
<th>FWHM* (eV)</th>
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<td>TiO2</td>
<td>Ti 2p3/2</td>
<td>459.90</td>
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<td>–</td>
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<tr>
<td>SiTi</td>
<td>Mg 1s</td>
<td>1,303.98</td>
<td>–</td>
<td>0.65</td>
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<tr>
<td></td>
<td>Si 2p</td>
<td>101.0</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td></td>
<td>Ti 2p3/2</td>
<td>459.71</td>
<td>0.19</td>
<td>0.30</td>
<td>3.5</td>
</tr>
<tr>
<td>SiTi*</td>
<td>Mg 1s</td>
<td>1,303.98</td>
<td>–</td>
<td>0.49</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>Si 2p</td>
<td>101.3</td>
<td>–</td>
<td>–</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Ti 2p3/2</td>
<td>460.21</td>
<td>0.12</td>
<td>0.25</td>
<td>3.4</td>
</tr>
<tr>
<td>SiTi**</td>
<td>Mg 1s</td>
<td>1,303.98</td>
<td>–</td>
<td>0.57</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Si 2p</td>
<td>101.5</td>
<td>–</td>
<td>–</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Ti 2p3/2</td>
<td>459.93</td>
<td>0.15</td>
<td>0.27</td>
<td>3.2</td>
</tr>
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</table>

*Full width at half maximum intensity.

---

### Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degussa P25</th>
<th>SiO2</th>
<th>SiTi</th>
<th>SiTi*</th>
<th>SiTi**</th>
<th>1 Mg - SiTi</th>
<th>2 Mg - SiTi</th>
<th>10 Mg - SiTi</th>
<th>25 Mg - SiTi</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBET (m² g⁻¹)</td>
<td>56</td>
<td>272</td>
<td>280</td>
<td>265</td>
<td>272</td>
<td>292</td>
<td>294</td>
<td>304</td>
<td>382</td>
</tr>
<tr>
<td>Dp (nm)</td>
<td>4.8</td>
<td>20.1</td>
<td>20.1</td>
<td>17.6</td>
<td>19.2</td>
<td>20.1</td>
<td>19.8</td>
<td>18.5</td>
<td>16.8</td>
</tr>
<tr>
<td>Vp (cm³ g⁻¹)</td>
<td>0.07</td>
<td>1.5</td>
<td>1.95</td>
<td>1.67</td>
<td>1.82</td>
<td>0.45</td>
<td>0.23</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>λ (nm)</td>
<td>371.2</td>
<td>136.3</td>
<td>696.6</td>
<td>407.9</td>
<td>486.3</td>
<td>696.6</td>
<td>700.56</td>
<td>708.57</td>
<td>720.93</td>
</tr>
<tr>
<td>Εg (eV)</td>
<td>3.54</td>
<td>9.1</td>
<td>1.78</td>
<td>3.04</td>
<td>2.55</td>
<td>1.78</td>
<td>1.77</td>
<td>1.75</td>
<td>1.72</td>
</tr>
<tr>
<td>ζ (mV)</td>
<td>–3.6</td>
<td>–24</td>
<td>–36.4</td>
<td>–27.8</td>
<td>–30.7</td>
<td>–16.4</td>
<td>–16.7</td>
<td>–20.2</td>
<td>–22.3</td>
</tr>
<tr>
<td>Rg1 (nm)</td>
<td>0.33</td>
<td>6.67</td>
<td>2.75</td>
<td>0.66</td>
<td>0.83</td>
<td>0.49</td>
<td>0.39</td>
<td>0.33</td>
<td>0.23</td>
</tr>
<tr>
<td>Rg2 (nm)</td>
<td>0.43</td>
<td>9.54</td>
<td>8.55</td>
<td>5.95</td>
<td>6.26</td>
<td>7.53</td>
<td>11.60</td>
<td>14.30</td>
<td>7.30</td>
</tr>
<tr>
<td>α</td>
<td>4.00</td>
<td>3.73</td>
<td>3.95</td>
<td>2.24</td>
<td>2.03</td>
<td>3.40</td>
<td>3.34</td>
<td>3.04</td>
<td>3.72</td>
</tr>
</tbody>
</table>

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Figure 1 | Typical high resolution XPS spectrum in the Ti 2p region of the sample SiTi.

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region and for the sake of simplicity, the data for the Ti 2p3/2 signal is provided.

According to Table 1, the SiTi, SiTi* and SiTi** samples had a Ti/Mg atomic ratio of the 0.3, 0.25 and 0.27, respectively. The average Ti/Mg was 0.27 ± 0.03, indicating that there is little variation among the three residue lots. Moreover, the Ti 2p3/2 and 2p1/2 spin-orbital splitting photoelectrons for TiO2 are located at binding energies of 459.1 and 464.9 eV, respectively. This result indicates that the Ti elements primarily existed as Ti4⁺ (Erdem et al. 2001), and the 1,303.98 eV Mg 1s peak results from Mg-O bonding, indicating that the Mg element may replace the Ti site in the SiO2 lattice (Li et al. 2003). Moreover, the commercial catalyst (TiO2) exhibited a Ti 2p3/2 peak, which was assigned to an oxidation state +4 for Ti (Yu et al. 2001; Liu et al. 2002). The observed positive shift of 0.81, 1.31 and 1.03 eV in the binding energy of Ti 2p3/2 for SiTi (from 459.71 to 458.90 eV), SiTi* (from 460.21 to 458.90 eV) and SiTi** (from 459.93 to 458.90 eV), compared to TiO2 may be due to titania (Ti4⁺) and/or magnesium (Mg2+) incorporation into the SiO2 lattice (Grigorova et al. 2013; Sui et al. 2015). These results indicate that Ti moieties are more cationic than those of commercial Ti. Moreover, the full width at half maximum (FWHM) of the prepared supported photocatalysts are larger than that of commercial TiO2, suggesting an increased heterogeneity of the generated supported species.

The catalytic activity of the particle samples is also proportional to their specific surface area because this arrangement requires the adsorption of reactants and the transfer of photoexcited electrons into the adsorbed molecules (Bayal & Jeevanandam 2013). Among the essential properties of a photocatalyst, the electronic (band gap
energy, efficiency of charge separation) and physical (surface area, pore volume, morphology, crystallinity) properties must be considered (Liu et al. 2011a, 2011b, 2011c). Table 2 shows the surface area ($S_{\text{BET}}$), pore diameter ($D_p$), pore volume ($V_p$), band gap energy ($E_g$), zeta potential ($\zeta$) and SAXS parameters of the prepared catalysts. For comparison, the results of the TiO$_2$ and SiO$_2$ were also determined.

According to Table 2, the specific surface area of SiTi was larger than that of the other samples prepared with different lots of the petrochemical residue. Nevertheless, the atom density is roughly similar among the three supported systems (i.e. 0.322 (SiTi), 0.288 (SiTi*) and 0.307 (SiTi**) Ti atoms nm$^{-2}$, respectively (mean 0.306 ± 0.02)).

Regarding the photocatalyst doped with magnesium, the 25 Mg-SiTi sample exhibited the highest surface area of the doped photocatalysts and TiO$_2$. The difference in their surface area was due to the synergetic effect among the components, such as MgO (Avasarala et al. 2011; Abed et al. 2015). The increase in the surface area was significant. Therefore, the larger surface area of 25 Mg-SiTi may be beneficial to the spatial separation of redox sites on the surface, which may enhance the electron transfer properties of the photocatalysts (Sharma & Jeevanandam 2012; Veréb et al. 2012; Pozan & Kambur 2013). Furthermore, the isotherms are type IV with H3 hysteresis curves (not shown) according to the classification of Brunauer, Deming, Deming, and Teller, and the pore diameter distribution suggests mesoporous structures (2–50 nm).

The energy band gap ($E_g$) is a relevant parameter for photocatalytic processes because for a smaller $E_g$, less radiation energy is required for activation of the process, which in turn may reach into the visible light region. Furthermore, $E_g$, which can be calculated by the extrapolation method, is the tangent of the steep absorption curve that intercepts the abscissa (wavelength) axis. The optical band gaps of both photocatalysts prepared with different lots of petrochemical residue as well as the samples doped with magnesium were determined using the following formula (Ren et al. 2010; Zhang et al. 2010).

$$E_g(eV) = \frac{1.240}{\lambda_g}$$  \hspace{1cm} (4)

where ‘$\lambda_g$’ is the wavelength of the intercept. The optical band gap values of the photocatalysts prepared ranged from 1.72 to 1.78 eV (Table 2). All the Mg–SiTi samples exhibited a band gap adsorption edge at 700–721 nm, which provides adsorption in the visible region. Moreover, as the Mg content increased, the Mg–SiTi samples exhibited enhanced light absorption in the visible range, which may be due to the transition of the excitation of the 2p electrons from the Mg$^{2+}$ ions to the conduction band of SiTi (Boltersdorf et al. 2015). The observed enhanced visible light absorbance is expected to considerably increase the utilization of visible light for photocatalytic reactions. Moreover, oxygen vacancies and electron concentration increase with magnesium doping, leading to infiltration of the Fermi level (Anilkumar et al. 2015) into the conduction band of the degenerate semiconductor causing a decrease in the polarization of its neighboring O$^{2–}$ ion. This decrease leads to a shift in the conduction band and valence band levels to the same degree in relation to the oxygen vacancy level, providing a reduction in the energy band gap of the catalyst (Vadivel & Rajarajan 2015), as shown in Figure 2.

Measurement of the zeta potential is also an important tool for evaluating the surface charge distribution and stability of photocatalysts because compatibility between the surface potential and the charge of the molecule to be degraded may improve the photocatalytic activity (Gaya & Abdullah 2008). The zeta potential ($\zeta$) of the photocatalysts is listed in Table 2. The SiTi, SiTi* and SiTi** particles exhibited a negative surface potential that ranged from –27.8 to –56.4 mV. However, the samples doped with magnesium have a less negative to positive surface potential, confirming that the surface doped with MgCl$_2$ is beneficial to the surface charge. Moreover, RhB, paracetamol and diclofenac sodium are characterized by their cationic nature, and the compatibility between the surface potential

![Figure 2](https://iwaponline.com/wst/article-pdf/74/10/2370/457041/wst074102370.pdf)
of the photocatalyst and the charge of the molecule to be degraded can improve the photocatalytic activity (González-Rodríguez et al. 2002; Chatchawalsaisin et al. 2004; Bertram & Bodmeier 2006).

The samples were further analyzed by SAXS, which provides structural information (i.e. a broader and clearer view of support and photocatalyst formation and aggregation) (Stoeckel et al. 2014; Chen et al. 2015a, 2015b). The multi-hierarchical organization of these materials as well as their particle radius (Rp), shape, fractal structure (α) and topography were investigated through the Unified approach in the Guinier and Power-law regions. By analyzing Level 1, which is located in a q region greater than 4 nm\(^{-1}\), the radius of gyration (Rg) of the primary particles can be determined. Level 2, which is located in a q region between 0.2 and 4 nm\(^{-1}\), can be used to determine the radius of gyration (Rg) of the secondary particles. Level 3, which is located in a q region below 0.2 nm\(^{-1}\), provides information on the organization of these particles (i.e. the structure of the fractal clusters (secondary particles) resulting from aggregation of primary particles) (Fouilloux et al. 2010). The structure of the clusters of the primary particles that constitute Level 3 can be obtained by analyzing the power law exponent (α) of the scattering curve. When the exponent of the power law is between 1.0 and 3.0, the particles have a dense core and a uniform surface (Adán et al. 2007). In the current study, the SAXS curves for all the systems revealed the presence of three distinct organizational levels. The results obtained from the unified set of SAXS curves for the prepared photocatalyst samples are provided in Table 2.

As shown in Table 2, taking into account Level 1, a decrease in the Rg of the commercial silica particles was observed after catalyst preparation, and this result was independent of the petrochemical residue lot that was used. The Rg of the primary particles of the photocatalysts ranged between 0.23 and 2.75 nm. The highest value of Rg (2.75 nm) was observed for SiTi, and the lowest value (0.23 nm) was observed for 25 Mg-SiTi. By comparing Level 3, a decrease was observed in α after catalyst preparation (with the exception of SiTi) compared to commercial silica, suggesting that a more ramified system has been formed. Regarding the organization of particles in terms of α, values between 2.03 and 3.95 were observed. For SiTi\(^{=}\) and SiTi\(^{==}\), the formation of particles with less condensed structures (mass fractals) was observed because the α values were between 2.03 and 2.24. For the SiTi and doped photocatalysts, the formation of particles with characteristics of a fractal surface was observed because the α values were between 3.04 and 3.95. This reduction in the particle size may lead to a larger surface area, which would increase the available surface area of the active sites (Shi et al. 2006).

### Photocatalytic activity of the photocatalysts prepared from different lots of petrochemical residue

Figure 3 shows the photocatalytic performance of the samples SiTi, SiTi\(^{=}\) and SiTi\(^{==}\) for the photodegradation of RhB and two drugs (paracetamol and diclofenac) under UV radiation.

According to Figure 3, SiTi exhibited better photocatalytic activity than the two other supported photocatalysts for the degradation of the respective target molecules. To study the effect of the Mg-doping concentration on the photocatalytic property of the photocatalyst prepared from petrochemical residue, the photocatalytic property of the photocatalyst prepared from the first lot of petrochemical residue (SiTi) was further studied, and the results are discussed in the following section which follows.

### Photocatalytic activity of the photocatalysts doped with magnesium

The photocatalytic activities of the composites were further investigated after addition of an external Mg source. For comparison, the photocatalytic activities of Mg–SiTi and the as-prepared SiTi were conducted under the same conditions. As shown in Figure 4, the Mg–SiTi samples exhibited higher photocatalytic activity than the undoped photocatalyst. Among the doped photocatalysts, 25 Mg–SiTi exhibited the best performance. After 60 min of irradiation, conversion ratios of 87% for RhB, 60% for paracetamol and 55% for diclofenac were observed under UV radiation. The efficiency of photodegradation decreased as the irradiation time increased. However, the percentage of degradation varied based on the dopant amount. For example, 50% RhB dye degradation was observed at 22.5, 28, 34 and 37.5 min for 25 Mg–SiTi, 10 Mg–SiTi, 2 Mg–SiTi and 1 Mg–SiTi, respectively.

Furthermore, few studies have reported the use of synthesized photocatalysts in the degradation of paracetamol and diclofenac sodium by heterogeneous photocatalysis (Da Silva et al. 2015). In general, TiO\(_2\) is used as a catalyst, and a high concentration of catalyst is required. In addition, considerable irradiation time and intensity of light are also
Figure 3 | Photocatalytic degradation of RhB (a), paracetamol (b) and diclofenac sodium (c) by SiTi, SiTi* and SiTi** under UV irradiation after 60 min of reaction ($C_{\text{Catalyst}} = 0.70 \text{ g L}^{-1}$, $C_{\text{Solution}} = 20 \text{ mg L}^{-1}$, $T = 30 \text{ °C}$, natural pH, UV radiation of $30 \text{ W m}^{-2}$, SD = 5%).

Figure 4 | Photocatalytic degradation of RhB (a), paracetamol (b) and diclofenac sodium (c) by SiTi, 1 Mg-SiTi, 2 Mg-SiTi, 10 Mg-SiTi and 25 Mg-SiTi under UV irradiation after 60 min of reaction ($C_{\text{Catalyst}} = 0.70 \text{ g L}^{-1}$, $C_{\text{Solution}} = 20 \text{ mg L}^{-1}$, $T = 30 \text{ °C}$, natural pH, UV radiation of $30 \text{ W m}^{-2}$, SD = 5%).
necessary (Andrezzi et al. 2004; Perez-Estrada et al. 2005; Tungudomwongsa et al. 2006; Dalrymple et al. 2007; Borges et al. 2015). Moreover, we observed a direct relationship between the photodegradation (%) of the studied photocatalysts and the Ti/Mg atomic ratio as well as the binding energy (eV) and the degradation constant ($\kappa$).

According to Figure 5, the photocatalytic efficiency of the doped photocatalysts varies in the following order: 25 Mg–SiTi > 10 Mg–SiTi > 2 Mg–SiTi > 1 Mg–SiTi for all target molecules. For example, a direct correlation was identified between the photocatalytic activity (and degradation constant) of the photocatalysts prepared from different lots of industrial residue and the Ti/Mg atomic ratio under UV and visible radiation (Figures 6 and 7). The effect of external Mg addition on the crystallinity of the sample was further analyzed by XRD, and the diffractograms are shown in Figure 8.

According to Figure 8, both the bare and doped photocatalysts exhibited diffraction peaks at 25.23°, 37.72° and 62.51°, indicating the presence of the anatase phase of TiO$_2$. The peaks were indexed to a tetragonal-type structure with 141/amd symmetry (Horn et al. 1972), and the results are in good agreement with the standard Joint Committee for Powder Diffraction Standards (JCPDS) data (card no: 21-1272 – Anatase TiO$_2$). Moreover, all diffractograms exhibited a crystalline peak corresponding to periclase (MgO). It is important to note that the peak intensity decreased as the Mg concentration increased (0–25 wt%), which may be due to the substitution of Ti$^{4+}$ ions at the Mg$^{2+}$ ion lattice sites. The lattice parameters of anatase TiO$_2$ were estimated to be $a = b = 3.7842$ Å and $c = 9.5146$ Å. These values decreased to $a = b = 3.7209$ Å and $c = 9.5057$ Å after Mg doping (Table 3). The observed variation in the lattice parameters is consistent with the smaller radius of the Mg$^{2+}$ ion (72 pm) with respect to the Ti$^{4+}$ ion radius (88 pm) (Bayati et al. 2011; Miranda et al. 2014) and the small amount of Mg concentration used for doping. The average crystalline sizes of the Mg–SiTi photocatalysts were calculated using Scherrer’s equation (Parthibavarman et al. 2015).

$$d(\text{nm}) = \frac{K \lambda}{\beta \cos \theta}$$

where $d$ is the mean crystallite size, $K$ is the shape factor taken to be 0.89, $\lambda$ is the wavelength of the incident beam (0.1540 nm), $\beta$ is the full width at half maximum and $\theta$ is the Bragg angle. The average crystalline size of SiTi was determined to be 21 nm, which further decreased to 14.2 nm for the 25 wt% Mg doped SiTi photocatalysts. This result suggests that the grain growth is suppressed due to doping of Mg into the Ti sites.
Figure 6 | Correlations between the photodegradation (%) of RhB (a), paracetamol (b) and diclofenac (c) and the Ti/Mg atomic ratio under UV (square) and visible (triangle) radiation.
Figure 7  |  Correlations between the binding energy (eV) and the degradation constant (k) of RhB (a), paracetamol (b) and diclofenac (c) under UV (square) and visible (triangle) radiation.
Figure 9 shows the proposed effect of Mg as a dopant in the current titania-based photocatalysts. When Mg is doped into the catalyst, the Mg particles can act as electron traps to facilitate electron hole separation and subsequent transfer of the trapped electrons to the absorbed $O_2$, acting as an electron acceptor on the surface of the Mg–SiTi. Simultaneously, more RhB molecules are adsorbed on the surface of the Mg–SiTi photocatalysts, enhancing the photoexcited electron to the conduction band and increasing the electron transfer to the adsorbed $O_2$. Moreover, the smaller band gap energy due to the Mg dopant may play an additional role in enhancing the visible light photocatalytic activity of the SiTi catalysts. The same behavior occurs in the degradation of the paracetamol and diclofenac sodium drugs.

CONCLUSION

Doping Ti-based catalyst with an additional amount of Mg altered the structural, textural, optical and photocatalytic properties of Mg-SiTi samples compared to those of SiTi (starting photocatalyst). For instance, an increase of 36% and 33% in surface area and the zeta potential, respectively, and a decrease of 4% in the energy band gap was observed in the systems after Mg doping. Regarding the degradation of the pollutants, doping with Mg resulted in an increase of 30% and 33%, 51% and 72%, and 60% and 73% on the degradation RhB, paracetamol and diclofenac sodium under UV and visible radiation, respectively. Mg can act as a photosensitizer for photocatalysts prepared from petrochemical waste and perhaps may hinder the recombination of electron–hole pairs. The present results suggest that the support (from the Ziegler-Natta catalyst) here has a positive effect on the development of such titania-based catalysts. One possibility is that the sites of the SiTi lattice replaced by Mg may generate an intermediate energy gap between the valence and conduction bands of SiTi to promote the absorption of photons and create more electron–hole pairs. The Mg-doped SiTi photocatalysts are promising for practical use in pollutant decomposition as effective photocatalysts that are prepared from industrial waste.

ACKNOWLEDGEMENTS

The authors wish to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for financial support of this work. The authors
also wish to thank the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) for analysis of SAXS (Project SAXS1 - 16993) and the Braskem S.A. (Triunfo, Brazil) company for the petrochemical waste used in this study.

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First received 16 May 2016; accepted in revised form 21 July 2016. Available online 6 September 2016