Photocatalytic Removal of Eriochrome Black T Dye over ZnO Nanoparticles Doped with Pr, Ce or Eu

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Wastewaters coming from textile industries produce serious problems because they contain a lot of pollutants such as organic dyes. Heterogeneous photocatalysis is a promising and efficient approach to remove dye pollutants from wastewater. ZnO is an excellent and promising photocatalytic material to decompose organic pollutants by transforming them into CO₂ and H₂O. In order to enhance the photocatalytic activity, ZnO could be doped with metal and non-metal ions. In this work, the doping with chemical elements belonging to the lanthanide group, such as praseodymium (Pr), cerium (Ce) and europium (Eu) is reported. ZnO nanoparticles doped with Pr or Ce or Eu were prepared by a modified precipitation method. The chemical-physical characterization data evidenced that that dopant ions were successfully incorporated into the ZnO lattice because the doped ZnO samples presented band-gap values of about 3.0 eV, lower than undoped ZnO (3.3 eV). Photocatalytic activities of the synthesized samples under UV or visible irradiation were investigated in the degradation of Eriochrome Black T (EBT) in aqueous solutions. Photocatalytic results showed that the total EBT discoloration was reached after 120 min under UV irradiation for all the photocatalysts and the complete mineralization was achieved after 180 min only for the Pr and Ce doped ZnO samples. The best photocatalytic performances in terms of EBT discoloration and mineralization have been found for Pr doped-ZnO photocatalyst, both under UV and visible light.

1. Introduction

Wastewaters produced by textile industries are highly hazardous to aquatic living and human beings because they cause serious damage to the surrounding environment. They contain a lot of contaminants such as organic dyes which are widespread used in the industrial processes but they are toxic and not biodegradable compounds. Organic dyes are also difficult to remove because they are stable to the light and to the oxidizing agents (Bhatt and Rani, 2013). It is reported that the conventional treatments like biological, physical and chemical processes are very expensive and they lead to dangerous secondary pollution, including toxics sludge, heavy metals or other solid wastes (Aouni et al., 2012). For this reason, heterogeneous photocatalysis is one of the most important efficient technologies used to remove organic contaminants from wastewaters. In particular, photocatalytic processes with TiO₂ have been always preferred in the past years (Sannino et al., 2013). Recently, zinc oxide (ZnO) appeared as an efficient candidate in the photocatalytic applications due to its chemical stability in nature, not toxicity and highest photocatalytic activity compared to widely used TiO₂ catalyst (Vaiano et al., 2015). ZnO is also known as a promising material for the removal of organic contaminants including dyes such as Eriochrome Black T (EBT) (Vaiano et al., 2016). Belonging to the azo dye class, EBT is a water soluble dye that is classified as a hazardous dye due to its large molecular structure and its chemical stability. It is widely used in the textile industry but it is difficult to remove from the aqueous phase always for its complex molecular structure (Bedoui et al., 2009). To enhance the photocatalytic activity, the doping is an important and effective way to improve the photocatalytic properties of the semiconductors (Vaiano et al., 2015a). In the previous studies, metal ions such as Cu (Gupta et al., 2016), Ag (Wang et al., 2004), Co (Kuriakose et al., 2014), Fe (Ba-Abbad et al., 2013) or noble metal (Pt, Pd) (Rao and Tarakarama Rao, 1999) were incorporated into the ZnO lattice showing an enhancement of photocatalytic performances compared to undoped ZnO. Some studies have reported that ZnO doping with rare earth ions showed enhancement in light absorption due to the creation of impurity energy levels within the band gap.

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Karunakaran et al., 2010). However, the literature concerning the use of ZnO doped with rare earth ions in photocatalytic systems is still scarce. In this sense, the aim of this work is to evaluate the photocatalytic performance of ZnO doped with Ce, Eu and Pr (all of them belonging to the lanthanide group) to remove EBT dye from aqueous solution under UV or visible light irradiation.

2. Experimental
2.1 Photocatalysts preparation and their characterization
Undoped ZnO catalyst was prepared by the precipitation method. 8 g of ZnSO₄ (Aldrich, 99%) was dissolved in 50 mL of distilled water and the precipitate was obtained through the slow addition of an aqueous solution of 25 mL of distilled water containing 4 g of NaOH (Aldrich, 99%) at room temperature. Afterward, the generated sample was centrifuged, washed and calcined at 450 °C for 30 min. With the same procedure, Ce, Eu and Pr-doped ZnO were prepared maintaining constant the molar ratio between the dopant and zinc element being 0.46 mol%. In particular, Pr(NO₃)₃·6H₂O (Aldrich 99.9%), Ce(NO₃)₃·6H₂O (Aldrich 99.9%) or Eu(NO₃)₃·5H₂O (Aldrich 99.9%), used as dopant sources, were dissolved into the solution of ZnSO₄ before to induce the precipitation with NaOH. All the synthesized photocatalysts were listed in Table 1. The photocatalysts were characterized by X-ray diffraction analysis (XRD) and UV–Vis diffuse reflectance spectra (UV–Vis DRS).

2.2 Photocatalytic tests
The photocatalytic tests were conducted in a photoreactor (ID = 2.6 cm, LTOT = 41 cm and VTOT = 200 mL) supplied with an air distributor device (flow rate of 142 Ncc·min⁻¹), a peristaltic pump (Watson Marlow) to ensure a continuous mixing of the photocatalyst in the solution. Four UV or visible lamps (Philips, nominal power at 8W each and main emission peak at 365 nm and 440 nm for UV and visible lamps respectively) were positioned around the photoreactor external surface. In 100 mL of aqueous solution containing 100 mg·L⁻¹ of EBT concentration, 0.3 grams of photocatalyst were dispersed. The suspension was left in dark conditions for 120 min until the adsorption phenomenon is fully developed. After that, the photocatalytic test under UV or visible light was performed up to 240 min. 4 mL of solution were taken with a syringe and then they were centrifuged to remove the catalysts powders before the concentration measurement. Moreover, the pH of the solutions was not modified and it was about 6.5 for all the photocatalytic tests. To measure the dye concentration, UV–vis spectrophotometer (Evolution 201) was used to analyze the absorbance of EBT at the wavelength of 580 nm while the total organic carbon (TOC) was measured by the high temperature combustion method on a catalyst (Pt-Al₂O₃) in a tubular flow microreactor operated at 680 °C, with a stream of hydrocarbon free air to oxidize the organic carbon (Sannino et al., 2011).

3. Results
3.1 Characterization of the photocatalysts
Figure 1 shows the XRD patterns of the photocatalysts in which there are five peaks at 2θ 32.06°, 34.74°, 36.53°, 47.85° and 56.97° respectively indexed to the (100), (002), (101), (102) and (110) planes of hexagonal wurtzite crystal structure (Vaiano et al., 2016). No signal due to praseodymium (Khataee et al., 2015), cerium (Mahmoud, 2010) and europium (Phuruangrat et al., 2014) oxides was detected, confirming the success of the synthesis. The average crystallite sizes of the prepared photocatalysts, reported in Table 1, were calculated using the peak at 2θ 36.53° through the Debye–Sherrer’s equation. The crystallite size values of the doped photocatalysts are decreased in comparison to undoped ZnO (25 nm) and the lower value was obtained for the Eu-ZnO sample (20 nm). Figure 2 reports the UV-Vis DRS spectra of the photocatalysts. It is evident the absorption threshold of undoped ZnO sample occurring at about 390 nm. All the doped samples demonstrated a shift toward the visible light region. In fact the value of band gap decreased slightly for all photocatalysts in comparison to the undoped ZnO (Table 1).

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Dopant nominal loading [mol%]</th>
<th>Crystallite size [nm]</th>
<th>Equivalent band gap energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped ZnO</td>
<td>0</td>
<td>25</td>
<td>3.4</td>
</tr>
<tr>
<td>Pr-ZnO</td>
<td>0.46</td>
<td>21</td>
<td>3.2</td>
</tr>
<tr>
<td>Ce-ZnO</td>
<td>0.46</td>
<td>24</td>
<td>3.2</td>
</tr>
<tr>
<td>Eu-ZnO</td>
<td>0.46</td>
<td>20</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure 1: XRD patterns of the photocatalysts

Figure 2: UV–Vis diffuse reflectance spectra of the photocatalysts
Photocatalytic activity results under UV light. Figure 3 shows the results of EBT discoloration as a function of irradiation time. With respect to undoped ZnO with, a slight increase of EBT discoloration rate was obtained for all doped photocatalysts. An important effect of the presence of dopant into ZnO structure was evident by the behavior of total organic carbon (TOC) showed in Figure 4. In particular, Pr-ZnO sample demonstrated higher photocatalytic performance than Ce-ZnO and Eu-ZnO samples, allowing to reach the complete mineralization after 120 min under UV light (Figure 4).

![Figure 3: Photocatalytic EBT discoloration (a) and EBT mineralization (b) under UV light](image1)

![Figure 4: Photocatalytic EBT discoloration under visible light over photocatalysts](image2)

**3.2 Photocatalytic activity results**

Figure 3a shows the results of EBT discoloration as a function of irradiation time. With respect to undoped ZnO with, a slight increase of EBT discoloration rate was obtained for all doped photocatalysts. An important effect of the presence of dopant into ZnO structure was evident by the behavior of total organic carbon (TOC) showed in Figure 3b. In particular, Pr-ZnO sample demonstrated higher photocatalytic performance than Ce-ZnO and Eu-ZnO samples, allowing to reach the complete mineralization after 120 minutes under UV light (Figure 3b). The photocatalytic discoloration of undoped and doped ZnO under visible light is reported in Figure 4. It is worthwhile to note that undoped ZnO did not show photoactivity in comparison to the all doped samples, as expected. From the comparison of the results in terms of TOC removal (Figure 5), Pr-ZnO sample
was the best photocatalyst because the highest value of TOC removal after 240 minutes of visible irradiation has been achieved.

![EBT mineralization under visible light over photocatalysts](image)

**Figure 5: EBT mineralization under visible light over photocatalysts**

**4. Conclusions**

From the characterization results it was evident that the dopant into ZnO structure induced a shift toward the visible region with a slightly decrease of the band gap value in comparison to undoped ZnO. Photocatalytic activity results demonstrated that the highest photocatalytic activity was attributed to Pr-ZnO sample achieving the complete discoloration and mineralization of EBT in aqueous solution after 120 min under UV light. Moreover, Pr-ZnO photocatalyst demonstrated also the best under visible light irradiation if compared to Ce and Eu-doped ZnO samples.

**Reference**


