



Sonophotocatalytic degradation of Acid Blue 113 in the presence of rare earth nanoclusters loaded TiO₂ nanophotocatalysts



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ABSTRACT

A simple, convenient and one-step sonochemical treatment was adopted for the loading of rare earth (RE) nanoclusters such as Sm³⁺, Pr³⁺ and Er³⁺ into the TiO₂ surface to enhance the sonophotocatalytic degradation of Acid Blue 113 (AB113). The prepared catalysts were characterized using various analytical techniques to prove that the expected modification can occur at the surface which leads to tailor the optical properties of the resulting nanocatalysts. In this study, it is proved that the visible light is sufficient for the band gap excitation of the synthesized nanocatalysts and to improve the efficiency of the mineralization process the sonicator producing 42 kHz ultrasound was combined with the photocatalysis technique. Among the experimented nanocatalysts Pr³⁺ loaded TiO₂ exhibit the higher rate of decolorization and mineralization of AB113 during sonocatalytic, photocatalytic and sonophotocatalytic processes. The synergy index for the combination of sonolysis and photolysis i.e., two advanced oxidation processes (AOPs) were calculated using the observed rate constants for the individual and combined AOPs.

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1. Introduction

TiO₂ photocatalysis ensues through the formation of hydroxyl radicals and hence its mechanistic studies towards the removal of aqueous pollutants are well understood [1]. TiO₂ considered as a good host candidate for doping of metal [2,3], non-metal [4] and rare earth (RE) nanoparticles [5–7]. However the comparison of efficiency of all the doped TiO₂ catalysts is very difficult since the process of photocatalytic degradation of organic contaminants depends on numerous experimental factors [1,2]. Recently trivalent lanthanide ions doped TiO₂ was found to be an interesting photocatalysts for the visible light induced degradation of organic contaminants [8–11] since the addition of rare earth materials as dopant into the TiO₂ (host) leads to tailor the optical properties

[5–7]. It is evidenced from the previous studies that the concentration of surface adsorbed hydroxide ions increased in the case of rare earth doped TiO₂ nanophotocatalysts [12]. The surface adsorbed hydroxide ions are expected to produce large number of hydroxyl radicals at the nanophotocatalysts reaction sites. In other words, surface adsorbed hydroxide ions reduced the recombination of electronic charges and increased the photocatalytic activity of the respective nanophotocatalysts by increasing the production of effective radicals [3,12,13].

The other possible reason for the enhancement in photocatalytic activity of rare earth doped TiO₂ may due to the formation of new energy levels which is closer to the conduction band. Therefore the electronic excitation of TiO₂ can be possible by the illumination of visible light. However the efficacy of the mineralization of organic contaminants during visible light assisted photocatalysis needs to be further improved. The combination of advanced oxidation processes (AOPs) enhances the degradation of non-biodegradable recalcitrant pollutants [14–18]. Among various AOPs, the combination of sonolysis with photocatalysis received much attention from the environmental perspectives [19–21]. The extreme conditions

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produced during the sonication are of current interest for the degradation of environmental contaminants [22–24]. Recently, Wang et al., [25] and Drosou et al., [26] reported that the commercial ultrasonic bath used for the cleaning in the laboratories can be used as the source for the sonochemical degradation of organic contaminants. The combination of the sonicator with the visible light assisted photocatalysis technique is expected to reduce the operating cost needed for mineralization of organic contaminants. In this study rare earth metals (RE) such as Samarium (Sm^{3+}), Praseodymium (Pr^{3+}), and Erbium (Er^{3+}) loaded TiO_2 nanophotocatalysts were prepared by a simple sonochemical processes. The efficiency of the nanophotocatalysts was monitored by following the degradation kinetics of Acid Blue 113 (AB113) in the presence and absence of the sonicator producing ultrasonic waves (42 kHz) and the visible light source illuminating spectral range ≥ 420 nm.

2. Experimental

2.1. Materials and methods

Titanium dioxide nanopowder and nitrates of Samarium (Sm), Praseodymium (Pr) and Erbium (Er) were purchased from Sigma–Aldrich and used as the starting materials for the preparation of rare earth doped TiO_2 nanocatalysts. Acid Blue 113 (di azo dye, $\text{C}_{32}\text{H}_{21}\text{N}_5\text{Na}_2\text{O}_6\text{S}_2$; C.I. 26360) was received from Sigma–Aldrich and used without further purification. Unless otherwise specified, all reagents used were of analytical grade and the solutions were prepared using double distilled water. The particle size of the prepared nanoparticles was calculated from the X-ray diffraction data (Philips PW1710 diffractometer, $\text{CuK}\alpha$ radiation, Holland) using Scherrer equation. Surface morphology, particle size, and various contours of the nanocatalyst powders were analyzed by Transmission Electron Microscopy (FEI TITAN G2 80-300) operated at 300 KeV. Diffuse reflectance UV–Vis spectra of the nanocatalysts were recorded using a Shimadzu 2550 spectrophotometer equipped with an integrating sphere accessory employing BaSO_4 as reference material. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301 spectrofluorophotometer. The surface area, pore volume and pore diameter of the samples were measured with the assistance of Flowsorb II 2300 of Micrometrics, Inc. The total organic carbon (TOC) for all the samples was analyzed by direct injection of the filtered sample solutions into a TOC analyzer (Vario TOC cube, Cientec Instrumentos S.A). Prior to the analysis, the instrument was calibrated with potassium hydrogen phthalate. TOC_0 is the TOC measured after the equilibrium adsorption of the dye on the nanocatalysts surface and TOC_t obtained at various irradiation times is denoted as TOC_t .

2.2. Preparation of nanocatalysts

The nitrate precursors (1 mol%) of rare earth metals (Sm^{3+} , Pr^{3+} and Er^{3+}) was added to the 100 ml aqueous suspension containing one gram of TiO_2 and stirred for 30 min. The suspension was irradiated with ultrasound (42 kHz) continuously for 2 h at room temperature then filtered and the solids were redispersed in 100 ml of distilled water under vigorous stirring (1200 rpm) for 15 min at 50 °C. The above procedure was repeated several times and then dried at 110 °C for 12 h followed by calcination at 550 °C for 5 h in order to get pure nanocatalysts. Similarly the bare TiO_2 was treated using the same methodology and calcinated at 550 °C for comparison.

2.3. Photocatalysis and sonophotocatalysis

A desired concentration of AB113 was prepared by dissolving the appropriate amount of dye in 250 ml of water and 250 mg of

nanocatalysts ($\text{RE-TiO}_2/\text{TiO}_2$) was added to the dye solution. The degradation of Acid Blue 113 (AB113) was studied under ambient atmospheric conditions and at natural solution pH (~ 6.0). In order to ensure the adsorption/desorption equilibrium, the dye/nanocatalyst slurry was stirred for 45 min in dark condition prior to irradiation. After that, the lamp and/or the sonicator were turned on and this was taken as “time zero” for the degradation reactions. The photocatalytic studies were performed using a light source (Cole-Parmer, USA) illuminating spectral range ≥ 420 nm with the intensity of incident irradiation $\geq 100,000 \pm 100$ Lux measured by Lux meter purchased from Cole-Parmer instrument company, USA and all the sonochemical reactions in this study were carried out by using a commercially available sonicator (8890, Cole-Parmer, USA) producing 42 kHz ultrasonic waves. The experimental setup and conditions used for photolysis, sonolysis, and sonophotolysis were identical. During the degradation studies, the target substance (organic contaminants) was sonicated in the presence and absence of catalysts and visible light. The apparent kinetics of disappearance of the substrate (AB113) was determined by following the concentration of the substrate ($\lambda_{\text{max}} = 574$ nm) using Shimadzu UV–Vis 2550 spectrophotometer. Prior to the analysis, the nanocatalysts were separated from the suspension by using a 0.45 μm Polytetrafluoroethylene (PTFE) filter.

3. Results and discussion

3.1. Characterization of the nanocatalyst

The crystal structure of pristine TiO_2 and 1 mol% RE^{3+} (Sm, Pr and Er) loaded TiO_2 nanocatalysts are shown in Fig. 1. The appearance of a strong intense peak at $2\theta = 25.3$ confirms the predominant existence of TiO_2 anatase phase in all the synthesized nanocatalysts. There is no specific diffraction belongs to RE^{3+} dopant was observed in the XRD pattern. The substitution of the rare earth ions into the TiO_2 may get suppressed due to the large mismatch in the ionic radius of host and guest molecules [27,28]. The doping of RE^{3+} ions does not change the crystal structure of TiO_2 and concurrently the calcination of the sonochemically synthesized nanophotocatalysts at 550 °C ruled out the possibility of replacement of Ti^{4+} ions [29]. The specific surface area (S_{BET}) of the prepared nanocatalysts are listed in Table 1, RE^{3+} loaded TiO_2 particles show the enhanced specific surface area when compared to the bare TiO_2 may be due to the ionic radius of RE^{3+} -ions prevented its penetration into the TiO_2 . Concomitantly, the charge

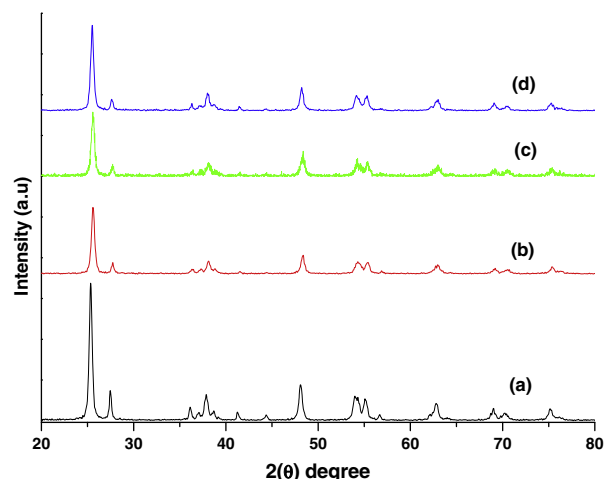


Fig. 1. X-ray diffraction pattern of bare (a) and RE ((b) Sm^{3+} , (c) Pr^{3+} and (d) Er^{3+}) loaded TiO_2 nanocatalysts.

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