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Low frequency ultrasound (42 kHz) assisted degradation of Acid Blue 113 in the presence of visible light driven rare earth nanoclusters loaded TiO_2 nanophotocatalysts

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ABSTRACT

An attempt has been made to render the visible light driven photocatalytic activity to the TiO_2 nanocatalysts by loading 1 wt% of rare earth (RE) nanoclusters (Gd^{3+}, Nd^{3+} and Y^{3+}) using a low frequency (42 kHz) producing commercial sonicator. The STEM-HAADF analysis confirms that the RE nanoclusters were residing at the surface of the TiO_2. Transmission electron microscopic (TEM) and X-ray diffraction (XRD) analyses confirm that the loading of RE nanoclusters cannot make any significant changes in the crystal structure of TiO_2. However, the optical properties of the resulted nanocatalysts were significantly modified and the nanocatalysts were employed to study the sonocatalytic, photocatalytic and sonophotocatalytic decolorization as well as mineralization of Acid Blue 113 (AB113). Among the experimented nanocatalysts maximum degradation of AB113 was achieved in the presence Y^{3+}-TiO_2 nanocatalysts. The decolorization of AB113 in the presence and absence of Y^{3+} loaded TiO_2 ensues the following order sonolysis < photocatalysis < sonocatalysis < sonophotocatalysis. The sonophotocatalytic decolorization of AB113 shows 1.4-fold (synergy index) enhanced rate when compared with the two corresponding individual advanced oxidation processes. The sonophotocatalytic mineralization shows that 65% of total organic carbon (TOC) can be removed from AB113 after the 5 h of continuous irradiation however the mineralization cannot be able to show the synergetic effect.

1. Introduction

The nano-size semiconductor photocatalysts are modified using various dopants in order to increase the visible light responsive character of the subsequent nanocatalysts [1–5]. Recently it was reported that the loading of rare earth (RE) dopants into the semiconductor photocatalysts increases the charge imbalance of the resulting nanocatalysts which increased the number of adsorbed hydroxide ions on the surface of the nanocatalysts during the degradation processes and eventually the surface adsorbed hydroxide ions may convert into hydroxyl radicals ($^{\cdot}OH$) during the degradation of environmental contaminants [6]. Alternatively, it was reported that the loading of RE into the TiO_2 significantly increases the photocatalytic activity through the formation of the complexes between the *f*-orbital of RE dopants with the various organic contaminants which provided an effective environment for the better interaction among the organic contaminants and hydroxyl radicals [7,8]. Therefore, it was expected that the presence of the RE nanoclusters on the surface of the TiO_2 can alter the surface adsorption properties as well as the complexation with the organic contaminants through its *f*-orbital to bring the effective outcome for the environmental remediation. Furthermore, RE nanoclusters act as a sink for the electronic charges to minimize the recombination process during the sonophotocatalysis [9,10].

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On the other hand, the development of novel methodologies for the purification of water and wastewater released from the industrial sectors is essentially required in order to reduce the existing operating cost [11–13]. Concurrently, the modification or replacement of the expensive components from the existing technology can also make the degradation process cost-effective for the commercial applications [14–17]. The extended utilization of a low frequency ultrasound (42 kHz) for the degradation of recalcitrant organic contaminants reduces the operating cost of the sonication process. However the rate of low frequency assisted removal of organic pollutants is diminutive when compared with the high frequency supported sonication processes. Therefore the adaptation of other advanced oxidation process (AOP) such as photocatalysis with the 42 kHz assisted sonicator makes the sonophotocatalysis process more effective for the removal of organic contaminants [18,19]. The development of visible light responsive photocatalysts for the degradation of various organic contaminants is of current interest which further reduces the operating cost [20–23].

Furthermore, the RE doping could control the TiO_2 particle growth, crystal transformation, and cause negative shift of the conduction band, and thus increase the resulting photocatalytic activity of the nanocatalysts [24,25]. Therefore, based on the previous studies and the necessity to evaluate the sonophotocatalytic efficiency of the various RE dopants, in this study Gadolinium (Gd^{3+}), Neodymium (Nd^{3+}) and Yttrium (Y^{3+}) were loaded into the TiO_2 nanocatalysts by a simple low frequency assisted sonochemical process. The resulted nanophotocatalysts were employed to evaluate the sonocatalytic, photocatalytic, and sonophotocatalytic degradation of Acid Blue 113 (AB113). The elemental Yttrium was located in the "d block elements" of the modern periodic table however it shows the chemically equal character with the rare earth elements therefore, Y^{3+} was considered as a RE dopant in this study and the resulted catalytic activity was taken into account to compare with other RE dopants.

2. Experimental

2.1. Materials and methods

Titanium dioxide nanopowder and nitrates of Gadolinium (Gd), Neodymium (Nd) and Yttrium (Y) were purchased from Sigma–Aldrich and used as the starting materials for the preparation of rare earth doped TiO_2 nanocatalysts. Acid Blue 113 (diazo dye, $C_{32}H_{21}N_5Na_2O_6S_2$; 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, CuKα 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 obtained at various irradiation times is denoted as TOC_t.

2.2. Preparation of nanocatalysts

The nitrate precursors (1 mol%) of rare earth metals (Gd^{3+}, Nd^{3+} and Y^{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 (RE-TiO_2/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 $\geqslant$ 420 nm with the intensity of incident irradiation $\geqslant$ 100000 ± 100 Lux measured by Lux meter (Cole-Parmer, USA). 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

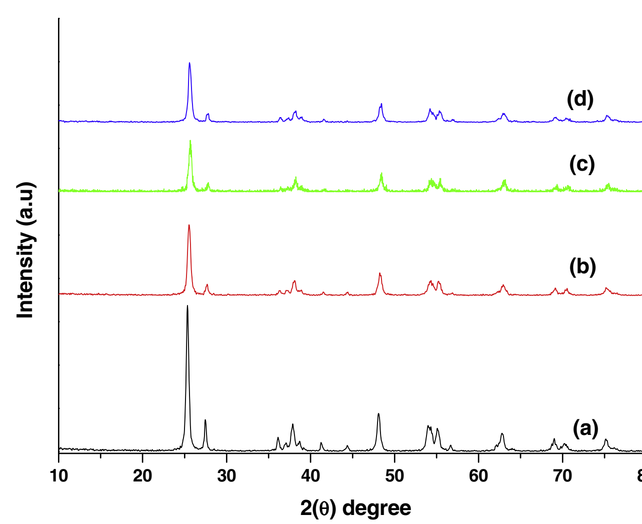

Fig. 1. X-ray diffraction pattern of bare (a) and RE ((b) Gd^{3+}, (c) $Nd^{3+}$and (d) Y^{3+} loaded TiO_2 nanocatalysts.

Table 1
Physicochemical characteristics of RE loaded TiO_2 nanocatalysts.

S. No	Nanophotocatalyst	Surface area (S_{BET} m^2/g)	Band gap (eV)
1	TiO_2	44.27	3.2
2	Nd^{3+}-TiO_2	47.98	2.67
3	Gd^{3+}-TiO_2	46.42	2.69
4	Y^{3+}-TiO_2	45.09	2.65