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Research paper

Hydrothermal Synthesis of TiO_2/Al_2O_3 Nanocomposite and its Application as Improved Sonocatalyst

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Abstract

The powder of $TiO_2/\alpha\text{-}Al_2O_3$ nanocomposite for Sonocatalysis decolorisation was successfully achieved in the Hydrothermal autoclave reaction for 6 hours and completely crystallized into Anatase phase at temperature of 220oC which more lower than normal required calcination temperature 500oC. The $TiO_2/\alpha\text{-}Al_2O_3$ nanoparticles examined using FT-IR, SEM, TGA, X-ray diffraction studies(XRD), The results indicate the formation of nanocomposite with tetragonal Anatase phase and average crystal size of 21.4nm for $TiO_2/\alpha\text{-}Al_2O_3$ while the average crystal size of 8.1nm for Al_2O_3, which are calculated according to Scherrer's equation. This powder was mixed with methylene blue to study the effect of nanocomposite on it, the prepared nanocomposite show highly decolorisation percentage of methylene blue solution.

Keywords: *Anatase, Hydrothermal, Methylene Blue, Nanocomposite, Sonocatalysis, $TiO_2/\alpha\text{-}Al_2O_3$.*

1. Introduction

Nanocomposites material formed by blending either polymers, metals, or ceramic with nanoparticles materials are attractive material due to create new material with new properties (D. C. C. Okpala 2014). Nanocomposite can classify into three different categories, according to their matrix materials to polymeric, metallic, and ceramic nanocomposites (T. Hanemann et al.,2010). The molecular structure and the stereo-hindrance of a matrix material play a major role in selection of the suitable matrix (I. Pleșa et al.,2016). The present of functional groups in the matrix molecular structure can ease the reaction with nanoparticles, while the stereo-hindrance of the matrix structure may prevent the nanoparticles from forming aggregation, thus enhancing the dispersion and uniformity of nanoparticles on the surface of matrix (J. Di *et al.*, 2014). There are numeric methods to synthesis nanocomposite, such as sol-gel, direct mixing of matrix and nanofiller, and Intercalation Method (M. Tanahashi 2010). Sol-gel is the most famous and flexible route for the production of nano metal oxides and nanocomposite especially, titanium oxides via the inorganic titanium tetra chloride (TiCl4) or organometallic titanium tetra alkoxide (Ti (O-alkyl)$_4$) precursors (T. K. Tseng et al.,2010). In a typical sol–gel process, organometallic precursors (Ti (O-alkyl)$_4$) is subjected to a hydrolysis–condensation reaction to form a colloidal suspension of titanium particles, subsequent to which these particles condense in a new gel form (H. S. Chen et al., 2012). in spite of simple the advantages of sol-gel, it has some drawbacks such as, shrinkage that happened during drying and sintering (M. Aparicio et al., 2012). The powder of TiO_2 formed by sol-gel route requires higher temperatures (>400°C) for completely crystallization of the final product (G. Yudoyono *et al.*, 2016). The crystallization step can be done by another technique through hydrothermal crystallization in supercritical water conditions pressures using Morey autoclave (K. Byrappa et al., 2007). Shuxi Dai et.al were reported that preparation of high crystalline TiO_2 nanoparticles through a facile inorganic acid-assisted hydrothermal treatment using The autoclave under heated and maintained at 150°C for 24 h(S. Dai et al., 2010).

The oxidation of organic compounds by ultrasound irradiation is one of the famous advanced oxidation process (AOP) that produce oxidative environment (i.e., produce reactive oxygen species) via cavitation process (B. Miljevic et al., 2014). Hydroxyl free radicals are one of these reactive oxygen species, which are unselectively attack the wide range of organic compounds in water (O. Moumeni et al., 2012). Highly reactive hydroxyl radicals which have one free electron pair are strong oxidizing agents and provide the main driving mechanism for degradation of various organic pollutants (M. M. Mahlambi et al., 2015). The presence of semiconductor (i.e., TiO_2, ZnO) particles enhanced the process of break up the micro bubbles created by the ultrasound irradiation into smaller bubbles, thus increasing the quantity of high of regions of high temperature and pressure, This leads to produce additionally amount of hydroxyl radicals which will attack the pollutant and resulting in degradation of the pollutant (D. Teresa et al., 2013). In this paper, we have study the focused on the Sonocatalytic of TiO_2–Al_2O_3 nanocomposite which prepared by hydrothermal method. As improving catalytic properties of prepared nanocomposite, the Sonocatalysis degradation of pollutant will be more efficient.

2. Materials and Methods

Materials: Hydrochloric acid (HCl, 37%), isopropyl alcohol ($(CH_3)_2CHOH$, 99.5%), and methylene blue were ($C_{16}H_{18}ClN_3S$, 99%) purchased from BDH. nano-alumina (Al_2O_3), and titanium (IV) tetraisopropoxide (abbreviation: TTIP; molecular formula: $Ti[OCH(CH_3)_2]_4$, 97%) and were purchased from Sigma-Aldrich and were used as received.

Synthesis of TiO_2/Al_2O_3 Nanocomposite: TiO_2/α-Al_2O_3 nanocomposite was prepared by the sol–gel method. Firstly, 1 mL of TTIP was added to 15 mL of isopropyl alcohol under constant stirrer and at room temperature for 15 min. secondly 1g of nano alumina was dispersed in TTIP solution to form white suspension. By adding 1mL of deionized water and adjusting pH to 3 (HCl used to adjusted pH) under vigorous stirrer for 30 min, the white gel was formed. Then, this gel was heated at 220°C for 6 h in a 20 mL Teflon-lined autoclave. Finally, the powder of TiO_2/α-Al_2O_3 nanocomposite was collected by dring the gel at 80°C for 2h.

Characterization: The crystalline phase of α-Al_2O_3 and TiO_2/α-Al_2O_3 nanocomposite were characterized by XRD using (Bruker AXSGmbh, Germany/D2 Phaser) with CuK_α radiation (λ=0.15040nm), the XRD pattern was recorded in range of (10-80)°. To determine the functional groups, α-Al_2O_3 and TiO_2/α-Al_2O_3 nanocomposite were performed using FTIR (Shimadzu, Japan, FTIR 8400s).

Experimental Procedure: TiO_2/α-Al_2O_3 composite was mixed with methylene blue. Then the suspensions were treated by vigorous stirring for 30 min in a dark place to make a good dispersion of catalysts and adequate adsorption of dye on the surface of catalysts. Afterwards, these suspensions were placed in an ultrasound apparatus (Q Sonica, 20 Hz, 55w) and irradiated. At certain time intervals, the degradation ratios were determined by UV-vis spectra. Synchronously, the influences of ultrasonic irradiation time and solution acidity on the sonocatalytic degradation were also investigated.

3. Results and Discussions

A major concern in the field of nanocomposite includes the study mixing state of its components, size, aggregation state of nanofiller, and morphology. Therefore, as represented by Fig.(1), the surface morphology of nanocomposites was examined by scanning electron microscopy (SEM type Zeiss DSM-960A). Al_2O_3 nanoparticles showed irregular shape without significantly homogenous distributions. According to SEM image, the prepared nanocomposite morphology observed the aggregation of TiO_2 nanoparticles and good mixing with Al_2O_3 matrix. The spherical shape in nanocomposite SEM image is for the TiO_2 nanoparticles which indicated to Anatase phase.

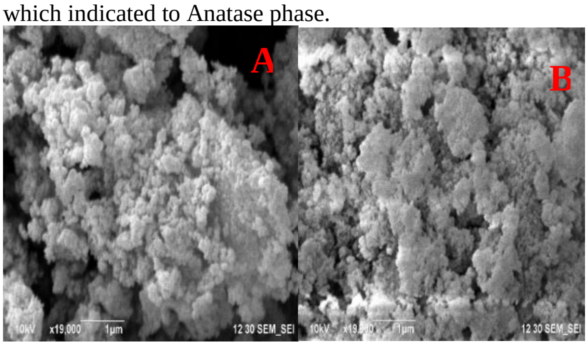

Fig. 1: SEM images of (A) Al_2O_3 nanocomposite.
(B) TiO_2/Al_2O_3 nanocomposite

The phase composition and crystal size of prepared nanocomposite and Al_2O_3 nanoparticles can be examined using the X-ray diffraction analysis. Fig. (2) Shows the diffraction Al_2O_3 peaks which can be well indexed to pure α -Al_2O_3 (JCPDS Card no. 880826) (H. S. Kim et al., 2012). The appearance of diffraction peaks in TiO_2/Al_2O_3 XRD pattern (Fig. 2) corresponding to (101) and other planes is in good agreement with the standard XRD peaks of Anatase TiO_2 (JCPDS Card No. 040477) (R. Abazari et al., 2014). According to Scherrer's equation (eq.1) (T. V. Kosmidou et al., 2008), the average crystal size of nanocomposite materials was calculated and placed in a table (1).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \text{(eq. 1)}$$

Where: *k*: is the shape factor which usually takes a value of about (0.94).
λ: is the incident x-ray wavelength (0.15040 nm for CuK).
β: is full width at half maximum (FWHM).
Θ: is diffraction angle at maximum intensity peak.

Table 1: represent the average crystal sizes of NPS.

NO.	Nanocomposite Materials	average crystal sizes (nm)	Reference
1	TiO_2	10.59	[19]
2	Al_2O_3	8.1	Current work
3	TiO_2/α-Al_2O_3	21.4	Current work

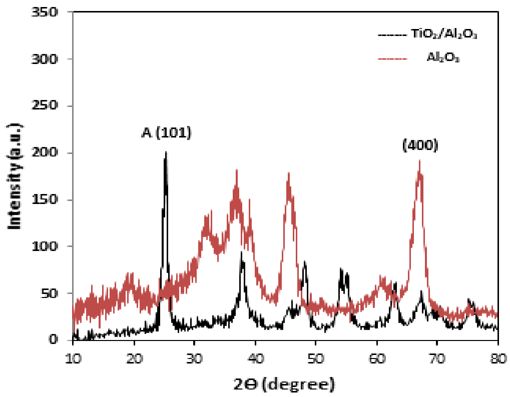

Fig. 2: XRD pattern of Al_2O_3 and TiO_2/Al_2O_3 nanocomposite.

From table we see that the average crystal sizes of nanocomposite materials for TiO_2/α-Al_2O_3 is different from TiO_2 and Al_2O_3 which is lead to get on a good mixing of NPS that was clearly in Fig.(1) for SEM images.

The FTIR spectrums of Al_2O_3, TiO_2, and TiO_2/Al_2O_3 nanocomposite were shown in Fig. (3). A broad band centered at 3419 cm^{-1} is assigned to the stretching vibration of the –OH on the oxides surfaces in different cases (S. S. Al-Taweel et al.,). The broad bands centered at 500-600 cm^{-1} in TiO_2 spectrum is assigned to the bending vibration (Ti-O-Ti) bonds (T. Mahalingam et al., 2017). The vibration modes of γ-Al_2O_3 shown in FTIR Al_2O_3 spectrum (Fig. 3) into two vibrational modes: Al-O-Al bending mode and Al-O stretching mode which located at ~821 cm^{-1} and ~552 cm^{-1}, respectively. In TiO_2/Al_2O_3 FTIR spectrum, the two Al_2O_3 (821 cm^{-1} and ~552 cm^{-1}) peaks may overlapping with TiO_2 vibration peak (500-600 cm^{-1}) and shift to higher wave number due to the size confinement effect (J. Gangwar et al., 2015).

The Thermogravimetric analysis results of Al_2O_3, TiO_2, and TiO_2/Al_2O_3 nanocomposite were as shown in Fig.(4). TGA and DTA curves of materials shown two steps in weight loss; firstly little weight loss at low temperature (<300°C) which was indicated to removal of physically adsorbed water (Y. L. Song et al., 2009), and secondly very little weight loss at higher temperature (300-800) °C which can related to strongly bonded OH groups (C. Y. Wu et al., 2017). According to TGA/DTA analysis, it appears that TiO_2/Al_2O_3 nanocomposite has more water adsorption capacity than other, and the result is compatible with FTIR result (Fig.3).

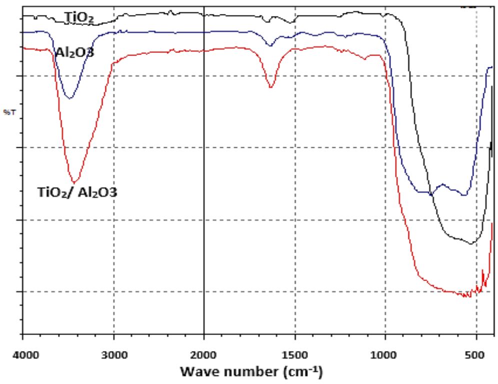

Fig. 3: FTIR *spectra* of Al_2O_3, TiO_2, and TiO_2/Al_2O_3 nanocomposite.

Sonochemical decolorisation of Methylene Blue (MB) was studied under initial concentrations of MB which was 5 mg /L. The experiments were conducted using ultrasonic processor at pH 7, contact time 60 min, and power density 3000 W/L. Fig. (5) Represent the Sonocatalysis effect of Al_2O_3, TiO_2, and TiO_2/Al_2O_3 nanocomposite on the decolorisation of methylene blue. the increase in the decolorisation of dye in presence of under studied nanoparticles due to these nanoparticles act as catalyst that increased the number of nucleation of the caviaty and improved the rate of dissociation of water into highly reactive hydroxyl radicals (•OH) (J. Wang *et al.*, 2007), TiO_2/Al_2O_3 nanocomposite show highly removal of MB dye than other Sonocatalysts due to highly dissociation rates H_2O molecules that yields more free radical generated, thereby increasing the rate of degradation of the organic compounds (Y. Song et al., 2007).

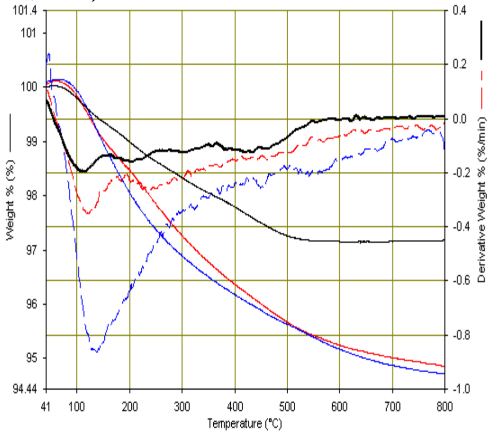

Fig.4: TGA/DTA curves of Al_2O_3, TiO_2, and TiO_2/Al_2O_3 nanocomposite.

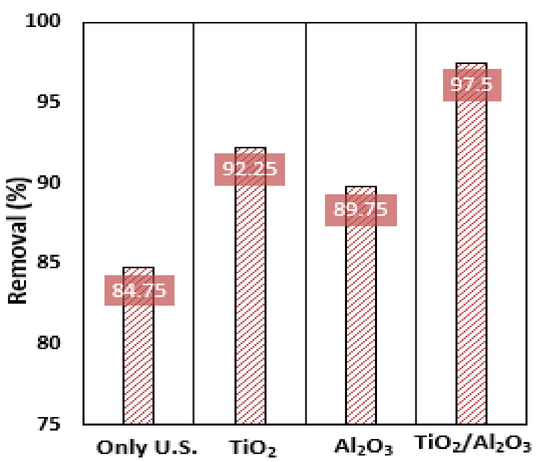

Fig.5: the sonocatalysis effect on MB decolorisation

4. Conclusions

In summary, we have prepared TiO_2/Al_2O_3 nanocomposite with Anatase phase of TiO_2 by hydrothermal method at 220°C and it was characterized by using different techniques. The synthesized nanocomposite was applied as successfully sonocatalyst to remove methylene blue form its aqueous solution and its sonocatalysis effect was compared with TiO_2 and Al_2O_3 nanoparticles. The sonochemical decolorisation results are expected to be highly related to the association between the dye removal and the water adsorption capacity of nanoparticles surface.

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