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Research Paper

Optimization of hydrothermal synthesis of Bismuth titanate nanoparticles and application for photocatalytic degradation of Tetracycline

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ABSTRACT

In this research, hydrothermal process was used to synthesize $Bi_4Ti_3O_{12}$ nanoparticles under supercritical water condition, and using Bi_2O_3 and TiO_2 as precursors. The prepared nanoparticles were analyzed by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and UV–vis diffuse reflectance spectroscopy. Hydrothermal synthesis of $Bi_4Ti_3O_{12}$ was optimized successfully via response surface methodology (RSM), and through Box-Behnken design. Effect of selected process parameters including temperature, reaction time, and pH were investigated on the production yield of Bi4Ti3O12 nanoparticles. Analysis of variance (ANOVA) demonstrated that the suggested quadratic model can interpret the experimental data, properly (R^2 = 0.9978 and R^2- adjusted = 0.9929). Moreover, the optimum conditions for the production yield was found to be the temperature of 497 °C, pH value of 11.8, and reaction time of 1.9 h. The production yield obtained from the RSM under the optimum condition was attained about 63.9%. Produced bismuth titanate nanoparticles were applied for degradation of Tetracycline antibiotic through photocatalytic process under visible and UV light irradiation. UV–visible diffuse reflectance spectroscopy showed that bismuth titanate has a band gap of 2.6 eV, and $Bi_4Ti_3O_{12}$ nanoparticles demonstrated a great photocatalytic activity for Tetracycline photo-degradation. Narrow band gap as the main advantage of bismuth titanate makes it an energy and cost effective photocatalyst which allows removing around 65% of tetracycline under visible light irradiation.

1. Introduction

These days, extensive use of pharmaceuticals has led to global pollution of numerous environmental matrixes. Tetracyclines (TCs) as one of the most widely-used antibiotics in aquaculture and veterinary medicines are due to their poor absorption excreted through feces and urine as un-metabolized parent compound. The most dangerous effect of antibiotics in the environment is the development of multi-resistant bacterial strains that can no longer be treated with the presently known drugs [1]. During the last decade, advanced oxidation processes (AOPs) have been proven to be substitute for removal of recalcitrant and non-biodegradable compounds. The most popular AOPs are heterogeneous photocatalysis with semiconductors [2,3]. Titanium based nanoparticles are known as the most effective photocatalysts for degradation of non-biodegradable compounds [4–6]. There are a lot of studied about photo-degradation of tetracycline using titanium based photocatalysts [7–9]. The wide band gap of TiO_2 as the most frequently used photocatalyst is the main drawback toward its application for degradation of pollutants in visible range irradiation. Numerous studies have carried out to achieve novel titanium based composites and structures with improved photo activity [10,11]. The main objective of these efforts is to alter the band gap of titanium based photocatayst by doping metals [12,13] and nonmetals [14] to TiO_2 structure. Bismuth compounds such as bismuth oxides [15] and oxyhalides [16] have shown to be effective photocatalysts in visible light range. As a class of promising photocatalysts which can respond under visible light, bismuth titanates have been widely studied. [17].

Nowadays, there is a growing demand for the advanced materials with high dielectric constant, low dielectric loss, good piezoelectric and also pyroelectric properties, which is due to the large scale use of Ferroelectric materials especially in capacitors, sensors, actuators, transducers, and memory applications. To avoid environmental

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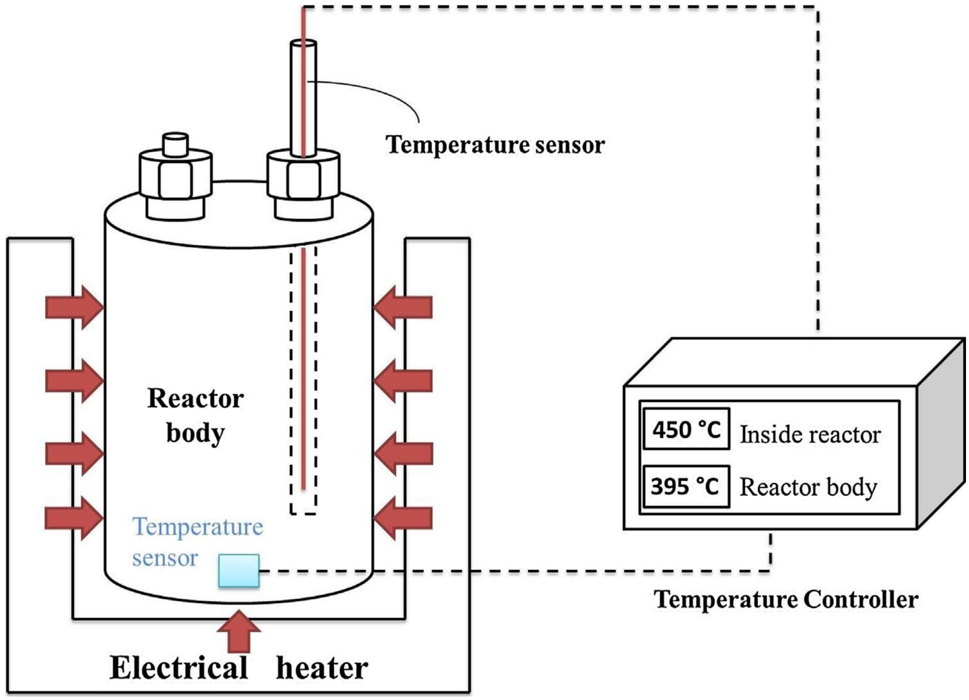

Fig. 1. Schematic drawing of hydrothermal reactor for BIT synthesis.

pollution by the product, lead-free materials are used while keeping the same applications. Therefore, among all lead-free piezoelectric materials, bismuth titanate ($Bi_4Ti_3O_{12}$) is selected as a new eco-friendly ferroelectric material [18,19]. As a member of the Aurivillius family with different chemical compositions such as $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$, $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, and $Bi_{20}TiO_{32}$ [20], Bismuth titanate (BIT) is made up from the stacking layers of $Bi_2O_2{}^{+2}$ (tetrahedron) and pseudo-perovskite layers of $Bi_2Ti_3O_{10}{}^{-2}$. It has a preferential direction of conductance along the $BiO_2{}^{+2}$ layers, making it difficult to obtain a high polarization on it [21]. Due to its low dielectric permittivity property regarding single crystal BIT accompanied by very high Curie temperature (T_c = 675 °C), BIT have attracted attentions as a useful material for high temperature piezoelectric applications in an extensive temperature range from 20 to 600 °C [17]. Besides, the important property of BIT which this study is focused on is related to BIT photo-activity. Owing to its narrow band gap [22], bismuth titanate is also used to remove pollutants as an effective photocatalyst under visible light irradiation [23–25]. This important feature of bismuth titanate would overcome the main constraint of TiO_2, and makes $Bi_4Ti_3O_{12}$ (BIT) an effective photocatalyst. For instance, Zhou and Hu [26] reported mass production of $Bi_{20}TiO_{32}$ Nanosheets and its application for photocatalytic degradation of azo dye in visible light irradiation. In another study, Hou et al. [27] synthesized Hierarchical bismuth titanate complex architectures using hydrothermal method. The produced particles showed a good performance in photocatalytic degradation of Rhodamine B under visible light irradiation.

There are various techniques for BIT powders synthesis such as hydrothermal method [28,29], sol–gel [30], co-precipitation [31], high-energy ball milling [32], metalorganic decomposition [33], Chemical Solution Deposition (CSD) [34], etc. The drawbacks of mentioned methods for the BIT nanoparticles production were being long-lasting, larger diameters, expensive raw materials, and high temperature for purification. Hence, in order to handle the mentioned problems, synthesis of BIT nanoparticles through a simple process seems inevitable.

Over the past two decades, there has been escalating attention to benefit from supercritical fluids (SCFs) as an alternative to organic solvents in industries [35]. Supercritical water is a promising green solvent which is recyclable, nontoxic and non-flammable. Hydrothermal synthesis processes under supercritical water conditions have been studied for production of metal oxide particles in nano-size range (1–100 nm typically) [36–38]. Supercritical hydrothermal synthesis process has been developed by Adschiri et al. [39–41], Hakuta et al. [42–45], and Li et al. [46]. They have also conducted different experiments to produce several single and complex metal oxide nanoparticles. They assumed that the nanoparticles were produced since the supercritical water causes the metal hydroxides quick dehydration before the significant growth of particles occurs.

The purpose of this study is to investigate the BIT nanopowder production via hydrothermal method under supercritical condition in a batch type reactor. The advantages of this technique are BIT desired shape preparation, the shortest possible residence time, lower cost of production and also lower temperature synthesis compared to the abovementioned synthesis methods [47]. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), and UV–vis diffusion reflectance spectrometer analysis were used for characterization of the nanoparticles. The prepared BIT particles were applied for photocatalytic degradation of tetracycline under UV and visible light irradiation.

2. Experimental

2.1. Materials

Bismuth (III) oxide (Bi_2O_3, purity ≥ 98.0%), Titanium dioxide (TiO_2, nanopowder, particle size < 25 nm, purity 99.7%), HNO_3 were supplied from Aldrich Chemical Company, and KOH was purchased from Merck Co. Double distilled water was used for the process. Tetracycline antibiotic was provided from Razak laboratories Co. Sodium hydroxide and hydrogen chloride were supplied from Sigma-Aldrich and Merck Co. respectively. 1N NaOH and 1N HCl was used to adjust the pH of the Tetracycline solution. Methanol solvent was purchased from Merck Co.

2.2. Methods

2.2.1. Hydrothermal synthesis of bismuth titanate (BIT) nanoparticles

The hydrothermal synthesis of $Bi_4Ti_3O_{12}$ nanoparticles was