Microwave-assisted synthetic method of novel Bi$_2$O$_3$ nanostructure and its application as a high-performance nano-catalyst in preparing benzylidene barbituric acid derivatives

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In this study, controllable and optimal microwave irradiation has been used to synthesize the novel nanostructures of Bi$_2$O$_3$ under environmental conditions. The final products had a thermal stability of 210°C, an average particle size distribution of 85 nm, and a surface area of 783 m$^2$/g. The high thermodynamic stability of Bi$_2$O$_3$ nanostructures was confirmed by TG and differential scanning calorimetry (DSC) analyses. The nanostructure nature of compounds, and most importantly, the use of an effective, cost-effective, and rapid synthesis route of microwave have created significant physiochemical properties in the Bi$_2$O$_3$ products. These unexpected properties have made the possibility of potential application of these products in various fields, especially in nano-catalyst applications. It is well-documented that, as Lewis acid, bismuth nano-catalyst exhibits a great catalytic activity for the green synthesis of some bio-active barbituric acid derivatives using precursors with electron-donating or electron-withdrawing nature in high yields (80%–98%). After incorporating this catalyst into the aqueous media, all the reactions were completed within 2–3 min at room temperature. The main advantages of this method are practical facility, the availability of starting materials, and low costs besides the catalyst reusability. Additionally, the catalyst synthesis process may be carried out in the aqueous media for a short period with medium to high yields. The obtained results have opened a new window for the development of a novel nano-catalyst with practical application.

KEYWORDS
Bi$_2$O$_3$ nanostructure, efficient synthesis route, novel catalyst, benzylidene barbituric acid, microwave
1 Introduction

Bi₂O₃ nanostructures are one of the most important products from transition metal oxides (Azizian-Kalandaragh et al., 2015). These structures, because of their special properties, have attracted particular attention to themselves in the recent decade (Wang et al., 2018). Among their extraordinary properties, the dielectric, piezoelectric, corrosion resistance, environmental compatibility, and low-cost properties can be mentioned (Kumari et al., 2007; Salim et al., 2014; Hashemi et al., 2019). The surface and physicochemical natures of Bi₂O₃ nanostructures are such that electron transfers are easily exchanged between photo-generated and electron-hole pairs; as a result, these compounds can be used as critical nanostructures in various fields (Ling et al., 2010; Kim et al., 2013).

Metal oxide nanostructures are produced by various methods, among which hydrothermal (Huang et al., 2019), ultrasonic (Zhang et al., 2006), sol-gel, and other conventional methods (Armelao et al., 1998) can be mentioned. Many of these methods require specific conditions that not only cause the reactions under controlled conditions but also leave many environmental impacts.

In order to overcome these problems, the microwave route has been proposed as an effective method to prepare various structures. Among the advantages of this method, it can be mentioned that the time duration of the synthesis process is reduced. The reactions are also carried out at low temperatures, and carbon dioxide emission is reduced when compared to other methods. In addition, the major difference in using microwave irradiation compared to other conventional methods is that in the usual methods, at first, heat is irradiated to the surface of the material; then, it is transmitted to the inside of the bulk. But in microwave methods, electromagnetic energy directly enters the structure of the material. As a result of the homogeneous irradiation of heat, the optimum use of energy is made, which creates desirable physicochemical properties in the structure.

As a cyclic amide, barbituric acid is the raw material in the synthesis of barbiturates. The mixtures of these derivatives of this material with alkyls and aryls exhibit hypnotic and sedative effects (Tanaka et al., 1988; Sokmen et al., 2013). Several derivatives of 5-arylidene barbituric acid have been more concerned as the raw material, which encompasses the intermediate in the synthesis of benzyl barbituric derivatives (Frangin et al., 1986) and heterocyclic compounds (Bojarski et al., 1985), asymmetrical disulfides (Tanaka et al., 1988), and oxadiazaflavines (Figueroa-Villar et al., 1992). Moreover, these derivatives have been extensively exploited in the pharmaceutical industry as anesthetics and central nervous system depressants (Vieira et al., 2011; Balas et al., 2011), local anesthetic, antispasmodic, sedative, hypnotic (Jursic, 2001), antimicrobial, antifungal, antitumor (Beres et al., 1974; Figueroa-Villar et al., 1992; Gulliya, 1999; Kidwai et al., 2005; Ikotun et al., 2011; Ma et al., 2011), anticonvulsant (Hastings and Long, 1991) and anticancer (Guerin et al., 1999), as well as complex and salt formation reagent (Golovnev et al., 2013; Golovnev et al., 2014; Golovnev et al., 2014; Golovnev et al., 2017; Golovnev et al., 2018), analgesic, bronchodilator, vasodilator, anti-parkinsonian, and antimalarial and anti-allergic agents (Davoll et al., 1972; Broom et al., 1976; Grivsky et al., 1980; Heber et al., 1993; Ghorab and Hassan, 1998).

Various synthetic methods have been introduced for the preparation of 5-arylidene barbituric acid derivatives, in which different catalysts, including solvent-free grinding using NH₄SO₃H (Li et al., 2006), microwave irradiation (Dewan and Singh, 2003), an infra-red promoted route (Alarreca et al., 2000), and condensation using ionic liquid media (Wang et al., 2005), are employed.

Although some researchers have reported this reaction with the use of no catalyst (Vieira et al., 2011; Figueroa-Villar and Vieira, 2013; Vieira et al., 2015), irradiation of visible light (Kumari et al., 2021), the following catalysts are used and introduced in this regard: [DABCO](SO₃H)₂Cl₂ (Shirini et al., 2015), [DABCO] (SO₃H)₂(HSO₄)₂ (Seyyedi et al., 2016), p-nanoporous MMT-HClO₄ (Mashhadinezhad et al., 2018), dodecylbenzensulfonic acid (DBSA) (Hosseini et al., 2016), FeCl₃·6H₂O (Kefayati et al., 2014), ethylenimine nitrate (Hu et al., 2004), silico-tungstic acid (Li and Sun, 2009), amino-sulfonic acid (Li et al., 2006), NaOH/β-ash (Gadekar and Lande, 2012), sodium p-toluene sulfonate (NaPPTS) (Kamble et al., 2010), CoFe₂O₄-NPs (Rajput and Karur, 2013), non-catalyst/infrared irradiation (Alarreca et al., 2000), BF₃/nano γ-Al₂O₃ (Mirjalli et al., 2015), succinimidinium N-sulfonic acid hydrogen sulfate ([SuSA-H]HSO₄) (Abedini et al., 2016), basic alumina (Khalafinezhad and Hashemi, 2001), Verjuice (Safari et al., 2019), sulfonic acid functionalized nanoporous silica (SBA-Pr-SO₃H) (Shirini et al., 2015), copper oxide nanoparticles (CuO-NPs) (Dighore et al., 2014), aminosulfonic acid (NH₂SO₃H) (Li et al., 2006), 2-amino-3-(4-hydroxyphenyl) propanoic acid (L-tyrosine) (Thirupathi et al., 2013), CoFe₂O₄ nanoparticles (Rajput and Kaur, 2013), sodium acetate (CH₃COONa) (Uttam, 2016), 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) (Wang et al., 2005), polyvinyl pyrrolidone stabilized nickel nanoparticles (PVP-Ni-NPs) (Kurhana and Vij, 2010), cetyltrimethyl ammonium bromide (CTMAB) (Ren et al., 2002), ethyl ammonium nitrate (EAN) (Hu et al., 2004), ZrO₂·SO₄·2H₂O (Jin et al., 2007), sodium p-toluene sulfonate (NaPPTS) (Kamble et al., 2010), Ce₂MgxZr₁−xO₂ (CMZO) (Rathod et al., 2010), taurine (Daneshvar et al., 2018), L-proline-N①-toluene sulfonate (Patil et al., 2020), PVC/NiFe₂O₄/PVP composite (Denho Khalaji, 2021), tartaric acid: choline chloride (Theresa et al., 2021), H₂O₂:HCl (2:1) (Sukanya et al., 2021), glacial acetic acid (Najafi et al., 2022), acetic acid (Deotale and Dholande, 2020), [H₂-Bpy][H₃PO₄] (Darvishzad et al., 2021), [nano-Fe₃O₄/SiO₂@(CH₃)₂-1-methyl imidazole]H₂SO₄ (Yadollahzadeh, 2022).
FIGURE 1
(A) TG and DSC curves (B) and XRD patterns of Bi$_2$O$_3$ nanostructures synthesized under optimal conditions of microwave route.

FIGURE 2
SEM micrograph of the Bi$_2$O$_3$ nanostructure by different magnification (A) 64 kx and (B) 58 kx. (C) TEM image of Bi$_2$O$_3$ sample synthesized under optimal conditions of microwave irradiation.
and potassium impregnated over mixed oxides (K2O/Al2O3-CaO) (Vaid et al., 2022). The methods adopted to produce these heterocyclic compounds have been useful and effective; however, the methods also have their own disadvantages and drawbacks, including expensive catalysts and reagents, harsh conditions for the catalyst synthesis, the use of contaminated organic solvents and/or corrosive inorganic acids, tedious laboring, non-reusability of the catalyst, and the need for extra amounts of the reagent or others as well as the incorporation of self-condensation and bis-addition.

Using water as the reaction medium, in addition to providing the advantage of organic synthesis in an aqueous medium, directs the procedure toward a more environmentally benign path. Moreover, in situ reductant generation decreases the purification steps and the waste generation, which facilitates the procedure and makes it more practical.

Cobalt nano-catalyst has been utilized successfully so that it leads to the desired results in the synthesis of arylidene barbituric acid derivatives.

In this work, novel nanostructures of Bi2O3 products are prepared under microwave irradiation with ideal physiochemical properties. For this purpose, final nanostructures were characterized by relevant analyses and the microwave process was optimized to select the desired products. Finally, the practical application of these nanostructures was investigated in the nano-catalyst reaction of the preparation of benzylidene barbituric acid derivatives.

2 Experimental section

2.1 Chemicals and reagents

Al2O3·4SiO·H2O (MW: 224.1450 g/mol, 99.99%), Bi (NO3)3·5H2O (MW: 485.0715 g/mol, 99.98%), and barbituric acid and aromatic aldehyde derivatives were supplied from Merck Chemical Company. The as-received materials were used with no purification.

2.2 Material characterization

The thermodynamic behavior of the Bi2O3 nanostructures was analyzed with 5 K/min using thermogravimetric analysis (TGA) and a differential scanning calorimetry (DSC) system (Netzsch QMS403C). The X-ray diffraction (XRD) patterns of the samples were analyzed on an X’Pert Pro PANalytical diffractometer using CuKa radiation. XRD was performed at a 2theta range of 10–90.

The surface morphology of the Bi2O3 nano-catalyst was evidenced by scanning electron microscopy (SEM, Hitachi, S-4800, 15-25 kV). The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) measurements were applied using Micrometrics ASAP 2010 analyzer to calculate the surface area and pore size distributions of crystals scratched from the Bi2O3 nanostructures. The magnetic hysteresis loops were recorded using a vibrating sample magnetometer (Changchun Yingpu, VSM-300). FT-IR
spectroscopy was performed by a PerkinElmer FT-IR 240-C spectrophotometer (KBr). \(^{13}\)C NMR and \(^1\)H NMR (400, 300, and 250 MHz) spectra were obtained by a Bruker Av-400 spectrometer in DMSO-d\(_6\) using tetramethylsilane (TMS) as the internal standard. Melting points were measured using Electrothermal 9100 apparatus and were then corrected. The progress of reactions was assessed using thin layer chromatography (TLC), and the products were identified based on their melting points and IR spectra in comparison to the authentic samples and those reported in the literature. The reaction yields were estimated with regard to the isolated products.

2.3 Bi\(_2\)O\(_3\) nano-catalyst preparation

In order to synthesize of Bi\(_2\)O\(_3\) nanostructures, the solutions including 2 mmol Bi (NO\(_3\))\(_3\).5H\(_2\)O in 10 ml ethylene glycol (Sol. A) and 2 mmol Al\(_2\)O\(_3\).4SiO\(_2\).H\(_2\)O in 10 ml ethylene glycol (Sol. B) were separately prepared under environmental conditions. The obtained solutions (Sol. A and Sol. B) were stirred at a temperature of 60°C for a period of 20 min. The obtained mixture has been entered into a microwave reactor and has been placed under the optimal conditions of 120 W for a time duration of 15 min at a microwave temperature of 26°C. Calcinations' procedures were then performed on the sample so that a pure Bi\(_2\)O\(_3\) nanostructure was created. At the end, the products were washed three times with distilled water to eliminate impurities existing in the structure. Also, in order to dry the products, they have been placed in the oven at up to 80°C. After 2 h, the primary nuclei related to the formation of Bi\(_2\)O\(_3\) nanocrystals were formed.

2.4 General procedure for the synthesis of benzylidene barbituric acid derivatives

A mixture of barbituric acid (1 mmol), aldehyde (1 mmol), and 20 W% (0.029 g) Bi\(_2\)O\(_3\) nano-catalyst in water (10 ml) was stirred at room temperature. The completion of the reaction was monitored by TLC [ethyl acetate: n-hexane (4:6)]. To gain pure benzylidene barbituric acid derivatives, when the reaction was completed, the mixture was filtered, and the solid retentate was washed three times with 10 ml of water.

3 Result and discussion

3.1 Characterization of Bi\(_2\)O\(_3\) nano-catalyst

3.1.1 Thermodynamic and nanocrystalline behaviors

Figure 1A shows the thermodynamic behavior of Bi\(_2\)O\(_3\) samples from environment temperature up to 700°C. Based on TG analysis, four observable peaks have been presented. The peak at the temperature of 60°C was related to the evaporation of surface water. In the second stage (91°C), the impurities and solvents trapped in the network vanished. In order to create a pure Bi\(_2\)O\(_3\) sample, it was better to heat up the samples to this temperature range. A considerable weight reduction occurred within the temperature of 214°C, which can be attributed to the destruction of the Bi\(_2\)O\(_3\) sample. The remaining sample components also collapsed at 368°C. Based on the DSC curve, the presence of endothermic peaks showed the energies required for weight reduction of the Bi\(_2\)O\(_3\) sample components in each one of the mentioned stages. Since each one of the DSC peaks was in accordance with the TG data, therefore, the product had not undergone phase change in the abovementioned temperature range (Sargazi et al., 2018). These results were consistent with the XRD data that confirmed the presence of pure single phase in the Bi\(_2\)O\(_3\) sample. The XRD patterns of the nanostructures have been presented in Figure 1B. The diffracted peaks indicated that the sample had been indexed in the BCC system with the Bi\(_2\)O\(_3\) crystalline phase (JCPDS no. 34-0097) (Hwang et al., 2018). Based on the results, no peaks
related to the presence of impurity or the formation of multiple phases have been observed, which confirmed the successful synthesis of the pure structure of Bi$_2$O$_3$ samples. The presence of some sharp peaks indicated that the samples had a high crystalline structure (Zhang et al., 2019). As a result, the effective microwave route affected the formation of Bi$_2$O$_3$ nano-catalyst with high purity and significant crystalline percentages.

3.1.2 Morphology and size distribution (before reaction)

The morphology and particle size distribution of the Bi$_2$O$_3$ sample (before reaction) with various magnifications have been shown in Figures 2A and B. According to these images, the SEM micrographs confirmed the formation of Bi$_2$O$_3$ crystals with tiny sizes. The size of crystals was in the

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**TABLE 1** Synthesis of 3j in the presence of different solvents and amounts of catalyst.

| Entry | Catalyst (W%) | Solvent | Time (h/min) | Temp. | Yield (%) |
|-------|---------------|---------|--------------|-------|-----------|
| 1     | –             | –       | N.R.         | r.t.  | –         |
| 2     | Bi$_2$O$_3$ 20% | –       | N.R.         | r.t.  | –         |
| 3     | –             | H$_2$O  | 24 h         | r.t.  | 33        |
| 4     | Bi$_2$O$_3$ 20% | H$_2$O  | 2 min        | r.t.  | 91        |
| 5     | Bi$_2$O$_3$ 20% | EtOH    | 3 min        | r.t.  | 40        |
| 6     | Bi$_2$O$_3$ 20% | EtOH/H$_2$O (1:1) | 3 min | r.t.  | 36        |
| 7     | Bi$_2$O$_3$ 20% | CH$_3$OH | 3 min        | r.t.  | 35        |
| 8     | Bi$_2$O$_3$ 20% | CH$_3$CN | 3 min        | r.t.  | 32        |
| 9     | Bi$_2$O$_3$ 20% | CH$_3$I  | 3 min        | r.t.  | 24        |
| 10    | Bi$_2$O$_3$ 20% | CH$_3$Cl  | 3 min       | r.t.  | 23        |
| 11    | Bi$_2$O$_3$ 20% | C$_6$H$_6$ | 3 min       | r.t.  | 18        |
| 12    | Bi$_2$O$_3$ 10% | H$_2$O    | 2 min        | r.t.  | 73        |
| 13    | Bi$_2$O$_3$ 15% | H$_2$O    | 2 min        | r.t.  | 87        |
| 14    | Bi$_2$O$_3$ 25% | H$_2$O    | 2 min        | r.t.  | 89        |
| 15    | Bi$_2$O$_3$ 30% | H$_2$O    | 2 min        | r.t.  | 58        |
| 16    | Bi$_2$O$_3$ 35% | H$_2$O    | 2 min        | r.t.  | 52        |
| 17    | Bi$_2$O$_3$ 20% | CH$_2$Cl$_2$ | 3 min    | r.t.  | 46        |

**TABLE 2** Benzylidene barbituric acid derivatives obtained via the Knoevenagel condensation of benzaldehyde derivatives and barbituric acid using Bi$_2$O$_3$ nano-catalyst.

| Entry | Ar X Product | Time (min) | Yield (%) | m.p. (°C) | Ref |
|-------|--------------|------------|-----------|-----------|-----|
| 1     | 2-OHC$_6$H$_5$- O | 3a         | 93        | 248-250  | 249-250 | Seyyedi et al. (2016) |
| 2     | 4-MeOC$_6$H$_4$- O | 3b         | 97        | 295-297  | 294-297 | Daneshvar et al. (2018) |
| 3     | 2-MeOC$_6$H$_4$- O | 3c         | 90        | 267-269  | 268-269 | Seyyedi et al. (2016) |
| 4     | P-(Me)$_2$NC$_6$H$_4$- O | 3d        | 97        | 277-279  | 278-279 | Seyyedi et al. (2016) |
| 5     | C$_6$H$_5$CH = CH- O | 3e         | 95        | 267-268  | 268 | Daneshvar et al. (2018) |
| 6     | 4-OHC$_6$H$_5$- O | 3f         | 98        | >300 >300 | Daneshvar et al. (2018) |
| 7     | 2-NO$_2$C$_6$H$_4$- O | 3g         | 97        | 271-274  | 271-273 | Daneshvar et al. (2018) |
| 8     | 4-NO$_2$C$_6$H$_4$- O | 3h         | 76        | 269-271  | 268-270 | Seyyedi et al. (2016) |
| 9     | 2-CIC$_6$H$_5$- O | 3i         | 96        | 250-252  | 249-251 | Daneshvar et al. (2018) |
| 10    | 4-CIC$_6$H$_5$- O | 3j         | 94        | 298-300  | 298-300 | Daneshvar et al. (2018) |
| 11    | C$_6$H$_5$- O | 3k         | 96        | 250-252  | 249-252 | Daneshvar et al. (2018) |
| 12    | 3,4,5-(OCH$_3$)$_3$C$_6$H$_2$- O | 3l        | 98        | 249-250  | 238-250 | Tomasic et al. (2018) |
| 13    | 2,4-CIC$_6$H$_4$- O | 3m         | 95        | 268-270  | 265-270 | Jin et al. (2007) |
| 14    | 4-OH-3-OCH$_3$C$_6$H$_3$- S | 3n       | 97        | 292-293  | 293-294 | Jin et al. (2007) |
| 15    | 4-MeC$_6$H$_4$- O | 3o         | 88        | 273-274  | 274-275 | Stojiljkovic et al. (2021) |
| 16    | 5-Br-2-OHC$_6$H$_5$- S | 3p       | 98        | 269-271  | 268-270 | Hosseini et al. (2016) |

*aIsolated yield.*
nanometric range, which was in accordance with the XRD results. Also, SEM results showed that the surface morphology of both samples was plate-like nanostructures and particles have been distributed uniformly without any evidence of agglomeration. In addition, the Bi$_2$O$_3$ samples showed a dense surface with good connections between the crystals. In order to obtain the particle size distribution of the Bi$_2$O$_3$ sample, a TEM image was obtained. According to this image (Figure 2C), Bi$_2$O$_3$ nanostructures have narrow particle sizes around 45 nm. This size distribution is with SEM results. Also, according to the TEM image, there is no evidence of an agglomeration process in the product, which confirmed the results obtained from SEM images.

3.1.3 Textural and magnetic properties

The N$_2$ adsorption/desorption isotherm and the porosity of Bi$_2$O$_3$ nano-catalyst synthesized under optimal conditions of microwave irradiation have been exhibited in Figures 3A and B, respectively.

According to classical isotherms (Wang et al., 2018b), the Bi$_2$O$_3$ sample had an adsorption/desorption behavior similar to the type IV isotherms, which indicated the mesoporous size distribution for them (Gao et al., 2019). Based on the BJH method, the Bi$_2$O$_3$ samples also had an average pore size distribution of 4 nm, which was in accordance with the type IV isotherms. As an important result, the Bi$_2$O$_3$ product has a mesoporous size distribution, which is significant compared to previous studies (Bakhshi et al., 2022; Wang and Lu, 2019) and bulk samples (non-porous system). This subject facilitated the potential application of products in the catalyst procedure. According to the results obtained from the BET technique, the sample had a surface area of about 783 m$^2$/g (Liu et al., 2018), which was considerable compared to the previous samples and bulk compound (about 100 m$^2$/g). The increase in surface area and porosity of the products can be attributed to the desirable conditions of nucleation, growth of crystals, and the effective impact of microwave synthesis parameters (Huy et al., 2019).

Figure 4 exhibits the magnetic hysteresis of the Bi$_2$O$_3$ nanostructures prepared by the microwave route under optimal conditions. The saturation magnetization of this novel nano-catalyst is about 65/4 emu/g. Also, it displays a small coercivity along with narrow hysteresis, which confirms the soft magnetic properties of this sample. This can be related to the results of the small crystalline size of Bi$_2$O$_3$ nanostructure that approved the inverse relation between coercivity and size distribution by D6 (Sargazi et al., 2018).

| Run                              | Yield of 3j (%) |
|----------------------------------|----------------|
| First of renewed catalyst        | 98             |
| Second of renewed catalyst       | 95             |
| Third of renewed catalyst        | 93             |
| Fourth of renewed catalyst       | 90             |

### Table 3
Reusability of the catalyst in the preparation of 5-benzylidene barbituric acid derivative of 4-chlorobenzaldehyde.

Scheme 2
Proposed mechanism for the synthesis of arylidene barbituric acid derivatives in the presence of Bi$_2$O$_3$ nano-catalyst.
3.2 Synthesis of benzylidene barbituric acid using Bi₂O₃ nanoparticles

This project mainly aimed to synthesize recyclable bismuth oxide nanoparticles using a facile, high-performance, and pro-environmental method. The nanoparticles were used as the catalyst in the production process of the arylidene barbituric acid derivatives (Scheme 1).

The performance of the Bi₂O₃ nano-catalyst was investigated using barbituric acid (2) and 4-chlorobenzaldehyde (1j) as the model substrate. In order to optimize the reaction conditions, various weight percentages of catalyst and diverse solvents were exploited.

First, the model reaction was performed solvent-free with no catalyst. As expected, the reaction did not happen noticeably. In addition, in another test, no reaction happened in the absence of the solvent and the presence of the catalyst (Table 1, Entry 1, 2).

Afterward, with the use of the catalyst (20 W%) and several solvents, which were different in terms of polarity and protic nature, such as methanol, ethanol, C₂H₅OH/H₂O, chloroform,

### Table 4 Comparison of various methods for the synthesis of (thio)barbituric acid.

| Entry | Catalyst | Amount of catalyst | Conditions | Time (min) | Yield (%) | Ref                      |
|-------|----------|--------------------|------------|------------|-----------|--------------------------|
| 1     | BF₃/nano-γ-Al₂O₃ | 60 mg             | Ethanol/r.t. | 30         | 84        | Mirjalili et al. (2015)  |
| 2     | PVP-Ni NPs   | 100 mg            | Ethylene glycol, 50°C | 10-15   | 93        | Khurana and Vij (2010)  |
| 3     | [bmmim]BF₄   | 0.2 ml            | Grinding-laying | 120      | 78        | Wang et al. (2005)       |
| 4     | EAN        | 2 ml              | r.t.        | 180        | 83        | Hu et al. (2004)         |
| 5     | CH₃COONa     | 100 mol%          | Gridding    | 10         | 91        | Uttam (2016)             |
| 6     | CMZO      | 200 mg            | EtOH, 60°C-70°C | 60        | 85        | Rathod et al. (2010)     |
| 7     | P-Dodecylbenzene sulfonic acid (DBSA) | 30 mol% | H₂O, reflux | 67        | 62        | Hosseini et al. (2016)   |
| 8     | [H₂-pip][H₂PO₄]₂ | 5 mol%        | H₂O/EnOH (1:1) 80°C | 9        | 96        | Darvishzad et al. (2019) |
| 9     | Taurine    | 20 mol%           | H₂O, 90°C  | 9          | 96        | Duaeshvar et al. (2018)  |
| 10    | FeCl₃.6H₂O  | 15 mol%           | H₂O, reflux | 35         | 80        | Kefayati et al. (2014)   |
| 11    | NP MMT-HClO₄ | 10 mg           | H₂O, 70°C  | 4          | 94        | Mashhadimezhad et al. (2018) |
| 12    | NaPTSA/r.t. | 50 mol%           | r.t.       | 4          | 92        | Kamble et al. (2010)     |
| 13    | Verjauice  | 10 ml             | 60°C       | 7          | 96        | Safari et al. (2019)     |
| 14    | Co₃Fe₂O₄ NPs | 1 mol%         | H₂O, EtOH/r.t. | 2–6      | 94–80     | Rajput and Kaur (2013)   |
| 15    | [SuSA-H]HSO₄ | 5 mol%         | H₂O/r.t.   | 2–12       | 80–98     | Abedini et al. (2016)     |
| 16    | Co₄O₆ nano-catalyst | 20 W% | H₂O/r.t. | 3–25       | 98        | Yahyazadehfar et al. (2019) |
| 17    | Bentonite (Al₂O₃.4SiO₂.H₂) | 25 mol% | 90/C₂H₂O | 5–25       | 90–98     | Yahyazadehfar et al. (2020) |
| 18    | Bi₂O₃ nano-catalyst | 20 W% | H₂O/r.t. | 3         | 98        | This work                |

![FIGURE 5](image-url)  
(A) SEM micrograph and (B) XRD image of the Bi₂O₃ nanostructure after the catalytic reaction.
toluene, dichloromethane, and acetonitrile, the reaction was reassessed. Monitoring the reaction revealed that the polar solvents such as methanol, ethanol, and acetonitrile were much more effective than the non-polar ones. This might be attributed to the much better dispersion of the catalyst as well as the much better solubility of the reagents in the polar solvents. In the next experiment, water as a green solvent was used, and the reaction progress was assessed. It was found that the synthesis of arylidene barbituric acid catalyzed by Bi$_2$O$_3$ nanostructure progressed with higher yields (Table 1).

Optimizing the consumption of Bi$_2$O$_3$ nano-catalyst showed that its concentration plays a decisive role in the reaction efficiency. As such, increasing the catalyst concentration from 5 to 20 W% raised the product yield. On the other hand, the catalyst concentrations above 20 W% reduced the yield. Consequently, the optimum level of the catalyst was set as 20 W% for the reaction at room temperature (Table 1).

After optimizing the catalyst, the reactions of different aldehydes with both electron-donating and electron-withdrawing substitutions were studied. It was noticed that the nano-catalyst can catalyze their conversion to the corresponding products in high yields during a short reaction time (Table 2). In fact, electron-donating and electron-withdrawing functional groups on the aromatic ring of aldehydes have no considerable effect on their reaction yields.

Compared to our previous reports on the production of benzylidene barbituric acid in the presence of Co$_3$O$_4$ nano-catalyst at 90°C, the results of this experiment are quite remarkable and promising in terms of the reaction conditions (i.e., aqueous medium, room temperature, and short periods of time). In most cases, the magnet was stopped as soon as the catalyst was introduced into the reaction medium, and in most cases, the reaction was completed in less than 3 min.

All the products were identified by infrared (IR) spectroscopy, and their melting points were compared with the reference data. For more certainty, the structure of the product $3m$, $3n$, and $3o$ was verified using $^1$H NMR spectroscopy as well.

For compound $3i$, the main absorption peaks in the FT-IR spectrum appeared at the wavenumbers of 1,654, 1,733, 1,751, 3,240, and 3,629 cm$^{-1}$, which are attributed to the C=O bond, two groups of C=O stretching vibration, sp² C-H stretching, and the secondary N-H stretching, respectively. In $^1$H NMR spectral analyses of this compound, it was observed that two characteristic singlets in $\delta$ 11.33 and 11.20 ppm for the NH groups of the pyrimidine ring and other singlets at $\delta$ 8.24 and 7.81 ppm due to aromatic protons and CH = C olefin proton and aromatic protons, respectively. Also, two signals for the methoxy groups appeared at $\delta$ 3.77 and 3.80 ppm. It indicated that barbituric acid was added successfully to 3,4,5-trimethoxy benzaldehyde and the compound "3i" was prepared.

5-(4-Hydroxy-3-methoxybenzylidene)pyrimidine-2,4,6 (1H,3H,5H)-trione (3n): Yield: 95%. MP = 268–270°C. IR (KBr, cm$^{-1}$): 3,207, 1,748, 1,696, and 1,664. $^1$H NMR (250 MHz, DMSO-d$_6$) $\delta$: 3.77 (s, OCH$_3$), 3.80 (s, 2 OCH$_3$), 7.81 (s, H-Ar), 8.24 (s, 1H, CH = C), 11.20 (s, NH), and 11.33 (s, NH).

5-(3,4,5-Trimethoxybenzylidene)pyrimidine-2,4,6 (1H,3H,5H)-trione (3l): Yield: 98%. MP = 249–250°C. IR (KBr, cm$^{-1}$): 3,240, 1,733, and 1,654. $^1$H NMR (250 MHz, DMSO-d$_6$) $\delta$: 3.77 (s, OCH$_3$), 3.80 (s, 2 OCH$_3$), 7.81 (s, H-Ar), 8.24 (s, 1H, CH = C), 11.20 (s, NH), and 11.33 (s, NH).

Reusability of the heterogeneous catalyst is an important characteristic that shows the compatibility of a catalyst with the green chemistry rules and put an end to the use of harmful and costly metal catalysts while decreasing the cost of products. These factors are of crucial importance from an environmental, economic, commercial, and industrial point of view.

To investigate the potential of this catalytic procedure and to fulfill the requirements of green chemistry and industrial application, the catalyst reusability was evaluated for the synthesis of 5-benzylidene barbituric acid derivative and Knoevenagel condensation using 4-chlorobenzaldehyde and barbituric acid as model reaction under the optimized reaction conditions. For this purpose, after completion of each run of reaction, the product of each step was dissolved in warm ethyl acetate, and the catalyst was subsequently recovered by centrifuging. In order to remove tars more efficiently from the catalyst surface, it was rinsed with H$_2$O twice, dried in an oven at 70°C overnight, and used in the next run. On the other hand, the solvent was removed by evaporation, and the product residue was gathered. The yields of four successive cycles from the first to fourth runs at room temperature were 98%, 95%, 93%, and 90%, respectively (Table 3). The results show no significant decrease in the performance of the recovered catalyst compared to the fresh state, excellent yields were produced with a recovered catalyst in four successive runs, and the average isolated yield for four runs was 94%, which clearly demonstrates the practical recyclability of this catalyst several times successively.

The possible mechanism of the barbituric acid and aryl aldehyde reaction, known as "Knoevenagel condensation," is illustrated in Scheme 2. The barbituric acid structure first converts to the enol form (keto-enol tautomerism in the first step), and it then attacks the aldehyde (second step) activated by Bi$_2$O$_3$ nano-catalyst as a Lewis acid. Finally, the dehydration process leads to the final product (last step).

3.2.1 Comparison of the catalytic ability

With the aim of demonstrating the potential and the performance of the proposed method in preparing this type of
compound, the method was compared with some other previously reported methods. Table 4 summarizes the results of the comparison. It can be seen that this novel method is superior to many others, especially in terms of reaction time, catalyst reusability, and bio-environmental considerations.

3.2.2 XRD and SEM of nanostructures after the reaction

In order to characterize the nanostructures after catalytic activity, the Bi$_2$O$_3$ nanostructures were analyzed by XRD and SEM (Figure 5). By comparing the results obtained from these analyses with the previous section (3.1.2), it is concluded that the morphology (A) and crystallinity behavior (B) of the samples did not significantly change after the reaction. Also, based on the SEM image, the particle size distribution of the sample has not changed much. As an important result, the structural stability of the Bi$_2$O$_3$ nanostructures is not affected by catalytic applications.

4 Conclusion

In this work, an effective strategy of the microwave route has been proposed to synthesize Bi$_2$O$_3$ nanostructures with a single phase over a short period of time and with optimal energy. This cost-effective, efficient, and environment-friendly route has created controlled properties of products that affect their catalytic applications with high efficiency. The results of the related analyses indicated that the Bi$_2$O$_3$ samples had high thermal stability (210°C), narrow particle size distribution (nanoscale distribution), and a desirable surface area (783 m$^2$/g). These properties differentiated the Bi$_2$O$_3$ nano-catalysts developed in this study from the previous samples. The results showed that the application of optimal conditions of microwave irradiation also affected the catalytic efficiency of the Bi$_2$O$_3$ products.

So, the prepared Bi$_2$O$_3$ nano-catalyst is introduced as an efficient nano-catalyst to catalyze the synthesis of benzylidene barbituric acid derivatives. The short reaction time, facile work-up process, recyclability of the catalyst, economic advantage, and aquatic medium make this method promising. This method is attractive due to its safe and environment-friendly process. The novel Bi$_2$O$_3$ nano-catalyst developed in this study opens up new options for further application in potential fields.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

MY: completed the experiment, analyzed the result data, and wrote the manuscript, ES: proposed the ideas, analyzed the result data, and reviewed and edited the manuscript, SA and DG: played the roles of consultants in the research stages. This article has been read by all authors and agreed to be published.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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