



# Sonochemical Facile Synthesis of Bismuth Oxide Nanoparticles Using Citrus Lemon Extract and Its Catalytic Activity on Azo Dye Degradation

G. Kumaravel Dinesh · R. Saranya

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**Abstract** The synthesis of bismuth oxide nanoparticles through sono-cavitation using citrus lemon extract as a simple, eco-friendly and cost-efficient method was evaluated. The aqueous extract of citrus lemon acted as a bio-reducing and capping/stabilizing agent in the single-step biosynthesis of bismuth oxide nanoparticles. Different instrumental techniques have been used to characterize the biosynthesized bismuth oxide nanoparticles, including UV–vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy (EDS). UV–vis spectroscopy revealed the formation of stable bismuth oxide nanoparticles at  $\lambda_{\text{max}}$  of 400 nm with a surface plasmon resonance (SPR) band. TEM revealed that the biosynthesized bismuth oxide nanoparticles were rod shaped with a particle

size of 26 nm. A potential mechanism for the formation of bismuth oxide nanoparticles with the influence of sono-cavitation has been suggested based on the observed findings. These catalytic capabilities of the bio-synthesized bismuth oxide nanoparticles were then evaluated by degradation of toxic azo dyes under different laboratory conditions. The azo dye Congo red (CR) was effectively degraded to 86% within 30 min under optimum experimental conditions using 0.12 g/mL catalyst. Thus, the phytochemical citrus lemon offers a cheap and eco-friendly solution for the synthesis of catalytic nanoparticles to degrade highly toxic organic compounds such as azo dyes.

**Keywords** Sono-cavitation · Bismuth oxide · Citrus lemon · Azo dye

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## 1 Introduction

The need of our world in a healthy, clean, and hygienic state for human survival is one of the biggest challenges faced by the researchers. Water plays a crucial role in sustaining life from living cells to the whole environment. Sadly, vast quantities of hazardous industrial waste are being dumped into natural water bodies water without adequate treatment, damaging the ecosystem. Among organic pollutants, 20% of dyes present in textile effluents are released into the environment as a result of urbanisation and industrialization (Deng et al., 2019). The toxicity and

turbidity caused by most synthetic dyes are particularly harmful to aquatics and other living organisms. Nearly 70% of the dyes used last year in industries belong to the azo dyes group. Azo dyes molecules consist of a group of (-N=N-) aromatic rings (Liu et al., 2018; Rawat et al., 2018). Due to their low biodegradability and toxicity, treating these industrial effluents is a major challenge and the development and implementation of efficient processes is therefore necessary. Among the most polluting dyes, congo Red ( $C_{32}H_{22}N_6O_6S_2Na_2$ ), a high-molecular, complex molecular structure synthetic diazo dye compound, is commonly used in textile and plastics industries and has significant impacts on the environment. This dye is very toxic, carcinogenic and resistant to traditional wastewater treatment (Askarniya et al., 2020; Shen et al., 2017). Furthermore, traditional treatment methods could produce secondary pollutants which are more difficult to monitor and screen after discharge.

Recently, advanced oxidation processes (AOPs) has emerged to achieve total mineralization of organic pollutants in wastewater. Among AOPs, heterogeneous catalysis became of great interest due to its environmentally friendly nature and the possibility of recycling the catalyst after treatment (Ma et al., 2019). The advanced oxidation method focuses on the formation of hydroxyl radicals on the catalyst surface, which attack and degrade the contaminants. In the presence of energy sources such as ultraviolet light or ultra-sonication, active hydroxyl radicals can be produced by chemical oxidizing agents such as ozone or peroxide (Boczkaj et al., 2018). This treatment provides efficient degradation of textile dye effluents by cavitation process through the cyclic growth and collapse of gas bubbles. Extremely high pressures and temperatures are achieved in the centre of collapsing bubbles, called 'hot spots'. Hot spots enhance the chemical activity where the formation of active reactive radicals like  $\bullet OH$  happen (Soltani et al., 2019). The addition of catalysts during the cavitation process further improves the degradation performance (Jia et al., 2019). This method provides better performance in controlling the contaminants present in aquatic environment.

Semiconductor oxides are mostly used in environmental remediation due to their stability, high activity, low cost and non-toxic nature. Among semiconductor oxides, bismuth oxide ( $Bi_2O_3$ ) has a range of desirable characteristics, including high band gap

(2–3.93 eV), and is used in wide range of applications as electrochemical sensor, conductivity, optical, photocatalytic and biomedical devices (Hou et al., 2013; Labib, 2017). Due to its large specific surface area and higher efficiency of the electron-hole splitting,  $Bi_2O_3$  photocatalytic activity is highly influenced by single layered structure and its morphology. Based on the morphology and structure nanoparticles exhibit different catalytic properties in wastewater remediation (Xiao et al., 2013). Despite several synthetic techniques have been investigated to synthesize  $Bi_2O_3$  nanoparticles with different morphologies (Cheng & Kang, 2014; Yan et al., 2014), finding a simple and low-cost method to obtain  $Bi_2O_3$  scaffold nanostructure is still a challenge.

In recent years, research is focusing on developing effective green chemistry techniques, such as the use of microbial agents, fungi and plant extracts, for nanoparticle synthesis. Plant mediated nanoparticles are worthy of attention because of their simplicity, fast synthesis, and environment-friendliness, and they are able to potentially make treated molecules biocompatible. The usage for biosynthesis of bismuth nanoparticles of naturally available citrus fruit extract has not been investigated so far. A classic example of the readily available natural fruit is Citrus limon, Citrus reticulata and Citrus sinensis. It has been reported that the lemon extract containing citric acid and ascorbic acid acts as a reducing agents and helps in anti-oxidant activity (Ortega et al., 2021). Citric acid is a reducing agent and helps in the formation of metal ions that improves the overall efficiency in catalytic cycles (Mahiuddin & Ochiai, 2022) by enhancing and stabilizing the reduction of metal ions.

Sonochemical synthesis of catalysts offers numerous advantages over conventional methods in terms of environmental friendliness, control over particle properties, catalytic performance, and efficiency (Adamou et al., 2023; Li et al., 2021). Firstly, it eliminates the need for hazardous solvents and allows for finer control over the catalyst's particle size and morphology (Li et al., 2021). Secondly, sonochemical synthesis leads to improved catalytic activity and selectivity as it produces catalysts with higher surface areas at shorter reaction times and offers better dispersion of active sites. In this study, citrus fruit extract is used, for the first time, as a surfactant for the synthesis of  $Bi_2O_3$  with different size and morphology. The obtained  $Bi_2O_3$  polymorphs have been

extensively characterized by XRD, FT-IR, EDS, XPS, SEM and HR-TEM. Furthermore, their catalytic activity in oxidation of congo red dye and the respective degradation rate constants, were also evaluated.

## 2 Experimental Methodology

### 2.1 Materials

Bismuth (III) oxynitrate ( $\text{Bi}_5\text{H}_{17}\text{N}_4\text{O}_{22}$ , Merck) was used as a starting material to synthesize  $\text{Bi}_2\text{O}_3$ . High purity analytical reagents were used for sample solution preparation: hydrochloric acid (HCl, Merck), sodium hydroxide (NaOH, Merck) and ethanol (99.9%  $\text{C}_2\text{H}_5\text{OH}$ ). Congo red dye was obtained from Sigma-Aldrich and used as supplied. All the solutions were prepared using ultrafiltered Millipore water from Milli-Q integral. Ultrasonic Processor (Sonics, VCX 500) was used for sonolysis and sonocatalysis experimental study.

### 2.2 Methods

The citrus fruit was washed using deionized water and then finely cut into small pieces. These sections had been squeezed to remove the juice later strained over a fine nylon pore screen. The extract was centrifuged at 12000 rpm for five minutes to eliminate any impurity and used as a stock solution for the experiments.

### 2.3 Synthesis of $\text{Bi}_2\text{O}_3$ Nanoparticles

Nanosized  $\text{Bi}_2\text{O}_3$  catalyst was synthesized by preparing an aqueous solution of 0.05 M bismuth oxynitrate solution in 100 mL of Millipore water. The hydrothermal treatment was conducted by stirring for 60 min while adding the citrus extract dropwise, and subsequently heating to 110° C. For the sonochemical method, the solution was irradiated with ultrasound about 30 min for the reaction to take place. The ultrasonic processor used was equipped with a probe tip of 13 mm diameter and had an operating frequency of 20 kHz and a total active surface area of 1.33 cm<sup>2</sup>. A yellow colour solution containing  $\text{Bi}_2\text{O}_3$  nanoparticles was formed. for the nanoparticles were then harvested by precipitation and discarding the supernatant. The precipitate was purified by washing several times

with ethanol upon magnetic stirring. Subsequently, it was filtered, dried in a hot air oven at 105 °C for 24 h, and grinded for further use.

### 2.4 Characterization Study

The X-ray diffractometer (XRD) data was recorded using a Bruker diffractometer (AXS D8 Advance) Cu K $\alpha$  (40 kV, 30 mA) as the radiation source and NaI as the detector. The synthesized particles were analysed in powder form in the  $2\theta$  range from 10° to 80°. The Fourier transform infrared (FT-IR) spectra was obtained in the range 400–4000 cm<sup>-1</sup> by a Bruker spectrophotometer (IFS 66v) with 4.0 cm<sup>-1</sup> resolution by the KBr pellets technique.  $\text{Bi}_2\text{O}_3$  nanoparticles imaging was obtained by a Zeiss Ultra plus high-resolution field emission scanning electron microscopy (SEM) at an accelerating voltage of 30 kV. A 20 mm<sup>2</sup> Oxford Inca EDX detector with an energy resolution of 129 eV was used to perform the elemental qualitative analysis. The morphology, microstructure and selected-area electron diffraction (SAED) patterns were analysed using a JEOL LaB 2100 High-Resolution Transmission Electron Microscopy (HRTEM) at an accelerating voltage of 200 kV. A Shimadzu-1800 spectrometer was used to monitor the UV–visible absorption spectrum. High resolution Raman spectroscopic analysis was carried out to confirm the presence of  $\text{Bi}_2\text{O}_3$  by using a Renishaw microRaman spectrometer with 514 nm excitation wavelength (Argon ion laser).

### 2.5 Sonocatalytic Degradation Study

An ultrasonic Processor (ultrasonic probe / sonotrode) Sonics VCX 500 with an operating frequency 20 kHz and maximum power output of 500 W was used in the experimental set-up for degradation studies. The various parameters like ultrasound power, catalyst loading, pH solution, dye concentration and various inorganic salts was conducted on the degradation of congo red dye based on removal efficiency in the sample. Initially, the adsorption rate was studies by means of stirring the catalyst without the application of sono-cavitation. Later, the sonocatalytic degradation experiments were performed in 250 mL glass bottles containing 100 mL of 20 ppm CR solution. A small aliquot was extracted from the sonocavitation treated dye solution at 30 min intervals to evaluate

the congo red dye degradation using an UV–Visible spectrophotometer (Perkin Elmer, Lambda 35) at a  $\lambda_{\text{max}}$  of 488 nm. The sonocatalytic degradation efficiency of congo red dye was evaluated using the following equation:

$$\text{Degradation efficiency(\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

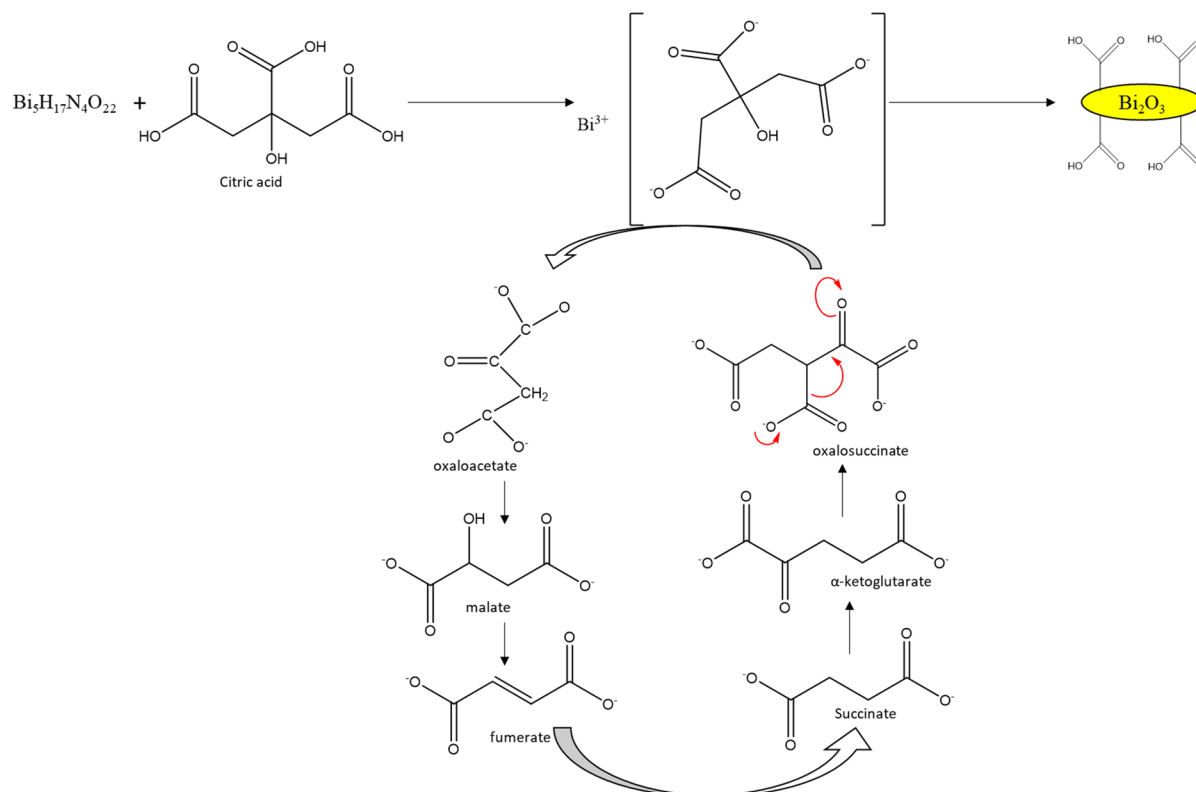
### 3 Results and Discussion

The research emphasis more on the synthesis of nanoparticles by sonocavitation mediated bio synthesis method. The reduction reaction of antioxidants phytochemicals presents in lemon extract, especially polyphenolics, ascorbic acid, flavonoids, citric acid follows tautomerization mechanism to bind the heavy metals. The presence of phenolic hydroxyl groups and citric acid as natural tricarboxylic acid (González-Molina et al., 2010) in the lemon extract increases the bonding of O–Bi–O and favours the formation of  $\text{Bi}_2\text{O}_3$  nanoparticles. The role of citric acid present in the lemon act as both reducing as well as stabilizing (capping) agent. Ascorbic acid and flavonoids in lemon extract act as chelating, stabilizing agent that facilitates the binding of metal ions and stabilization of metal nanoparticles. They reduce the reactant to metal (bismuth)  $\text{Bi}^{3+}$  and the stability of the metal depend on the weak van der Waals forces of attraction and electrostatic repulsion between the molecules present in the mixture. The ligand present in the citric acid function to make a bonding between  $\text{Bi}^{3+}$  ions and citrate molecules present creating a bismuth organic ligand complex (Milde et al., 2014). Similarly, the  $-\text{COOH}$  groups present in the solution binds easily with the metal ions forming bismuth citrate complex ion. The free carboxyl group available in the solution is deprotonated  $[(\text{citrate})^{-3}]$  therefore no hydrogen bonding occurs. The resulting citrate molecules can grab  $\text{Bi}^{3+}$  to the surface, resulting in irregular-shaped particles (Jiang et al., 2009). Volatile essential oils present in the extract acts as surfactants in the catalytic process (Mahiuddin & Ochiai, 2022). The formation of ion association with the  $\text{Bi}^{3+}$  have a reduced heteropoly form and less stable state which accelerates the reaction of bismuth with oxygen via hydrolysis to form bismuth oxide (Fig. 1). This

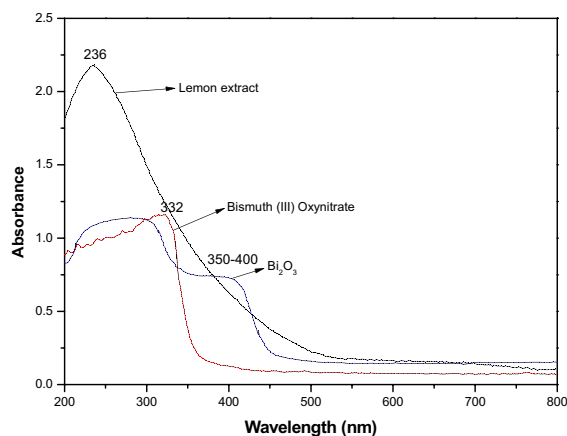
reaction mechanism enhances the appearance of yellow colour solution.

The bismuth oxide nanoparticle formation was suggested by visual observation of a yellow colour in the solution and confirmed by surface plasmon resonance (SPR) band via UV–vis spectrophotometry (Fig. 2). The lemon extract showed a strong peak at 236 nm while bismuth oxynitrate showed a strong peak at 332 nm. The absorbance intensity shifted to a longer wavelength 350 to 400 nm confirming the formation of bismuth oxide. This shift is due to the electron–hole transition occurred during  $\text{Bi}_2\text{O}_3$  formation. The optical band gap obtained for the synthesized bismuth oxide found to be 2.46 eV by Tauc equation, as previously reported (Dinesh et al., 2016; Vignesh et al., 2013).

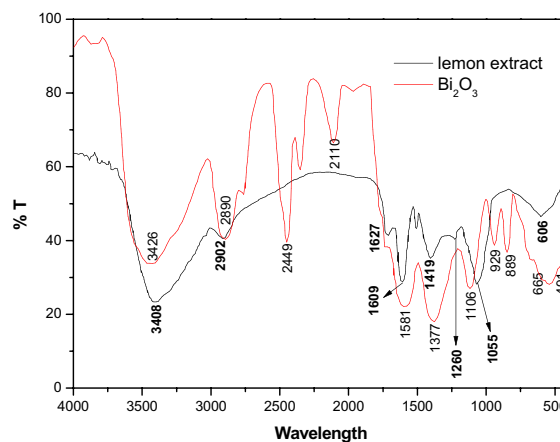
The FTIR results (Fig. 3) of the lemon extract helps in detecting the functional groups potentially involved in the chemical modifications of bismuth oxy nitrate to  $\text{Bi}_2\text{O}_3$  nanoparticles. The peaks at  $3408 \text{ cm}^{-1}$  indicate the presence of alcohol and phenol functional groups. The O–H stretch and H–bond vibrations denote the presence of flavonoids, polyphenols derived from the lemon extract (Yu et al., 2016). The band at  $2902 \text{ cm}^{-1}$  may be attributed to the incorporation of water molecules with C–C stretch and C–H stretch from hydrocarbon chains like sugars present in the plant. The bands located at 1627, 1609 and  $1419 \text{ cm}^{-1}$  were assigned to the C=O stretch carbonyl group, N–H bend primary amide from protein carboxyl sugar and C–O–H bending vibrations related to alcohol, carboxyl and ester groups, respectively. All the functional groups associated with the flavonoids, carotenoids and citric acid present in the lemon extract act as eco-friendly bioactive capping agents in bismuth oxide nanoparticle synthesis (Jeevanandam et al., 2017). The FTIR results of formed bismuth oxide was confirmed by the presence of absorption band at 929, 889, 665 and  $491 \text{ cm}^{-1}$  which are typical Bi–O–Bi bond stretching and bending vibrations (Khairnar & Shrivastava, 2019). In particular, the presence of absorption band at  $889 \text{ cm}^{-1}$  indicates the  $\delta(\text{C}=\text{O})\text{--Bi--O--Bi}$  vibrational stretch and bend due to the reduction reactions of phytochemicals and stabilization of  $\text{Bi}_2\text{O}_3$  nanoparticles (Jeevanandam et al., 2017). The band at 1377 indicate the intermediate bismuth nitrate formation during the reduction from bismuth oxy nitrate. The absorption bands at 3426 and  $1581 \text{ cm}^{-1}$  were assigned to the  $-\text{O--H}$  stretching and bending vibrations. The



**Fig. 1** Possible reduction and stabilization mechanism of  $\text{Bi}_2\text{O}_3$  nanoparticles in the presence of citrus lemon extract



**Fig. 2** UV-Vis spectra of citrus lemon extract, Bismuth (III) Oxy nitrate and  $\text{Bi}_2\text{O}_3$  nanoparticles



**Fig. 3** FTIR spectra of citrus lemon extract and  $\text{Bi}_2\text{O}_3$  nanoparticles

absorption peak at  $1106\text{ cm}^{-1}$  is characteristic from O–H stretching vibration of water molecules attached to the -Bi-Bi- compound. The weak bands emerged at

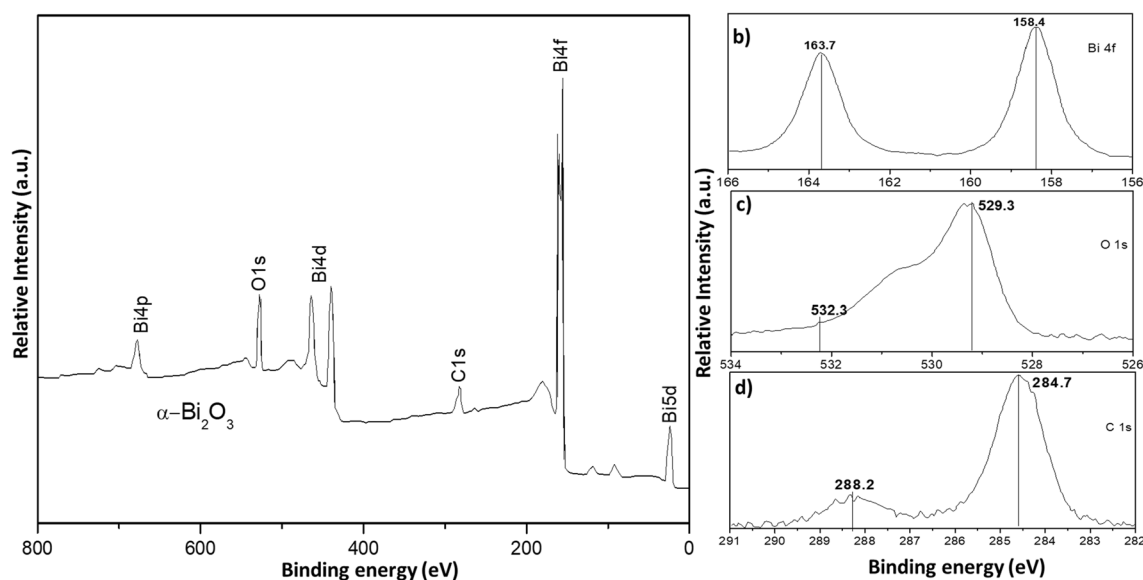
$1260\text{ cm}^{-1}$  is attributed to wagging and rocking C–H vibrations from asymmetrical stretching (C–H) bands of D-limonene. The relatively small weak associated

band at  $1055\text{ cm}^{-1}$  and  $606\text{ cm}^{-1}$  correspond to C-O stretching vibrations of citric acid and C=C bending vibrations of  $\alpha$ -Pinene (Toprakçı et al., 2023). Characteristic C-O vibrations at  $2890\text{ cm}^{-1}$  in  $\text{Bi}_2\text{O}_3$  corresponds to the weak C-O bond stretching of citric acid. The strong peak at  $1377\text{ cm}^{-1}$  corresponds to the presence of  $\text{H}_2\text{O}$ . The remarkable peaks at 2449 and  $2110\text{ cm}^{-1}$  represents the symmetrical bands of C-C of  $\alpha$ -Pinene and C-H combined with metal Bi ions respectively (Oruç et al., 2019).

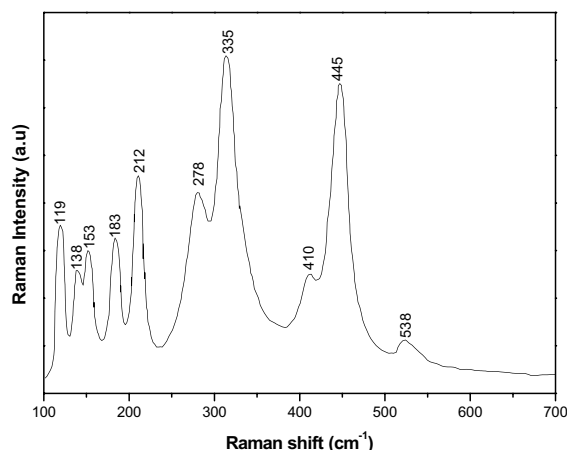
Surface analysis was performed using the XPS technique to further elucidate the elemental composition and chemical states present on the surface of  $\text{Bi}_2\text{O}_3$  nanoparticle synthesized through lemon extract. Figure 4 showed a typical XPS survey spectrum of the  $\text{Bi}_2\text{O}_3$  nanoparticle, with peaks revealing the presence of Bi, O, C elements which confirmed the purity of the prepared  $\text{Bi}_2\text{O}_3$ . The C 1s signal at 282.7 eV was assigned to the carbon species present and used as a reference to calibrate the binding energies of other elements. Figure 4b showed high-resolution XPS spectra of Bi 4f. The peaks Bi 4f<sub>7/2</sub> at 158.4 eV and Bi 4f<sub>5/2</sub> at 163.7 eV are separated by 5.3 eV, which is characteristic of  $\text{Bi}^{3+}$  (He et al., 2018; Jiang et al., 2015). Those at 158.4 and 163.7 eV belonged to the  $\text{Bi}^{3+}$  species  $\alpha$ - $\text{Bi}_2\text{O}_3$ . Figure 4c presented the high-resolution O 1s spectrum which was attributed to the oxygen in the lattice (Bi-O) at

529.3 eV and surface-absorbed oxygen (Bi-O-H) at 532.3 eV. The peaks are observed between 532.3 and 529.3 eV, a noticeable shift to lower binding energies attributed to the increased electron density around oxygen atoms in Bi-O-Bi bonds as  $\text{Bi}_2\text{O}_3$  content rises. This phenomenon is associated with the high polarizability of  $\text{Bi}^{3+}$  ions, due to their large ionic radii and low cationic field strength. Additionally, an increase in  $\text{Bi}_2\text{O}_3$  content leads the electron density on the oxygen atoms averaged by the hybridization of Bi 6s and O 2p orbitals. The deconvolution from 532.3 to 529.3 eV indicates the presence of bridging and non-bridging oxygen atoms from the Bi-O-Bi (Oprea et al., 2013). Figure 4d presented the high-resolution C 1s where peaks at 284.7 and 288.2 eV represents the carbon from carbohydrates present in the lemon extract adsorbed to the surface of the formed  $\text{Bi}_2\text{O}_3$  nanoparticles. Thus, the XPS results further confirmed the existence of  $\alpha$ - $\text{Bi}_2\text{O}_3$  heterostructure (Fang et al., 2016).

The vibration and molecular structure of inorganic materials can be identified by Raman spectra. The intensity of Raman spectra obtained for the synthesized samples (Fig. 5) reveals a strong crystallinity. The peaks at  $119\text{ cm}^{-1}$  was attributed to the vibrations of Bi atoms, suggesting that most of the Bi is present in the crystal lattice of the prepared samples. The peaks at 138 and  $153\text{ cm}^{-1}$  indicate the stretch of



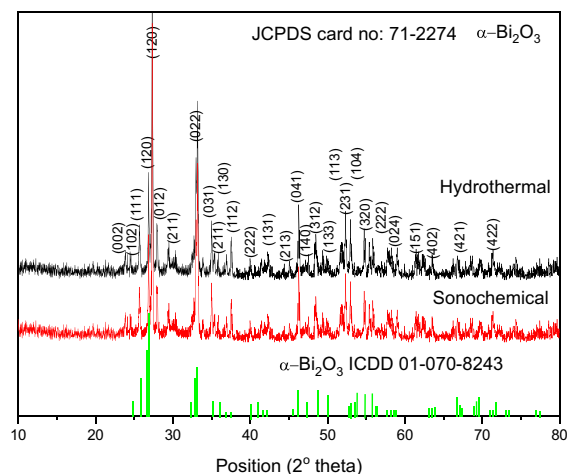
**Fig. 4** XPS spectrum of  $\text{Bi}_2\text{O}_3$  nanoparticles



**Fig. 5** Raman spectra of  $\text{Bi}_2\text{O}_3$  nanoparticles

both Bi and O atoms. Further peaks obtained at 183, 212, 278, 335, 410 and  $445\text{ cm}^{-1}$  are due to atomic vibration of the O atoms present in the monoclinic  $\alpha\text{-Bi}_2\text{O}_3$  crystalline lattice (Hao et al., 2017; In et al., 2011). The presence of  $538\text{ cm}^{-1}$  is attributed to the defects of oxygen vacancies with bismuth interstitials. The Raman spectra indicates grown  $\text{Bi}_2\text{O}_3$  with the fewer structural defects and monoclinic phase (Al-Ghamdi et al., 2017). The results suggest that all these peaks possess  $A_g$ ,  $B_g$  or both symmetries as identified by tensor selection rule using polarized micro-Raman spectroscopy. Most of the peaks reveal the crystalline nature of the synthesised product, which was mainly identified as  $\alpha\text{-Bi}_2\text{O}_3$ .

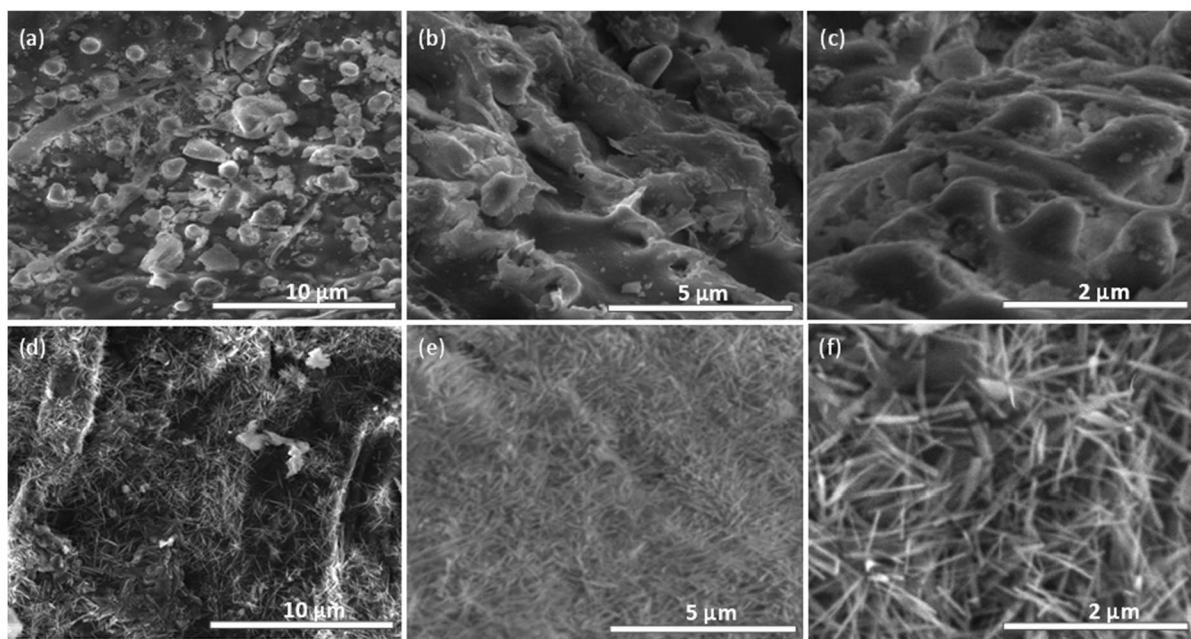
Figure 6 shows the XRD patterns of the synthesized  $\text{Bi}_2\text{O}_3$  by two different methods hydrothermal and sonochemical method. The strongest diffraction peaks (120) located at  $27^\circ$  further confirms the formation of  $\alpha\text{-Bi}_2\text{O}_3$  (Chen et al., 2012). The high Bi concentration is clearly indicated by the reflections at  $2\theta = 27.44^\circ$ ,  $27.46^\circ$  and  $33.32^\circ$  (Hameed et al., 2008). The crystalline form of the  $\alpha\text{-Bi}_2\text{O}_3$  was confirmed using the Scherrer equation, and the particle size of  $\alpha\text{-Bi}_2\text{O}_3$  was found to be 26 nm. The peaks indicating the presence of  $\alpha\text{-Bi}_2\text{O}_3$  at  $2\theta = 26.92^\circ$ ,  $28.00^\circ$ ,  $33.94^\circ$  and  $35.40^\circ$  represent the Miller indices of (111), (120), (022) and (031) which are indeed characteristics of  $\alpha\text{-Bi}_2\text{O}_3$ . The observed XRD spectrum matched with the JCPDS card no: 71-2274 (Vila et al., 2018). The XRD patterns shows 80% similarity with the  $\alpha\text{-Bi}_2\text{O}_3 \rightarrow \text{ICDD 01-070-8243}$  which revealed with the comparison. It aligns in agreement



**Fig. 6** XRD analysis of synthesized  $\text{Bi}_2\text{O}_3$  nanoparticles

similar to the synthesis experimented by Weber et al., 2016. The morphology of the synthesized  $\alpha\text{-Bi}_2\text{O}_3$  crystals was influenced by the sono-cavitation controlled reaction. The variations in the crystal morphology was attributed to the  $\bullet\text{OH}$  radicals formed upon ultrasound irradiation during the synthesis of  $\alpha\text{-Bi}_2\text{O}_3$ . The resulting  $\alpha\text{-Bi}_2\text{O}_3$  had a monoclinic structure with the point group 2/m, a polar crystal group. These crystals appear needle-like along the direction (001). The absence of other peaks confirms the purity of the formed  $\alpha\text{-Bi}_2\text{O}_3$ .

The SEM images in Fig. 7a, b and c refer to the  $\alpha\text{-Bi}_2\text{O}_3$  nanoparticles synthesised through the hydrothermal process. The Fig. 7d, e and f show the influence of sono-cavitation on the morphology of the  $\text{Bi}_2\text{O}_3$  nanoparticles. The formation of nano short-wire or nano short-rod facet-like structure ranging from 100–200 nm in length during sonochemical synthesis method was observed. This is attributed due to the reaction controlled by sono-cavitation where the materials get mixed up with the lemon extract. The growth of nano short-rod facet of monoclinic  $\alpha\text{-Bi}_2\text{O}_3$  occurs from the surface in clustered high-density environment. The formation of nano short rod facet needle-like structures can be attributed to a combination of Ostwald ripening and self-assembly processes, which are facilitated by the application of sonocavitation (Yue et al., 2020). During the sonochemical process, the nuclei generated grow into the distinctive nanorod facet needle-like structure. Also, sono-cavitation accelerates the uniform dispersion of the particles



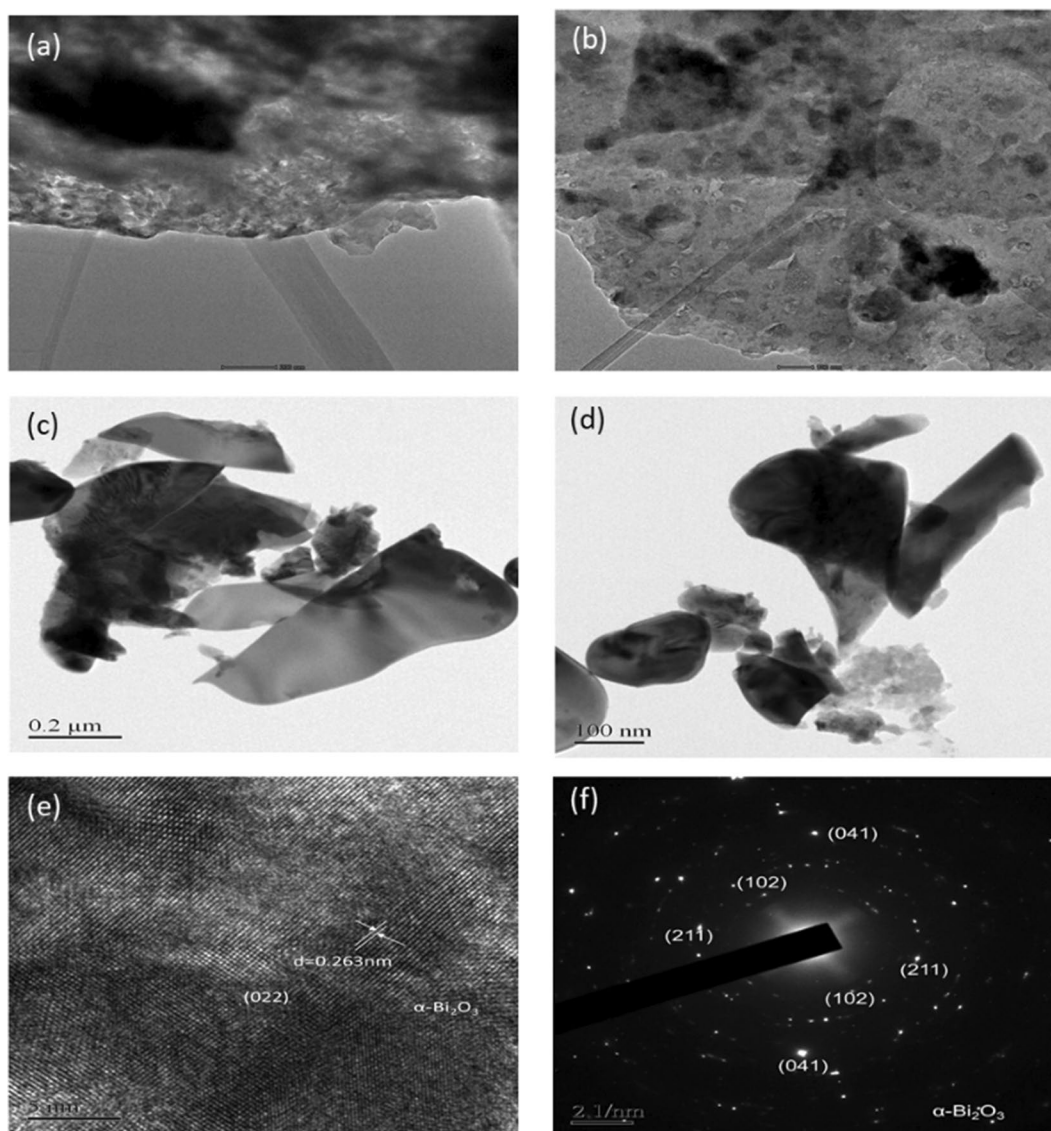
**Fig. 7** SEM images of synthesized  $\text{Bi}_2\text{O}_3$  nanoparticles through hydrothermal (a, b and c) and sonochemical (d, e and f) method

thereby improving the crystal lattice of the formed catalyst Shirsath et al. (2013) compared the particle size of  $\text{Bi}_2\text{O}_3$  photocatalyst synthesized using the sonochemical and conventional method and found that a smaller size was obtained through sono-cavitation. This effect was attributed to a fast-kinetic reaction obtained by sono-cavitation that limited nucleation and particle growth. Figure S2 shows the composition of pure  $\alpha\text{-Bi}_2\text{O}_3$ . The one-dimensional needle type facet crystal growth was attained through sono-cavitation method. Furthermore, the hydrothermal process involves the formation of nanoparticles through a mechanism of nucleation, dissolution, and recrystallization (Baumgartner et al., 2020; Yue et al., 2020).

Figure 8a and b shows the TEM image of  $\text{Bi}_2\text{O}_3$  synthesized through hydrothermal method, where the nanoparticles appear with an irregular shape. On the contrary, sono-cavitation resulted in a large amount of  $\alpha\text{-Bi}_2\text{O}_3$  nanoparticles with a nano shortrod facet morphology and dense thickness. The needle-like grain morphology formed during the growth changed to large facet via dissolution recrystallization process (Wu et al., 2013). TEM image of the synthesized catalyst as in shows clear fringes with an interplanar lattice spacing of 0.263 nm (Fig. 8e). This suggests the 120 plane of  $\alpha\text{-Bi}_2\text{O}_3$  (Ge et al., 2011), and the presence of needle-like  $\alpha\text{-Bi}_2\text{O}_3$  in

the formed facet crystals. The corresponding selected area electron diffraction (SAED) pattern (Fig. 8f) of a randomly chosen region confirms that  $\alpha\text{-Bi}_2\text{O}_3$  correspond to the interplanar spacing of 0.263 nm with the fringes matching the theoretical value for  $\alpha\text{-Bi}_2\text{O}_3$ . The morphology variation from needle-like grain to facet was due to the shielding effect of  $\text{OH}^-$  ions during the synthesis process. Despite the crystal change, the formed  $\text{Bi}_2\text{O}_3$  belongs to monoclinic structure with the formation of  $\alpha\text{-Bi}_2\text{O}_3$  in 120 plane.

The DRS spectra of  $\alpha\text{-Bi}_2\text{O}_3$  and the band gap calculations were given in the supplementary data S1. From the obtained data it can be revealed that the nano short-rod facet structure obtained through sonochemical synthesis method show a strong photo-absorption band in the visible light region (400 to 600 nm). This might be due to the intrinsic band gap absorption which corresponds to the band gap of 2.46 eV (Sood et al., 2015). The band gap obtained for the  $\text{Bi}_2\text{O}_3$  through hydrothermal method was 2.52 eV. The difference in band gap also confirms that the sono- influenced the synthesis process. This shows the catalytic effect of  $\alpha\text{-Bi}_2\text{O}_3$  catalysts when exposed to the solar spectrum. Hence,  $\text{Bi}_2\text{O}_3$  catalyst can drive photocatalytic oxidation of recalcitrant pollutants in the visible light (Ciciliati et al., 2015).

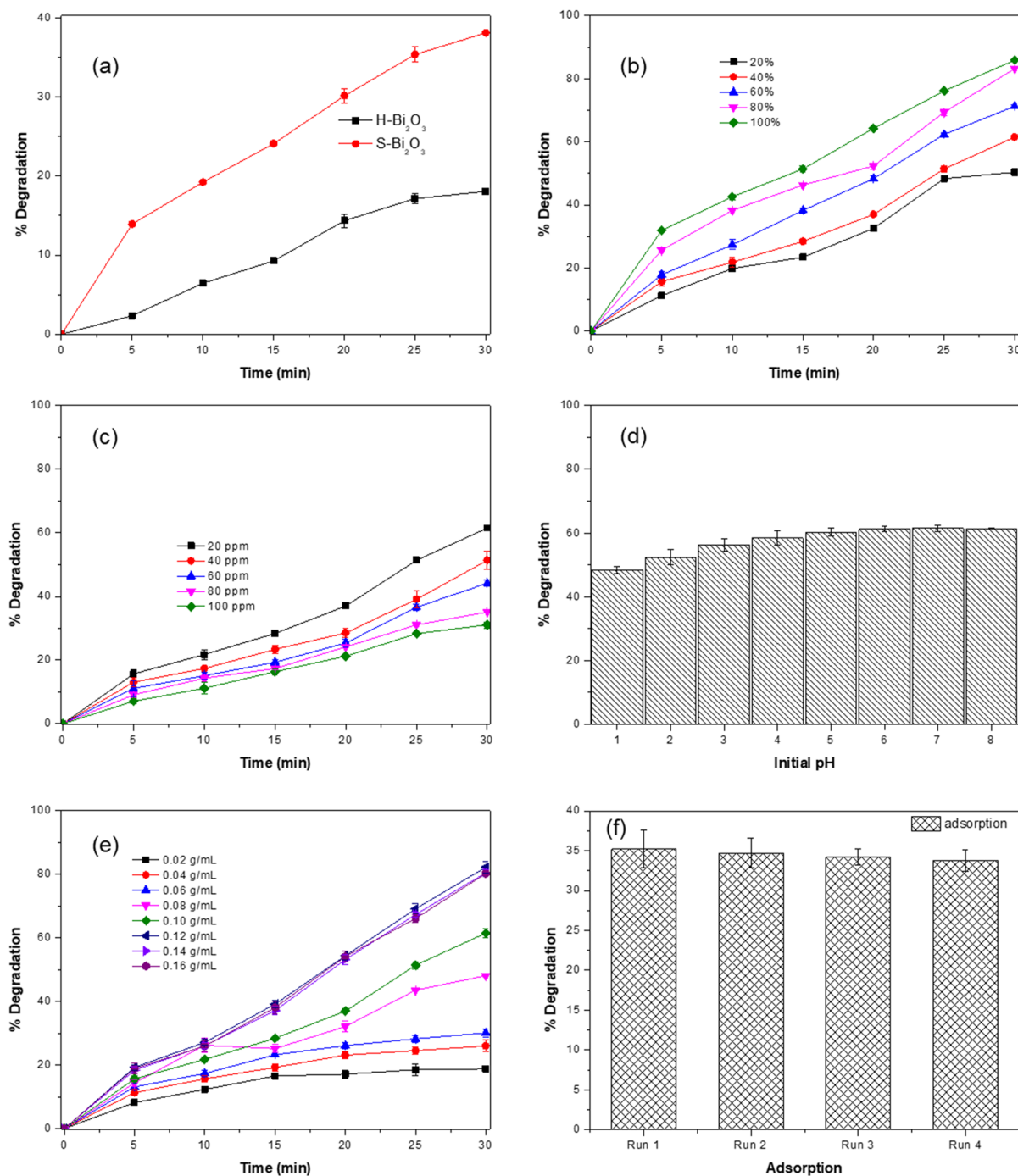


**Fig. 8** TEM images of synthesized  $\text{Bi}_2\text{O}_3$  nanoparticles through hydrothermal (**a** and **b**) and sonochemical (**c** and **d**) method; lattice spacing (**e**) and SAED pattern (**f**) for  $\text{S-Bi}_2\text{O}_3$

### 3.1 Catalytic Studies on Congo Red Dye

The adsorption of Congo red (CR) dye on the  $\text{Bi}_2\text{O}_3$  catalyst was studied by addition of 0.1 g  $\text{Bi}_2\text{O}_3$  to 100 mL of 20 ppm CR and incubation for various intervals of time ranging from 0 to 30 min. No degradation of the CR dye was obtained in the absence of  $\text{Bi}_2\text{O}_3$  nanoparticles, even after 60 min, suggesting that the reaction does not occur without the catalyst. A decrease of the dye concentration was detected

after the addition of 0.1 g/mL of  $\text{Bi}_2\text{O}_3$  nanoparticles, produced with both the hydrothermal and the sono-cavitation method, in the absence of sono-cavitation (Fig. 9a). The adsorption of the dye on the catalyst proceeded for 30 min, after that the reaction kinetics was slower due to the reduced interaction between the  $\text{Bi}^{3+}$  and CR dye molecules (containing various carboxyl, phenyl, azo groups). With the catalyst loading of 0.1 g/mL, the adsorption reached maximum of 38% beyond that there was no considerable change.



**Fig. 9** Degradation studies on methylene blue dye; (a) adsorption studies, (b) effect of sonication intensity, (c) dye concentration (d) initial pH, (e) catalyst concentration, and (f) reusability studies on adsorption

The adsorption effect is critical and dependent on the morphology of the catalyst used. The nanowire facet transformation by sono-cavitation caused

a rearrangement of the surface atoms, which likely increases the stability of the catalyst and increased the concentration of active sites favouring adsorption.

When sono-chemical synthesized catalyst was used, adsorption rate has reached 38%, whereas hydrothermal treated catalyst has only resulted in 18% (%) under the same experimental conditions (pH, initial dye concentration, contact time and temperature). However, it is significant that the sono-cavitation studies tend to offer maximum degradation of 86% within 30 min for higher concentration of dye 20 ppm. Thus, sono-cavitation improvise the degradation process in the presence of catalyst.

The intensity of sono-cavitation plays a major role in the degradation kinetic process. The amplitude of the instrument was increased from 20 to 100% to understand how the intensity impacts the degradation of CR dye. The experiments were carried out in the presence of 0.1 g/mL S-Bi<sub>2</sub>O<sub>3</sub> catalyst, volume 100 mL, reaction time of 30 min. At 20%, the CR degradation after 30 min was 50.4%. The increase in intensity dramatically increased CR degradation to 61.5%, 71.3%, 83.2% and 85.9% respectively, at 40%, 60%, 80% and 100% sonication intensity (Fig. 9b). This can be attributed to (i) the generation of more reactive radical species (radical  $\cdot\text{O}_2^-$  and radical  $\cdot\text{OH}$ ) during sono-cavitation at higher intensities (Lee et al., 2018), (ii) the physical effects like microjets, shock waves and microturbulence caused by intense sonication, which enhances the mass transfer rates of CR dye molecules and the number of active sites available on the catalyst surface (Dinesh et al., 2015), and (iii) the generation of cavitation bubbles and hotspots inducing the generation of a greater number of reactive radicals (Khataee et al., 2017).

The effect of the initial dye concentration on sonocatalytic degradation was experimented at a 20 kHz frequency, 40% power intensity and 0.1 g/L catalyst concentration. The degradation efficiency of CR declined when increasing the dye concentration (Fig. 9c). This can be related to the inhibition of O<sub>2</sub> absorption sites on the catalyst surface due to the presence of excessive dye molecules. The number of active sites for the generation of  $\cdot\text{O}_2^-$  and radical  $\cdot\text{OH}$  radicals with free conduction band electrons from Bi<sub>2</sub>O<sub>3</sub> declined, resulting in a decrease in the CR degradation efficiency. Moreover, the increased number of dye molecules adsorbed to the catalyst surface can restrict the absorption and transfer of cavitation energy. There would be a possible enhancement in the interaction between the intermediates produced during the oxidation of CR dye and reactive radicals

available for degradation. Thus, declining the efficiency of degradation kinetics.

Figure 9d shows the effect of pH on CR adsorptions and sonocatalytic studies on S-Bi<sub>2</sub>O<sub>3</sub>. As the initial pH of the solution was increased from 1 to 6, the adsorption percentage increased steadily from 48.4 to 61.2 percent. This is attributed to the electrostatic attraction between dye molecules and the catalyst surface. The point of zero charge for Bi<sub>2</sub>O<sub>3</sub> was found to be in the range from 6 to 7.5. In the pH range from 6 to 6.8, the catalyst surface of Bi<sub>2</sub>O<sub>3</sub> is protonated and thus CR dye gets more attracted towards catalyst. The acidic range pH favours higher degradation of CR dye. CR becomes dipolar and being an anionic dye, they get adsorbed more during acidic pH range. Results showed that adsorbent ionization and adsorbent surface load change with the pH of the solution.

One of the vital factors affecting the degradation efficiency of the catalytic process is the quantity of the catalyst added to the reaction mixture. Individuating the optimal catalyst quantity is crucial to avoid the use of excessive catalysts that may cause particle aggregation. Although there are many reports on the effect of catalyst loading, a straightforward comparison between these studies is difficult due to the various material morphologies, radiation fluxes and selected wavelengths chosen in each study. The impact of catalyst loading on the degradation of CR dye was investigated in the range from 0.02 to 0.14 g/L, at 20 ppm dye concentration, at 35 °C temperature and at an initial pH of 7. The CR degradation curves are presented in Fig. 9e. The degradation efficiency improved from 18.7 to 82.2 percent with an increase in the loading of the catalyst from 0.02 to 0.12 g/L, due to the increased availability of active sites on the catalyst surface. However, a further increase in catalyst loading to 0.14 g/L caused a decline by 2% of the degradation efficiency, which was due to the aggregation of catalyst and sudden reduction of active sites.

### 3.2 Comparison of Other Research Studies

The results obtained in the sonocatalytic degradation of CR dye from the use of Bi<sub>2</sub>O<sub>3</sub> nanoparticles were compared with some of the reported research articles to demonstrate the advantage of the catalyst synthesized through green method. It also helps to understand the synergistic effect of sonocavitation

on synthesis and degradation methodology. From Table 1, it is clear that the present procedure is more acceptable and gave better results with respect to the catalyst loading, the original dye concentration, and the degradation time. From the comparison it can be concluded that the degradation reaction requires longer reaction time and high catalyst loading.

### 3.3 Reusability and Stability

The stability of the prepared  $\text{Bi}_2\text{O}_3$  catalyst was measured by the adsorptive cyclical degradation of the CR dye. After each degradation cycle, the catalyst was collected by centrifugation, then washed with ethanol and sonicated for 30 min to clean the catalyst surface from

**Table 1** Comparison of catalytic activity of  $\text{Bi}_2\text{O}_3$  with different synthesis procedure and their degradation study on various dyes

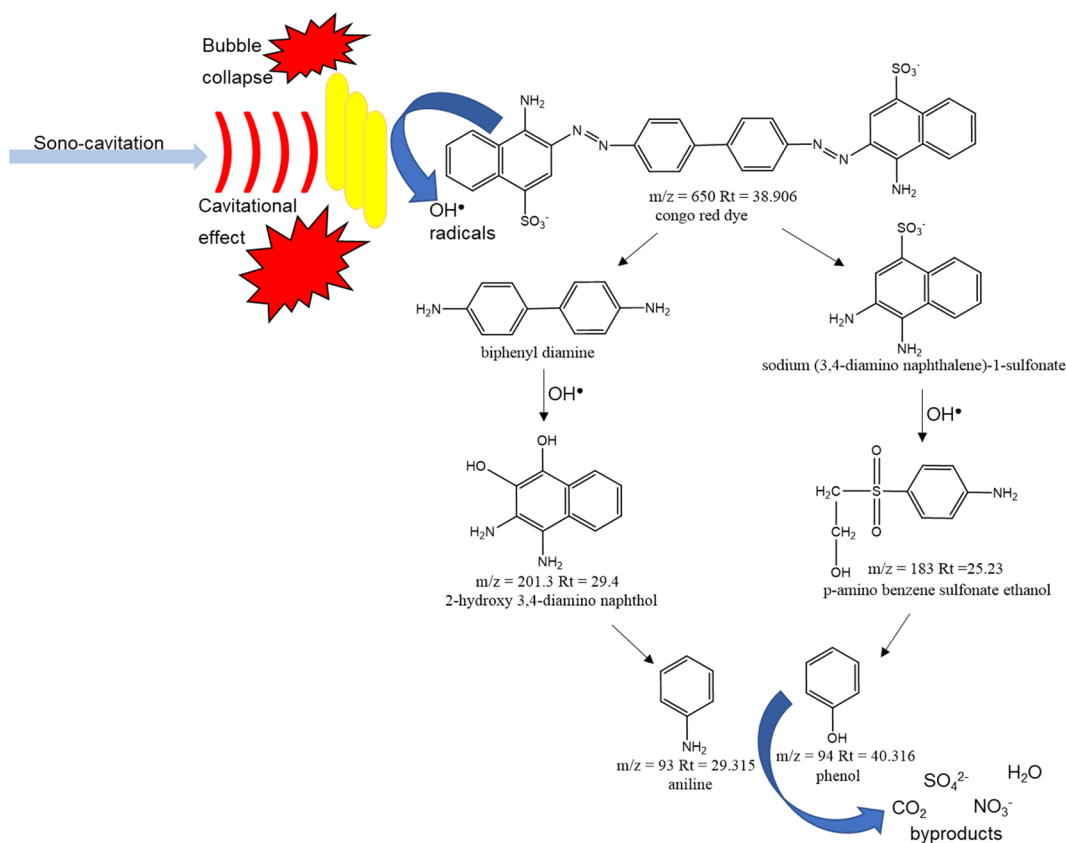
| S.No | Synthesis route            | Crystalline phase                                    | Morphology                                                      | Catalytic activity                                                                               | Reference                          |
|------|----------------------------|------------------------------------------------------|-----------------------------------------------------------------|--------------------------------------------------------------------------------------------------|------------------------------------|
| 1    | Sonochemical               | $\alpha$ -Monoclinic                                 | High aspect ratio nanorods (length in cm, diameters 100–120 nm) | Sunlight; Rhodamine Band 2,4,6, TCP degradation of 97% in 45 min and 88% in 180 min respectively | (Sood et al., 2015)                |
| 2    | Sonochemical               | $\alpha$ -Monoclinic                                 | Nanoparticles size ~60 nm                                       | Mercury vapor—UV light source 125 W, degradation of methyl orange 93% in 120 min                 | (Kusuma et al., 2022)              |
| 3    | Hydrothermal               | $\alpha$ -Monoclinic                                 | Nanoparticles size ~34 nm                                       | Sunlight, Methyl orange degradation 87% in 100 min                                               | (Yaou Balarabe et al., 2022)       |
| 4    | Hydrothermal               | $\beta$ -phase                                       | Spherical particles 22–31 nm                                    | 400 W halogen lamp Approximately 53% degradation of Rhodamine in 100 min                         | (Khan et al., 2024)                |
| 5    | Sonochemical               | $\beta$ -phase                                       | Rectangular cubic poly dispersive structure of 23 nm            | 80% of Rhodamine B in 180 min                                                                    | (Azizian-Kalandaragh et al., 2015) |
| 6    | Solvothermal               | $\alpha$ and $\beta$ -phase                          | Nano spheres with 90 nm diameter                                | 1000 W Xe lamp, Acetaminophen degradation of 93% in 180 min                                      | (Xiao et al., 2013)                |
| 7    | Chemical                   | $\alpha$ -Monoclinic                                 | Agglomerated crystals                                           | 500 W Xenon lamp, Methyl orange degradation rate 76% in 120 min                                  | (Iyyapushpam et al., 2012)         |
| 8    | Hydrothermal               | $\alpha$ -phase                                      | Flower shaped 100 nm                                            | 300 W xenon lamp, norfloxacin degradation of 33%                                                 | (Jiang et al., 2020)               |
| 9    | Femtosecond laser ablation | $\delta$ - $\text{Bi}_2\text{O}_3$ phase             | Nanoparticles size 10–60 nm                                     | LED 365 nm, Indigo carmine degradation ~50% in 90 min                                            | (Lin et al., 2010)                 |
| 10   | Electrospinning            | $\beta$ tetragonal                                   | Nanofibers (length in $\mu\text{m}$ s, diameters 200–300 nm)    | UV light, Rhodamine B degradation of 93% in 120 min                                              | (Wang et al., 2009)                |
| 11   | Hydrothermal               | Mixture of $\alpha$ -Monoclinic / $\beta$ tetragonal | Porous nanoflakes (113.8 nm)                                    | 99.6% Rhodamine B removal in 180 min using 0.5 g/L                                               | (Bera et al., 2018)                |
| 12   | <b>Sonochemical</b>        | $\alpha$ -Monoclinic                                 | Nano short rod facet of 23 nm                                   | Sonocatalytic degradation of CR dye to 86% in 30 min with 0.12 g/L catalyst loading              | <b>This work</b>                   |

the residual dye molecules. Then the catalyst was dried and used for the following degradation cyclic, while all the other reaction conditions were retained as stable. The  $\text{Bi}_2\text{O}_3$  demonstrated no substantial loss of adsorptive catalytic efficiency after four CR degradation loops, reaching degradation efficiencies of 35.2%, 34.7%, 34.2% and 33.8% over four cycles of 30 min each shown in Fig. 9f. The small reduction in CR degradation during the adsorption trials may be due to the reduction in the active sites of catalyst surface and further cleaning of catalyst would help in the recovery of catalytic activity. However, a reduction of approximately 2% in the CR degradation between the first run and the fourth run suggests that the prepared  $\text{Bi}_2\text{O}_3$  catalyst is extremely stable. Hence, the use of  $\text{Bi}_2\text{O}_3$  sample for practical application would be advantageous.

### 3.4 Possible Degradation Mechanism

The possible degradation mechanism can be inferred by identifying the intermediates formed during the

degradation of CR dye. The intermediate products of CR dye degradation were identified using an Agilent 6890 GC (injector temperature 250 °C; 1  $\mu\text{L}$  injected in splitless mode; carrier gas—helium 1 mL/min). The column details as—Agilent HP-5 ms Capillary GC Column with 30 m and 0.25 mm diameter, coated with 0.25 mm bonded 5% phenyl, 95% dimethylpolysiloxane. The column oven was programmed between 100 and 300 °C at the rate of 20 °C per minute with the injection temperature of 250 °C. An Agilent 5973 mass selective detector (MSD; EI mode, 70 eV;  $m/z$  40–450; source temp. 260 °C) were used to confirm the intermediate products during the degradation process. The possible degradation pathway of CR dye by sonocatalytic treatment process is shown in Fig. 10. The asymmetric cleavage of the C-N bond was likely caused by the hydroxyl radical ( $\bullet\text{OH}$ ) formed during the reaction, which breaks the CR dye structure to form biphenyl diamine and sodium (3,4-diamino naphthalene)-1-sulfonate as intermediates. Further,



**Fig. 10** Plausible degradation pathway through GC MS analysis data

biphenyl diamine undergoes hydroxylation to form 2-hydroxy 3,4-diamino Naphthol with a  $m/z$  of 201 with a base peak of 201.3 at retention time of 29.4 min. The aromatic ring of sodium (3,4-diamino naphthalene)-1-sulfonate is then opened to form p-amino benzene sulfonate ethanol with a  $m/z$  of 183, a base peak of 181.32 and a retention time (Rt) of 25.23 min. The compounds 2-hydroxy 3,4-diamino Naphthol and p-amino benzene sulfonate ethanol undergo further cleavage of chromophores to form aniline and phenol with  $m/z$  93 and 94 peak with a Rt of 29.315 min and 40.316 min, respectively. Further the attack on the aromatic, amino and hydroxy compounds by hydroxyl radicals to form  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic ions.

#### 4 Conclusion

In conclusion, a facile, efficient, and green sono-cavitation method was introduced to synthesise bismuth oxide nanoparticles. The formation of biosynthesized bismuth oxide nanoparticles has been demonstrated by the appearance of a surface plasmon resonance (SPR) band at 400 nm. Synthesized bismuth oxide nanoparticles were characterized via various spectroscopic techniques, such as FTIR, SEM, TEM, EDS, XRD, XPS and Raman spectroscopy to analyse the physicochemical properties and surface morphology. Results showed that the cavitation had a great influence on the phase structure, morphology and catalytic performance of the nanoparticles. The sample synthesized through cavitation method exhibited superior performance than the hydrothermal method on adsorption studies of CR dye. Moreover, it was observed that the catalyst owned a good stability. The study could provide a new route for the development of bismuth oxide catalyst for various applications such as wastewater treatment, removal of hazardous toxic substance with improved catalytic property and stability.

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**Data Availability** Data will be available on reasonable request.

#### Declarations

**Competing Interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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