



Improved direct synthesis of TiO₂ catalyst using sonication and its application for the desulfurization of thiophene

Ashlesha Tiple, Pankaj S. Sinhmar, Parag R. Gogate*

Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai 400019, India

ARTICLE INFO

Keywords:

Catalyst synthesis
Ultrasound
Characterization
Desulfurization
Combination approaches

ABSTRACT

TiO₂ catalyst was synthesized in the presence of ultrasound (ultrasonic horn at 20 kHz frequency and 70% duty cycle) at different power (80 W to 120 W) and durations as well as surfactant concentration with an objective of establishing best conditions for achieving lowest particle size of the photocatalyst. Detailed characterization in terms of crystal phase, crystallinity, functional groups and morphology of the photocatalyst has been performed using SEM, XRD and FTIR analysis. It was demonstrated that sonication significantly reduced the particle size with high degree of sphericity and homogeneity as compared to conventionally synthesized TiO₂ with similar crystallinity in both cases. The catalytic performance was subsequently evaluated for the deep desulfurization of thiophene. Different desulfurization approaches including individual US (ultrasonic horn at 20 kHz frequency, 110 W power and 70% duty cycle) and UV irradiations, US/UV, US/UV/H₂O₂, US/UV/TiO₂ and US/UV/H₂O₂/TiO₂ were applied to evaluate the catalytic activity. The best approach was demonstrated as US/UV/H₂O₂/TiO₂ and also activity of catalyst synthesized using ultrasound was much better compared to conventionally synthesized catalyst. The studies related to different model solvents demonstrated lowest reactivity for toluene whereas n-hexane and n-octane resulted in complete desulfurization in 60 min and 50 min treatment respectively. The desulfurization followed pseudo first order reaction kinetics irrespective of the solvent used. Overall the work clearly demonstrated the efficacy of ultrasound in improving the catalyst synthesis as well as desulfurization of thiophene.

1. Introduction

The refractory nature of thiophene for oxidation induced desulfurization is majorly due to the low electron density of sulfur and its aromaticity which imposes difficulty in oxidation, hence it is of immense importance to develop an effective catalyst for desulfurization [1] as well as hybrid method based on combined oxidation processes. For the application of titanium dioxide as an effective catalyst, it is very important to optimize the catalyst synthesis process [2]. The excellent properties like non-toxic nature, high stability, high mechanical resistance, high refractive index, long-term photo stability, effective electronic and optical properties makes this material a prime candidate for various applications [3] such as photocatalysis [4], dye sensitized solar cells [5], electrochemistry [6], semiconductors [7] and waste water treatment [8].

The photocatalytic activity of the TiO₂ catalyst for a variety of applications including photocatalysis and oxidation differs substantially based on its phase structure, composition, crystallinity and particle size

[1,9,10]. Various attempts have been reported for the enhancement of characteristics such as crystal phase, particle size, morphology and crystallinity of TiO₂ in order to ensure its remarkable activity [8,11]. For the synthesis of TiO₂ catalyst, different method such as sol gel [12], hydrothermal [13], precipitation [14], solvothermal [5] and direct synthesis [15] has been employed. Among these methods, sol gel is widely studied synthesis method because of its mild experimental conditions and simple preparation approach. Direct synthesis method also offers better control on particle size and crystal structure just by optimizing synthesis conditions like temperature, time, solvent, and precursor. Additionally, the surface based modifications can be achieved using the surfactant during the synthesis as it is believed to improve dispersibility and thermal stability of TiO₂ powder and also the use of surfactant modifies surface state of the photocatalyst. Cetyltrimethylammonium bromide (CTAB) is often used as cationic surfactant [16,17]. Ultrasound has a significant potential to improve the synthesis of nanomaterials mainly due to its easy applicability and the cavitation effects that can improve the synthesis approaches [18–20].

* Corresponding author.

E-mail address: pr.gogate@ictmumbai.edu.in (P.R. Gogate).

<https://doi.org/10.1016/j.ultsonch.2021.105547>

Received 14 November 2020; Received in revised form 28 March 2021; Accepted 29 March 2021

Available online 1 April 2021

1350-4177/© 2021 The Author(s).

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

The passage of sonic waves through the precursor and solvent mixture leads to the generation of high and low-pressure regions within the reaction mixture thus, propelling the various steps of cavitation. The typical effects of cavitation are formation of hot spots of high temperature and pressure [21] as well as the micro mixing which improves solute to solvent transfer within the reaction mixture and also the nucleation rate of the particle formation [8]. The primary reason for the lower particle size due to application of sonication is the collapse of cavitating bubbles aiding the deagglomeration and breaking of particles due to microjets and shock waves. There are few literature reports which confirms the favourable role of sonication to obtain lower particle size materials [8,19,21]. Considering the presented analysis, the present work focuses on sonochemically improved direct synthesis of titanium dioxide as the first stage of the work.

One of the interesting applications of TiO_2 as a photocatalyst has been reported as the desulfurization of thiophene and other alkylated derivatives of thiophene. The electrons available in valance band of titanium dioxide gets excited with photons from the ultraviolet light and these electrons travel to the conduction band leaving valance band holes on the surface of photo catalyst. The sulfur atom lone pair electrons of thiophene (TH) are then captured by the hole of TiO_2 resulting in the formation of ground state cation $[\text{TH}]^+$. Ground state cation $[\text{TH}]^+$ and hydroxyl radicals react to oxidize the thiophene to its sulfoxide form. The excited electron on the catalyst also reacts with the electron acceptor oxidant for the generation of highly active hydroxyl radicals with oxidation potential of 2.8 V which also individually oxidizes the sulphur compounds. So, titanium dioxide can enhance the overall rate of oxidation and generation of hydroxyl radicals thus overcoming the limitation of low reactivity due to the low density sulfur atom of thiophene. Indeed literature presents some illustrations for photocatalytic desulfurization involving titanium dioxide. Abdel-Wahab and Gaber [22] evaluated the photooxidation of dibenzothiophene in acetonitrile solution using TiO_2 and reported 75% sulphur reduction under 10 h of ultraviolet irradiation. Matsuzawa et al. [23] studied photooxidation of dibenzothiophene and 4,6 dimethyl dibenzothiophene in acetonitrile solution using commercial titanium dioxide powder in presence of H_2O_2 as oxidant and reported accelerated rate of desulfurization with the combinational approach. Dedual et al. [24] used P25 commercial TiO_2 for photocatalytic desulfurization of dibenzothiophene and benzothiophene dissolved in n-octane. 91% and 64% desulfurization were reported for dibenzothiophene and benzothiophene respectively in 3 h of treatment time. Keynejad et al. [25] studied the photocatalytic desulfurization of diesel fuel in batch reactor in presence of ultraviolet light using commercial TiO_2 as a photocatalyst and reported 90% of sulphur removal at optimum conditions of 30 W UV irradiation, 40 min time and 2 wt% H_2O_2 . Wang et al. [26] investigated the synthesis of TiO_2 in the presence of ionic liquids and subsequent use of the obtained nano TiO_2 particles on the desulfurization. It was reported that sulphur content of model oil was reduced by 98.2% and that of diesel by 94.3% under 10 h of UV irradiation. Zhu et al. [27] explored the catalytic activity of different forms of synthesized TiO_2 powder on the desulfurization of model oil in the presence of ionic liquid and reported that the form of TiO_2 can remarkably affect the desulfurization operation with 96.6%, 23.6% and 18.3% of desulfurization demonstrated using TiO_2 of different forms as amorphous, anatase and anatase-rutile combination, respectively. Li et al. [1] also confirmed that the form of TiO_2 significantly affect the desulfurization rate. Three different forms of TiO_2 (i.e. anatase, amorphous and anatase-rutile) were prepared by sol gel synthesis method and the application study illustrated that anatase nano TiO_2 particle exhibits highest catalytic activity for the desulfurization of dibenzothiophene as it resulted in complete desulfurization while amorphous TiO_2 and anatase-rutile TiO_2 showed only 25.7% and 48.1% sulphur removal efficiency. Huang et al. [15] synthesized mesoporous TiO_2 using phosphotungstic acid and different surfactants using direct synthesis method and evaluated their photocatalytic activity for the desulfurization of dibenzothiophene in n-octane reporting 98% DBT

removal. Zheng et al. [28] prepared TiO_2 using sol gel method and checked its catalytic activity for the desulfurization of different sulphur compounds in n-octane solution. It was reported that 99%, 52.8%, and 74.3% removal of dibenzothiophene, benzothiophene and 4,6 dimethyl dibenzothiophene respectively, is obtained in 90 min at 40 °C of temperature. Li et al. [29] prepared nano TiO_2 by sol gel method and carried out the photocatalytic desulfurization of model oil containing thiophene as standard sulphur compound while n-octane as standard diesel compound and reported around 90% desulfurization of thiophene in 3.5 h of treatment in the presence of UV irradiation and O_2 as oxidant.

Although lot of research has been done using TiO_2 as a photocatalyst including the synthesis and subsequent applications, their lies a gap in terms of developing use of ultrasound for the improvement of efficiency of the photocatalytic desulfurization process for thiophene. Very little literature reported with anatase TiO_2 required long reaction times and most of the studies were performed using n-octane as a key diesel compound. As per our best knowledge the catalytic oxidative desulfurization is still not performed for different solvent such as toluene, n-hexane, heptane etc. It is expected that the solvent can have a remarkable effect on the desulfurization efficiency of the thiophene. Along with this the development of efficient, simple and quick method of synthesis which can offer excellent particle size and improvement in surface properties over the conventional preparation methods is also a crucial factor. It is important to note that the catalytic activity for desulfurization of thiophene will strongly depend on the catalyst synthesis procedure which crucially affects the particle size, phase and morphology [8,10,11].

The present study deals with the application of ultrasonic treatment during the synthesis method to lower the particle size and enhance surface morphologies of the anatase TiO_2 , also comparing the characteristics with the conventionally prepared TiO_2 . The effect of different parameters including US power, US time and CTAB concentration on the catalyst size has been evaluated in details. The performance of the synthesized catalyst has also been investigated for different desulfurization approaches including individual as well as combinational schemes of desulfurization such as Sonication, UV irritation, US/UV, US/UV/ H_2O_2 , US/UV/ TiO_2 and US/UV/ H_2O_2 / TiO_2 . The kinetic analysis has also been performed for different solvents to understand its effect on the kinetics of the desulfurization of thiophene. Performing the desulfurization studies using combined approaches is also an important aspect of the study as such studies are not commonly reported in the open literature for the titanium dioxide synthesized sonochemically.

2. Materials and methods

2.1. Materials

The model diesel fuel used in present study was a mixture of thiophene (model sulfur compound) and n-hexane or toluene or n-octane (as the model key diesel compound). Industrial grade toluene was purchased from International Chemicals Pvt. Ltd Mumbai, India. Thiophene was obtained from Sigma Aldrich Chemicals Pvt. Ltd Bangalore, India whereas hydrogen peroxide (30% v/v), laboratory grade n-hexane (98%), n-octane (AR grade) and HPLC grade acetonitrile were purchased from Thomas Bakers Pvt. Ltd Mumbai, India. A structure directing agent cetyltrimethyl ammonium bromide (CTAB) was procured from Fisher scientific Pvt. Ltd India. The analytical grade ethanol (99%) was purchased from Changshu Hongsheng Fine Chemicals Co. Ltd, China. Freshly prepared distilled water was used for dilution and preparation of solutions.

2.2. Catalyst preparation

Synthesis of TiO_2 catalyst was carried out using titanium tetraisopropoxide as precursor, CTAB as modifying agent, acetic acid as catalyst, and ethanol as solvent. In a typical run, 10 mL of titanium tetra-

isopropoxide was dissolved in 65.58 g of ethanol and a known quantity of CTAB was added under magnetic stirring at 300 rpm to a 250 mL glass reactor. After 30 min of stirring, 0.4 mL of 0.3 M acetic acid was added. The resulting suspension was stirred for 3 h at room temperature. 13 mL deionized water was added drop wise to this suspension under constant magnetic stirring at 300 rpm. After addition of deionized water, the solution was irradiated using ultrasonic horn (at 20 kHz frequency and 70% duty cycle) for known time duration. During ultrasonic irradiation, the temperature was maintained at room temperature using water bath and then the resulted solution was evaporated on heating bath. The obtained solid product was washed twice by deionized water and dried at 373 K for 12 h and then calcined at 773 K for 3 h. For the studies involving the use of ultrasound for the catalyst synthesis ultrasonic horn (M/S Dakshin, Mumbai, frequency of 20 kHz) was used. The ultrasonic horn has two protruding rings placed at equal distance of 1 cm from the circular bottom of the tip to achieve maximum cavitation effect. The effect of different synthesis parameters such as US power (80–120 W), US irradiation time (15–60 min) and concentration of CTAB (0.052 to 0.104 g) was evaluated to optimize the particle size of TiO₂ photocatalyst. For comparative study, the catalyst was also synthesized in absence of sonication with 2 h magnetic stirring at 300 rpm under identical procedure. The schematic representation of the process used for catalyst preparation including the applied reactors has been represented in Fig. 1. A comparative study of the catalyst obtained using US treatment and conventionally prepared TiO₂ is very crucial aspect to establish the benefits of using sonication in terms of activity enhancement and improved surface morphology of the catalyst.

2.3. Experimental setup for desulfurization of thiophene

The desulfurization reaction was carried out in a 250 mL glass reactor equipped with lid. Thermometer was used to monitor the temperature. The water bath was used to maintain the temperature for all set of experiments. For all the desulfurization experiments, ultrasonic horn (M/S Dakshin, Mumbai, frequency of 20 kHz) was operated at constant power output of 110 W and a fixed 70% duty cycle to prevent the heating of horn tip, as per recommendations of the supplier. The schematic representation of the experimental setup has been represented in Fig. 2. For the combination studies, the reactor assembly including US horn was introduced into a UV chamber equipped with two 8 W UV lamps (Philips TUV-8 W /G8T5) which were placed opposite to

each other in such a way that the fuel mixture was completely exposed to UV light. The distance between UV lights and reaction mixture was kept constant as 20 mm.

2.4. Experimental methodology

All the experiments have been carried out at constant 200 ppm concentration of thiophene dissolved in required model diesel (toluene as organic solvent for all experiments except those related to effect of type of solvent). Initially, the catalyst was screened on the basis of particle size and the lowest particle sized TiO₂ obtained was further used for desulfurization of thiophene. For desulfurization process, the catalyst activity study was conducted using various individual as well as combinational approaches of desulfurization such as sonication, UV, US/UV, US/UV/H₂O₂, US/UV/TiO₂, and US/UV/H₂O₂/TiO₂ at fixed TiO₂ loading of 1 g/L and oxidant loading of 5 mL/L whereas the reaction temperature was maintained at 40 °C. For all the experiments, the intensity of UV light was kept constant while US was operated at a fixed power output of 110 W, 70% duty cycle and 20 kHz frequency. The reaction temperature was measured using thermometer and maintained by water bath. The effect of solvent on the extent of desulfurization was also evaluated using toluene, n-hexane and n-octane as key diesel component. At optimized conditions, the comparison of the catalyst synthesized in the presence of ultrasound and conventionally prepared TiO₂ has also been established in present study.

During the treatment, the samples were collected at a constant time interval of 10 min. From the obtained samples, the oxidized sulfones and sulfoxides were further extracted with DI water (for toluene) and acetonitrile (for n-hexane and n-octane) at 2:1 ratio (v/v). The organic and extractant phase were separated carefully and the obtained organic phase was used for analysis based on HPLC.

2.5. Analysis

High performance liquid chromatography was used to determine the concentration of thiophene in simulated diesel fuel. The HPLC unit used in this study was supplied by Thermo-Fisher Scientific Ltd. (Ultimate 3000). The unit was configured with in-built temperature controller, UV detector, Quaternary pump and C18 reverse phase column (4.6 mm × 150 mm). The mobile phase used was a mixture of HPLC grade acetonitrile and DI water (80:20) used at a constant flow rate of 1 mL/min

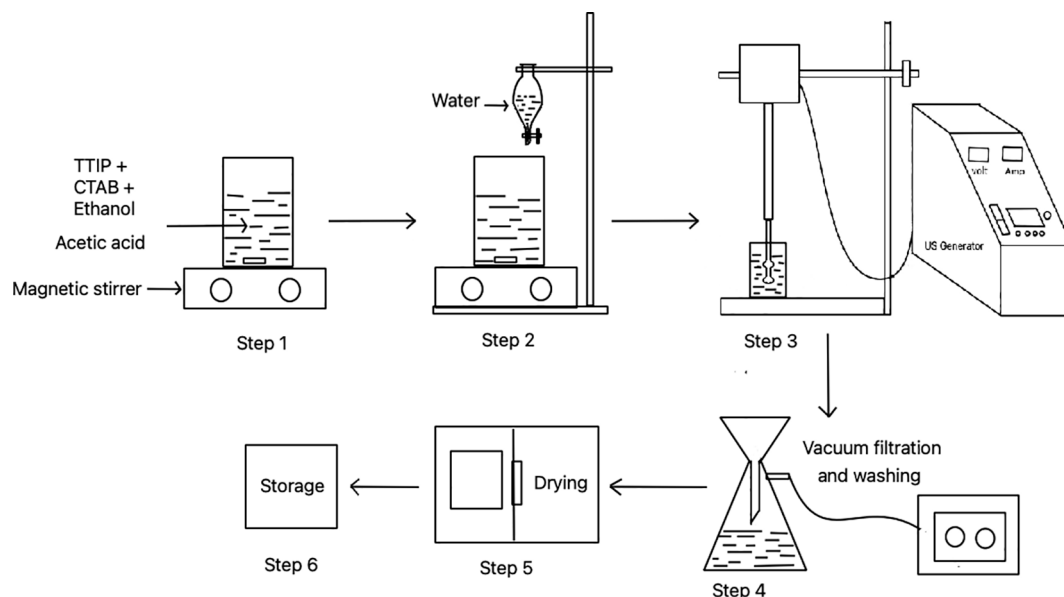


Fig. 1. Schematic representation of the catalyst synthesis process.

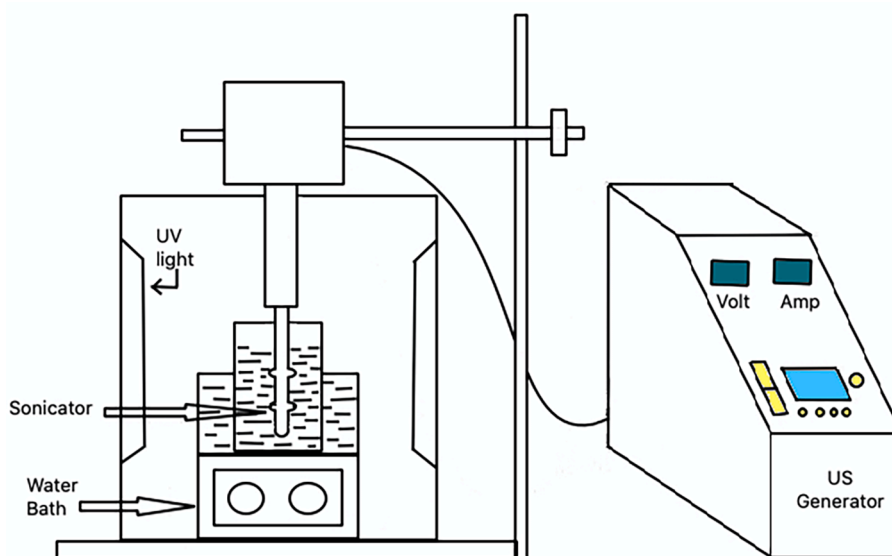


Fig. 2. Experimental setup for desulfurization of thiophene.

while the column temperature was maintained at 25 °C. The wavelength of 231 nm was used to detect the thiophene concentration in the solution.

Initially, thiophene solutions of known concentrations were used to prepare the calibration chart correlating the concentration and the observed peak area during the HPLC analysis. The obtained peak areas for the unknown samples were converted into the concentrations based on the calibration equation. Based on the concentrations of the withdrawn samples and the initial sample, extent of desulfurization has been calculated.

2.6. Catalyst characterization

The particle size of the obtained TiO₂ was quantified using Malvern Zetasizer Nano S model. To perform the particle size analysis, 1 µg of sample was added to 50 mL of water which was further diluted 10 times. The resulting solution was used to detect the particle size of titanium dioxide catalyst. XRD patterns were recorded on Bruker AXS X-ray diffractometer using Cu- α radiation of $\lambda = 1.5406 \text{ \AA}$ at room temperature. The diffraction patterns for TiO₂ catalyst were recorded at different 2θ angles in the range of 0–75°. The Scherrer equation used for estimation of the crystal size is represented as follows:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is average crystal size, K is dimensionless shape factor with value ranging between 0.9 and 0.94, θ is Bragg angle, β is the corrected line broadening at half the maximum intensity, and λ is the wavelength of X-ray.

The surface morphological characteristics of TiO₂ catalyst were analyzed using scanning electron microscope (JEOL – JSM 6380 LA instrument). For functional group determination, Perkin Elmer Spectrum 100 FTIR has been used. The spectra were recorded in the infrared region of 4000–400 cm⁻¹, using KBr pellets at a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Effect of synthesis conditions on catalyst particle size

Effect of various parameters on particle size of the obtained TiO₂ catalyst was studied in order to get the best conditions for obtaining the lowest particle sized catalyst. Subsequently the catalyst was also

prepared conventionally at an optimized CTAB concentration and compared to that obtained using ultrasonic approach.

3.1.1. Effect of US power on catalyst particle size

Experiments were performed to optimize the US power in such a way that the lowest possible particle size of TiO₂ catalyst can be achieved. The US power was varied from 80 W to 120 W of power output at constant conditions of 70% duty cycle, 20 kHz frequency, 30 min of sonication time and 0.065 CTAB loading at 40 °C temperature. The obtained results are depicted in Fig. 3 where it is seen that the particle size reduced from 780 nm to 361.4 nm as the ultrasound power increased from 80 W to 110 W. Subsequently, the particle size of TiO₂ reduced marginally to 352.9 nm as the US power increased from 110 W to 120 W. Since the difference in particle size was negligible for 110 W and 120 W, 110 W was considered as the optimum power for subsequent experimental sets of catalyst preparation. The obtained results clearly indicate dominant reduction of particle size with a positive change in US power till an optimum power dissipation level, beyond which the reduction is not significant. The decreasing trend of particle size at higher power dissipation till optimum can be postulated to the fact that at higher power dissipation, the intensity of bubble formation and collapse is increased leading to generation of more intense shock waves, acoustic streaming and micro turbulence which are responsible for particle breakage, deagglomeration and particle size reduction. The results obtained by Hassanjani-roshan et al. [30] also clearly demonstrated that ultrasonic power plays positive role in particle size reduction with the particle size reducing from 30 nm to 12 nm as the power increased from 1 to 9 W. Sabnis and Gogate [31] also reported a similar decrement in particle size from 22.02 µm to 18.87 µm with an increased power output from 50 W to 100 W. Kitamura et al. [32] reported that as the ultrasound power elevated from 0 W to 12 W, a reduction in average particle size from 12 µm to 1 µm was observed. Importantly, though the trends are similar, the actual quantitative effect on the particle size reduction and the best power condition for getting maximum benefits is dependent on the system as established using the literature comparison. This clearly explains the utility of the study reported in the current investigation.

3.1.2. Effect of US time on catalyst particle size

Synthesis of TiO₂ catalyst was also performed at varying conditions of the ultrasound irradiation time over the range of 5 min to 60 min under an optimized US power of 110 W. Fig. 4 shows the variation in

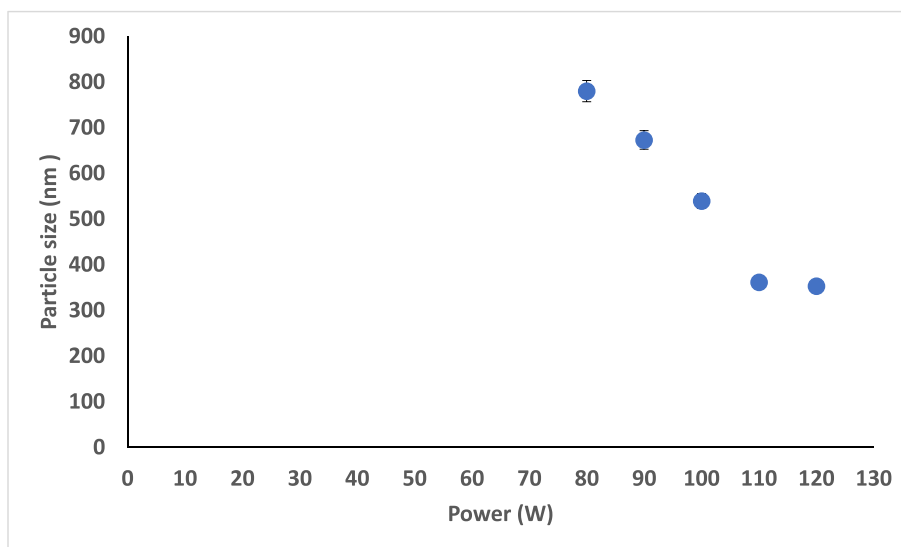


Fig. 3. Effect of US power on particle size of TiO₂ particles under constant conditions of 70% duty cycle, 30 min sonication and 0.65 g CTAB loading.

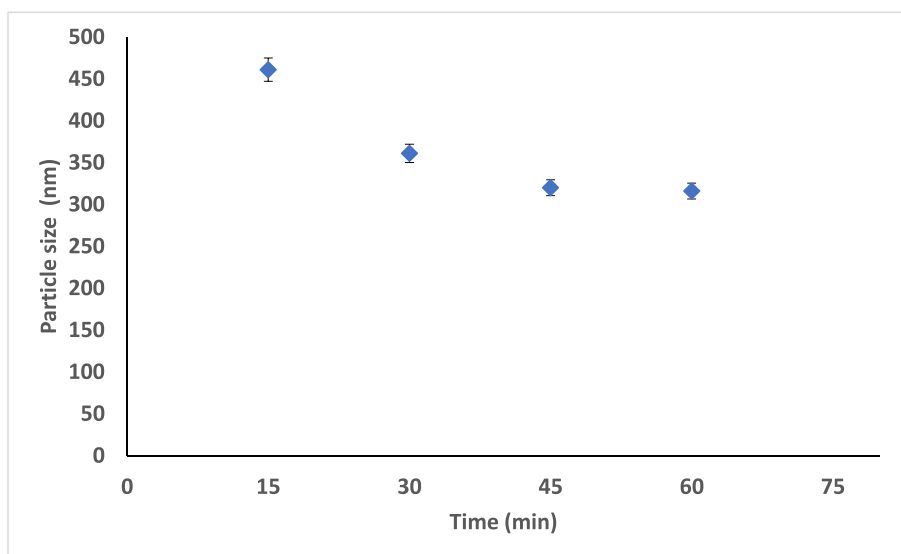


Fig. 4. Effect of US irradiation time on particle size of TiO₂ particles under constant conditions of 70% duty cycle, 110 W US power and 0.65 g CTAB loading.

particle size with respect to irradiation time and clearly signifies that the effective reduction in particle size of catalyst is strongly dependent on the irradiation time. It was seen that the particle size decreased drastically till 45 min of irradiation time with the further increase of irradiation time to 60 min giving a nominal change in the particle size. The particle size obtained for 5 min, 15 min, 30 min, 45 min, and 60 min treatment were 554 nm, 461 nm, 361 nm, 320 nm and 316 nm, respectively. From the obtained results, it can be established that the tendency in reduction of particle size was greater at the initial ultrasonic irradiation time in comparison with the prolonged irradiation time. The results revealed that negligible difference (actual values as 320 nm and 316 nm respectively) in the particle size of catalyst was observed for the irradiation time of 45 min and 60 min. Thus, to save energy of ultrasound processing and hence the cost of operation, 45 min as the irradiation time was chosen as an optimum irradiation time. The observed results can be justified on the basis of the fact that with an increase in irradiation time till optimum, the exposure of catalyst to the cavitation effect is increased which leads to increase in inter-particle collision of the TiO₂ particles and the fragmentation of particles. The inter-particle collision avoids the agglomeration of particles within the solution and

hence reduction in particle size is observed. The study conducted by Ambati and Gogate [8] also reported that increasing sonication time from 15 min to 60 min significantly reduced the particle size of Fe-TiO₂ from 480 nm to 99 nm. Neppolian et al. [19] also observed a particle size reduction from 16 nm to 12 nm as sonication time varied from 30 to 120 min. The grain size reduced from 5.5 nm to 4.9 nm in 30 min of irradiation and subsequent increase in time resulted in no significant change in grain size of TiO₂ establishing 30 min as optimum [21]. The specificity of the observed effects and the best treatment time on the type of catalyst synthesized and the ultrasonic reactor applied again has shown the importance of the current work.

3.1.3. Effect of CTAB loading on catalyst particle size

To understand the effect of CTAB loading on particle size obtained using ultrasound assisted approach, experiments were carried out at room temperature, 60% duty cycle, 110 W power and 45 min of irradiation time. Different loading of CTAB such as 0.052 g, 0.065 g, 0.078 g, 0.091 g and 0.104 g were used to evaluate the best possible loading of CTAB to achieve minimum catalyst particle size. Fig. 5 illustrates the obtained data for the variation of particle size with respect to CTAB

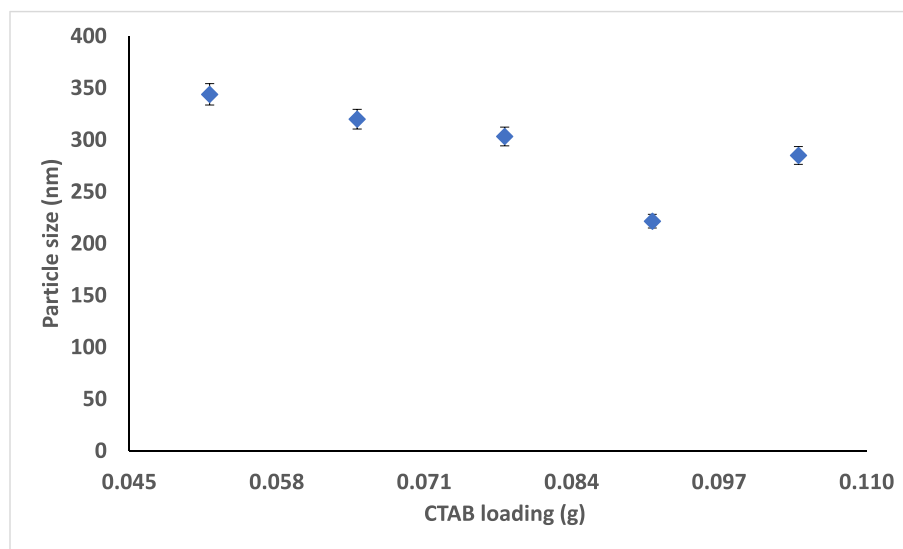


Fig. 5. Effect of CTAB loading on particle size of TiO_2 under constant conditions of 110 W power and 45 min sonication.

loading and it was illustrated that with an increase in CTAB loading from 0.052 g to 0.078 g, the particle size reduced from 344 nm to 303 nm and with a subsequent increase in the amount to 0.092 g, the particle size reduced remarkably to 222 nm. With a further increase in the amount to 0.104 g, an increase in particle size to 284 nm was observed. CTAB is a surfactant used mainly as a surface directing agent which is capable to reduce the surface tension of the mixture which in turn allows greater dispersion of the titanium precursor. Thus, with an increase in quantum of CTAB, the dispersion of precursor within the mixture is enhanced leading to reduction in the particle size. If the quantity used is increased beyond optimum, the viscosity of colloids becomes greater and the precursors of TiO_2 particles that have formed a nucleus tend to reunite easily, forming bigger particles and particles agglomerate to form larger particles [33]. The literature also demonstrated that the loading of CTAB is an important factor which influences the catalyst modification process [17,34]. Li and Tripp [35] reported that on the surface of TiO_2 the CTAB exists as micelles when the concentration of CTAB is above critical micelle concentration, leading to formation of agglomerates. Jiu et al. [16] established that CTAB is a favorable surfactant for the growth of TiO_2 crystallites based on the use of sol-hydrothermal process at elevated temperature in the presence of triblock copolymer F127 and reported that at low concentration of CTAB of 0.005 M and 0.03 M, irregular and short nanorods were obtained but by increasing the concentration to 0.05 M, long branched rods were seen with diameter of 20–30 nm and length of 500 nm. It was also reported that with a further increase in concentration to over 0.1 M, spherical nanocrystals can be obtained. The presented results and comparison with literature clearly illustrate the role of surfactant concentration in altering the morphology of the formed materials.

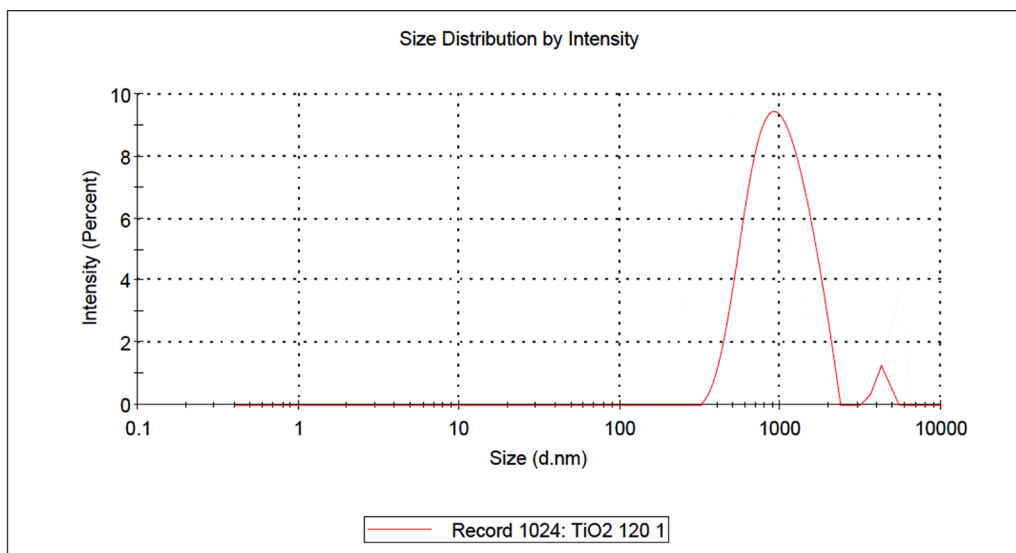
3.2. Comparative characterization of catalysts

The particle size analysis was performed for conventionally and ultrasonically synthesized TiO_2 particles. For the conventionally synthesized TiO_2 , particle size of 987 nm has been observed at optimum CTAB loading in absence of sonication. In the presence of sonication, the particle size obtained was 222 nm at optimized conditions. The particle size distribution curves have been illustrated in Fig. 6. It can be thus concluded that with the application of sonication, the particle size can be reduced significantly as compared to conventionally prepared catalyst at optimum reaction conditions. The size distribution was also narrow and uniform for the catalyst obtained using the ultrasound assisted synthesis.

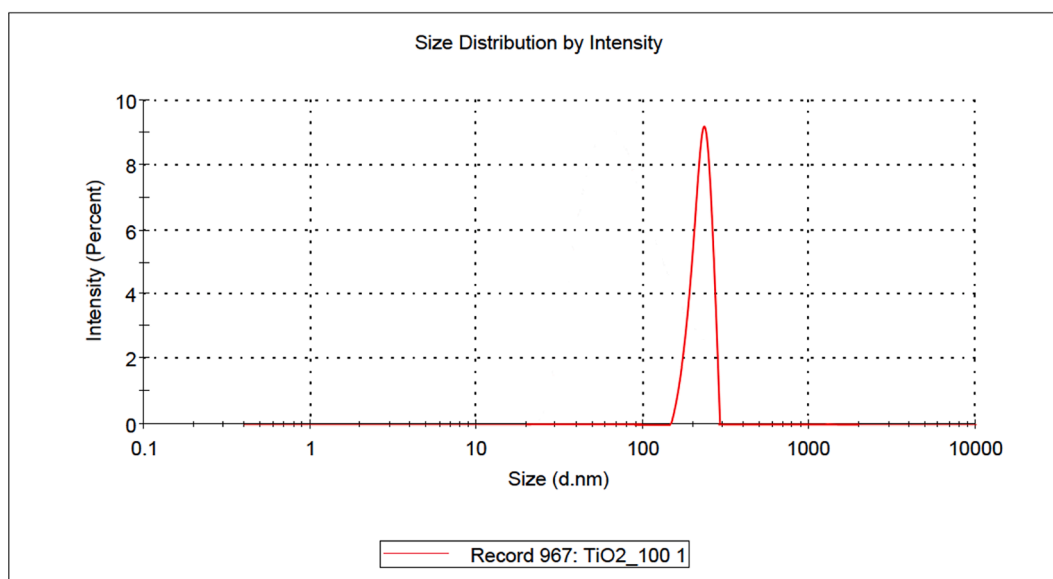
The external surface morphology of synthesized TiO_2 particles was also characterized using SEM analysis and the obtained images are shown in Fig. 7. It is seen that catalysts obtained using ultrasonic process and conventional approach both have a spheroidal shape though the surface of catalyst is more uniform in the case of ultrasonically prepared TiO_2 catalyst. The surface images clearly show that the usage of sonication resulted into lesser particle size, high degree of sphericity and homogeneous nature of particles compared to conventionally prepared TiO_2 . The results of SEM images are in agreement with the particle size analysis of both the catalysts. Thus, it can be concluded based on the results of particle size and SEM analysis that smaller particles with controlled size distribution can be produced using sonication.

FTIR transmittance spectra of conventionally and ultrasonically prepared TiO_2 catalysts with calcination at 500 °C for 3 h are illustrated in Fig. 8. The functional group analysis of catalyst was performed with FTIR spectroscopy. The spectra obtained for the catalysts represented peak at 757, 531, 659 480–484, 1384, 1631 and 2923 cm^{-1} respectively. The characteristic peak at 1631 cm^{-1} generally represents the bending vibration of OH indicating hydroxyl group attached on the particle surface due to the hygroscopic nature [17,36,37]. The absorption band in the region of 450–800 cm^{-1} is attributed to the vibrational absorption, bending and stretching of Ti-O-Ti linkage of TiO_2 catalyst [38]. The band at 480–484, 531 cm^{-1} and 1384 cm^{-1} can be more precisely ascribed to the bending vibration of Ti-O bond indicating that during calcination, all the organic ligand are completely removed [20]. The IR spectra at 757 and 659 cm^{-1} corresponds to the Ti-O-Ti stretching vibration. The weak band observed at 2923 cm^{-1} could be attributed to residual species frequency which was not completely removed by distilled water wash and can be assigned to C-H vibrational stretching of alkane group [39]. It was also established that compared to conventional TiO_2 , ultrasonically synthesized TiO_2 has a well distributed Ti-O stretching indicating the positive modification of TiO_2 particles by the application of sonication.

Before performing the X-ray diffraction analysis, the samples were dried overnight at 80 °C to remove trapped moisture from conventionally and ultrasonically synthesized TiO_2 . The powder X-ray diffraction peaks of TiO_2 catalyst for ultrasonically and conventionally synthesized TiO_2 has been depicted in Fig. 9. XRD of both samples showed sharp peaks validating the anatase nature of TiO_2 catalyst with high degree of crystallinity [40]. Nearly same crystal size of 31.5 nm was observed for both samples. No change in crystallinity and crystal size was observed for catalyst obtained with sonication. Eight crystal peaks were observed for ultrasonically prepared TiO_2 sample (similar to conventionally



(a)



(b)

Fig. 6. Particle size distribution: a) Conventionally synthesized TiO₂, b) TiO₂ synthesized in the presence of ultrasound.

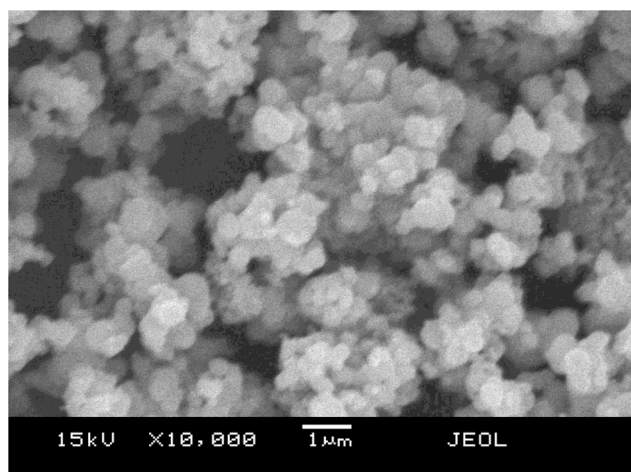
synthesized TiO₂) at 2 theta value of 25.37, 37.84, 48.06, 53.95, 62.73, 68.76, 70.36, and 75.02 which corresponds to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 0 4), (1 1 6), (2 2 0), and (2 1 5) orientations on crystallographic planes of anatase structure. The comparison clearly confirmed not negative changes in the crystal structure due to the use of ultrasound.

3.3. Catalyst activity study for desulfurization of thiophene using different approaches

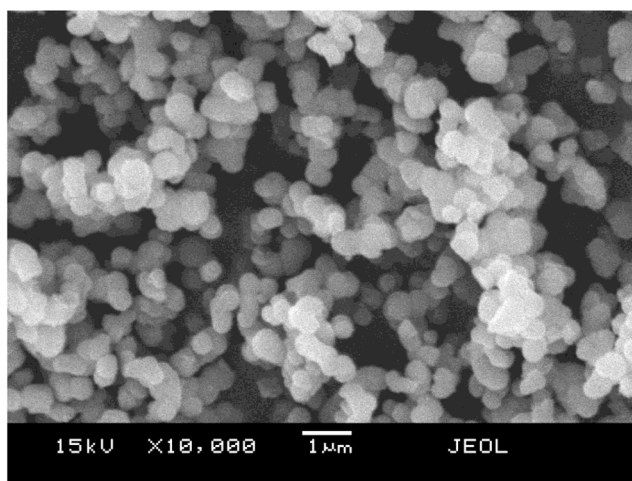
The catalyst with lowest particle size was selected to evaluate the catalytic activity in different desulfurization approaches. The catalytic activity study for desulfurization of thiophene was performed using individual and combinational approaches of UV and US irradiation in absence and presence of oxidant and catalyst with toluene as the organic solvent used. US horn was operated at constant power output of 110 W, 20 kHz frequency and 70% duty cycle. UV irradiation was provided

using two 8 W UV lights placed opposite to each other. H₂O₂ and TiO₂ were used as oxidant and catalyst respectively. The individual as well as combinational approach of US and UV were studied in absence of catalyst and oxidant to develop an understanding about the effectiveness of individual and combined US and UV irradiation on desulfurization of thiophene. Different combination studies performed with catalyst and oxidant were US/H₂O₂/UV, US/TiO₂/UV, and US/UV/H₂O₂/TiO₂.

Fig. 10 represents the obtained results for the different approaches used for desulfurization of thiophene in toluene at 60 min of treatment time, 40 °C temperature, 1 g/L TiO₂ loading and 5 mL/L of H₂O₂ loading as applicable in the specific approach. It is observed that individual approaches of UV and US irradiation resulted into lesser extent of desulfurization as 4.21% and 9.8% as compared to desulfurization obtained with the combinational approach of US/UV as 13.4%. Similarly, the combination of US/TiO₂/UV showed about 9% higher desulfurization than the combination of US/UV/H₂O₂. The maximum extent as 43%



(a)



(b)

Fig. 7. SEM images: a) Conventionally synthesized TiO_2 , b) TiO_2 synthesized in the presence of ultrasound.

was observed for the combinational approach of US/UV/ H_2O_2 / TiO_2 which is about 2 folds higher than individual combination of US or UV with catalyst or oxidant. From the obtained data it can be observed that the efficiency of desulfurization of thiophene was lower with only UV and US irradiation than the combinational approach of US and UV irradiation. The results can be due to combined effect between US and UV irradiations based on the complementary nature of the cavitation effects and chemical effects of the individual UV approach [41]. The combination approach of US/UV with oxidant or catalyst showed a significant improvement in desulfurization efficiency due to the additional generation of hydroxyl radicals and presence of active sites on the TiO_2 particles compared to that of approach of only US/UV. It can be thus said that the desulfurization efficiency can be improved with the addition of oxidant or catalyst [42]. Maximum efficiency was observed for the combinational approach of US/UV/ TiO_2 / H_2O_2 with respect to other approaches studied. This remarkable increment may be due to number of phenomena such as a) cavitation effect of sonication is responsible for continuous cleaning of TiO_2 particles which in turn increases active sites available for oxidation of sulphur compound, b) both ultrasound and UV irradiation promotes the faster dissociation of hydrogen peroxide to hydroxyl radicals, c) cavitation effects lead to enhanced mass transfer leading to better contact of oxidants with the thiophene and d) presence of catalyst enhances the cavitation intensity

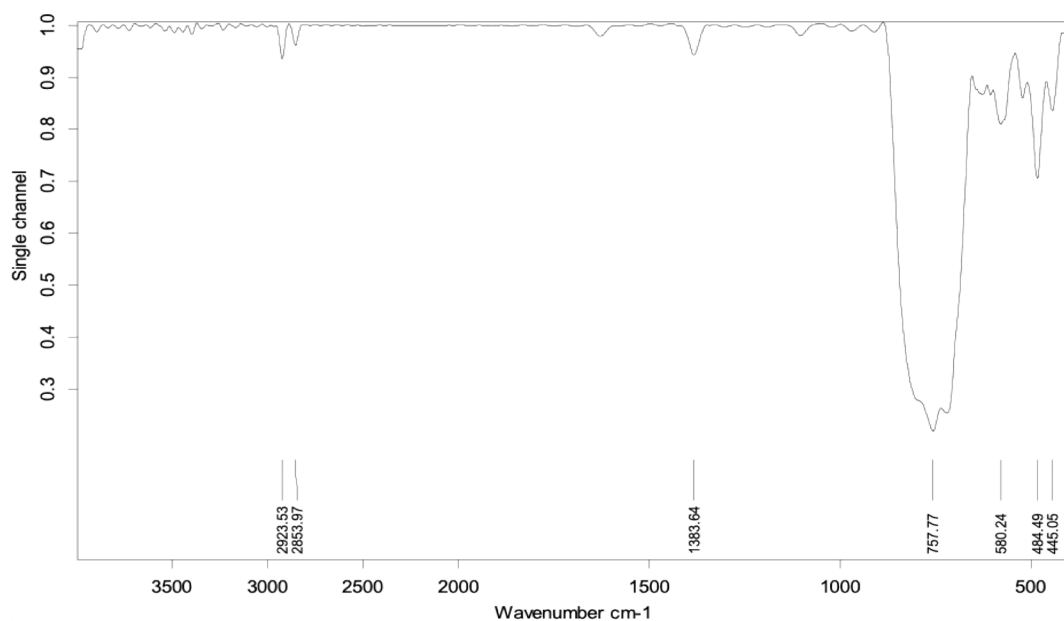
based on the surface cavitation effects [43]. Additionally, under the presence of UV irradiation the electrons available in valance band get excited with photons from the UV light and this excited electron then travel to conduction band leaving valance band holes on the surface of the photocatalyst [44]. These electron and holes on the surface of catalyst are the active sites for the oxidation of thiophene. The excited electron also reacts with the electron acceptor oxidant for the generation of highly active hydroxyl radicals with oxidation potential of 2.8 V which further oxidizes the sulphur compounds. Overall, in comparison to all other approaches, the maximum extent of desulfurization was obtained for the combinational approach of US/UV/ H_2O_2 / TiO_2 . Similar results were reported by Wang et al. [41] for desulfurization of FCC gasoline involving different model sulphur compounds and using 0.15 g of nickel-heteropoly acids supported on silica gel (NSW300) as the catalyst and 0.3 mL of hydrogen peroxide in different combinations of US and/or UV irradiation. It was reported that the combinational approach of US/UV/NSW-300/ H_2O_2 resulted into 100% and 95.5% desulfurization of model sulphur compounds (dissolved in n-octane) and FCC gasoline respectively in 30 min of treatment. Further, the study conducted by More and Gogate [42] also reported 98.9% thiophene (dissolved in n-hexane) desulfurization for the combinational approach of US/UV/ H_2O_2 / TiO_2 in 60 min of treatment at 0.3 g/L of catalyst loading and 300 ppm H_2O_2 loading. Clearly the results presented in the current work are important as it highlights the best treatment approach for oxidation of thiophene, specifically establishing the best treatment conditions for the catalyst obtained using direct synthesis method with assistance of ultrasound.

3.4. Comparative study of activity of conventionally and ultrasonically synthesized TiO_2 .

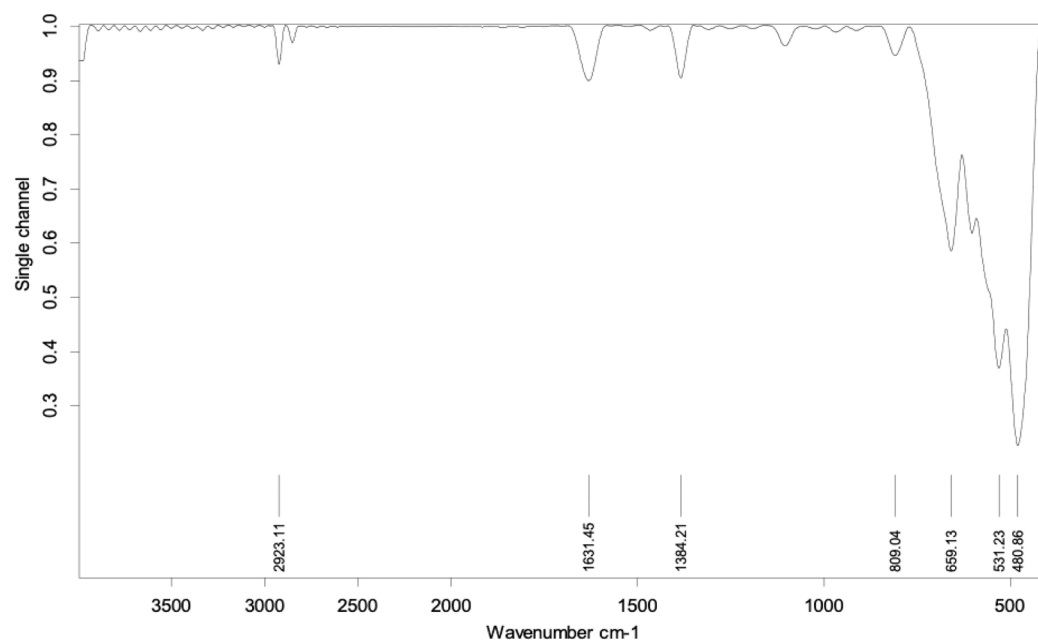
The comparative study was performed using ultrasonically and conventionally synthesized TiO_2 at treatment conditions of 1 g/L of TiO_2 loading, 5 mL/L of H_2O_2 dosage and 40 °C as the temperature using toluene as solvent. The obtained results are illustrated in Fig. 11. The extent of desulfurization for ultrasonically synthesized TiO_2 was found to be 43% in 60 min while that for the conventionally synthesized TiO_2 was only 29% in same treatment time. The observed higher activity for ultrasonically synthesized catalyst is attributed to fact that ultrasound gives lower particle size which gives higher surface area of the catalyst for oxidation reaction. Thus, it can also be said that the particle size of the catalyst has a remarkable effect on the extent desulfurization of thiophene. Overall, application of ultrasound during the synthesis of TiO_2 enhanced the catalytic activity of TiO_2 for desulfurization of thiophene.

3.5. Effect of solvent

In this research work, the nature of key diesel/ gasoline compound as selected organic solvent has been investigated to evaluate the effect on the extent of desulfurization. The study is important as the nature of organic solvent plays a significant role in deciding the thiophene removal efficiency [45]. The experiments were performed using three different solvents as toluene, n-hexane, and n-octane. 200 ppm thiophene was dissolved in the known solvent and the model diesel or gasoline thus obtained was treated using the best approach of US/UV/ H_2O_2 / TiO_2 . The obtained results for thiophene desulfurization in different organic solvents are represented in Fig. 12. It appears that changing the solvent remarkably affects the extent of desulfurization of thiophene. Toluene, as a solvent, showed lowest effectiveness with only 43% desulfurization while n-octane showed highest reactivity (100% removal in 50 min of reaction time) towards thiophene. The presented results confirmed that the nature of solvent has a greater impact on sulphur removal efficiency which may be attributed to the effect on the reactivity during the oxidation process. The order of extent of thiophene desulfurization with respect to organic solvent was observed as: n-



(a)



(b)

Fig. 8. FTIR spectra: a) Conventionally synthesized TiO_2 , b) TiO_2 synthesized in the presence of ultrasound.

octane > n-hexane > toluene. The aliphatic nature of solvents like n-octane and n-hexane aid easy desulfurization mainly due to the nature of solvent and polarity which affects the reactivity during the oxidation process while toluene is well known to offer resistance in oxidation reaction due to the presence of conjugated- π aromatic system [45,46]. The reactivity can also be explained on the basis of the dielectric constant (ϵ) which represents the solvent polarity and signifies that higher value of dielectric constants is equal to higher polarity. n-hexane ($\epsilon = 1.88$) and n-octane ($\epsilon = 1.9$) may be considered to exhibit lower polar character offering higher reactivity than toluene ($\epsilon = 2.4$) [45]. The cavitation effects are also expected to be with different intensity with respect to the solvent phase. It was thus clearly established that the removal of

thiophene is significantly different for different organic solvents with maximum desulfurization observed with n-octane compared to other solvents. Suryawanshi et al. [46] reported a study of non-catalytic desulfurization of thiophene using hydrodynamic cavitation using 3 different solvents and the order of reactivity and sulfur removal efficiency were observed as Toluene < n-octane < n-octanol. Jaimes et al. [47] also reported higher removal of the thiophene in n-octane compared to 1-octene at the temperature above 400 °C and 15 s as treatment time. In another study by Jaimes et al. [48], it was reported that for the FCC gasoline (prepared as mixture of thiophene and different solvents) desulfurization using ZSM-5 catalyst, thiophene conversions as 36.0% and 33.1% were seen for n-octane and 1-octene respectively and

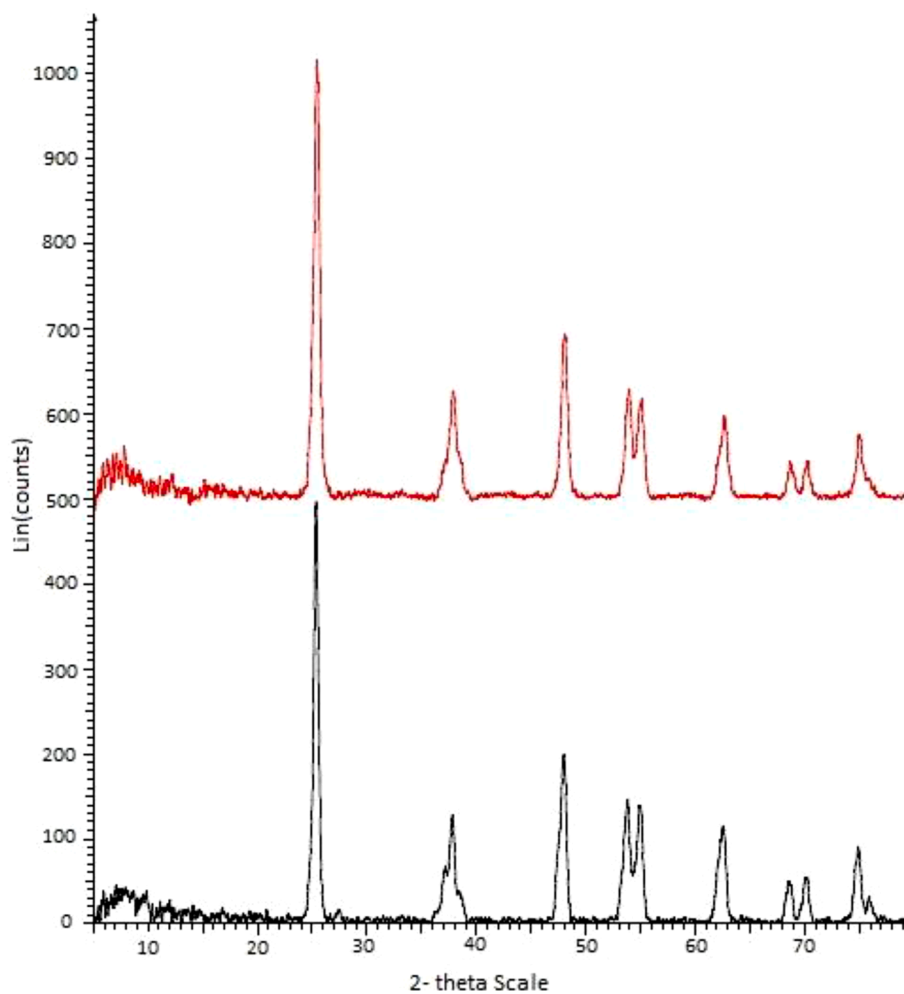


Fig. 9. XRD pattern: a) Conventionally synthesized TiO₂, b) TiO₂ synthesized in the presence of ultrasound.

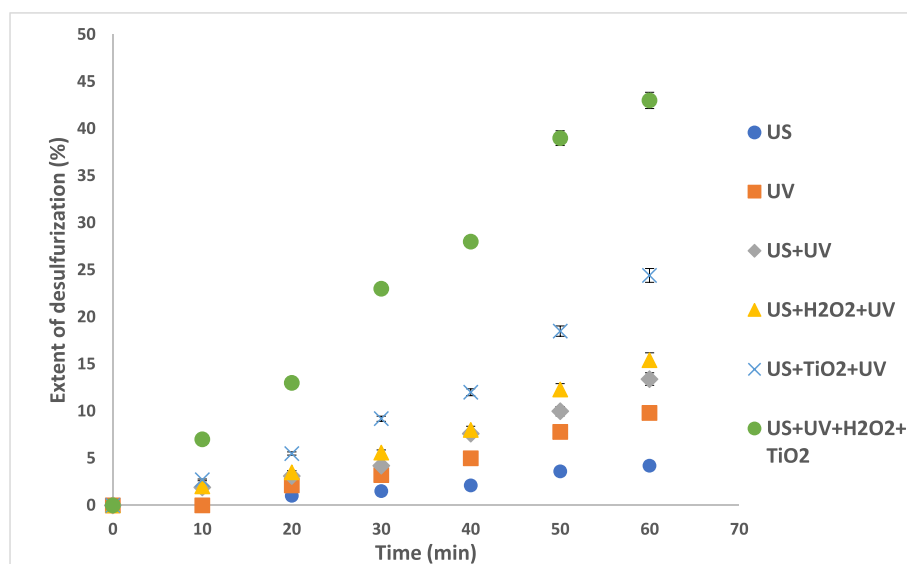


Fig. 10. Comparison of different approaches in terms of the extent of thiophene desulfurization using ultrasound and ultraviolet light with additives.

in the range of 0.56% to 6% for less reactive solvents, such as methyl-MCH, TMP and toluene. From the literature analysis it was observed that till date no study on the effect of solvent on the extent of thiophene desulfurization using the combined approach of ultrasound and UV

irradiation has been reported thus signifying the importance of the present work. The result of this study also clearly demonstrated the effectiveness of US/UV/TiO₂/H₂O₂ approach for different organic solvents as key diesel compound for the treatment of 200 ppm of thiophene

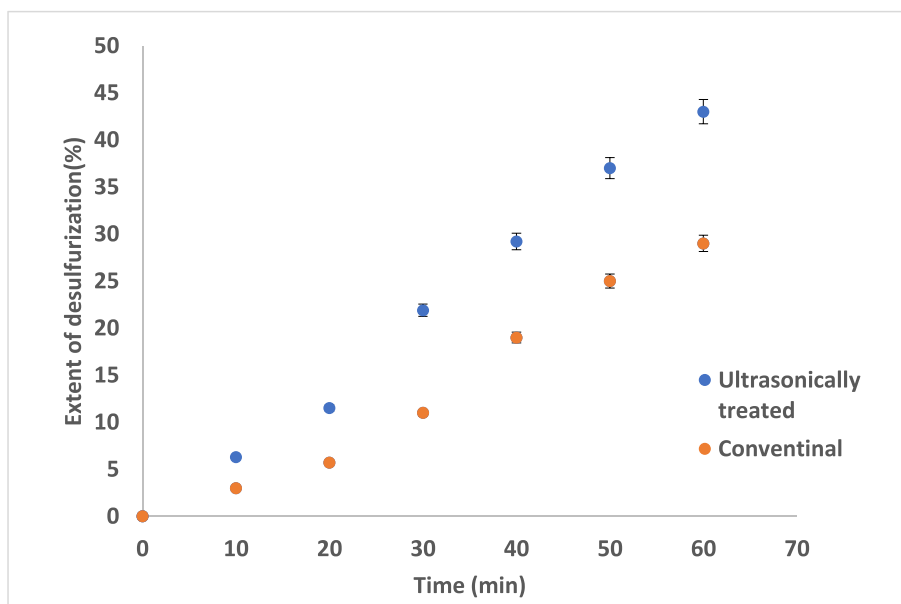


Fig. 11. Comparative study of ultrasonically and conventional synthesized TiO_2 for desulfurization of thiophene using US/UV/ H_2O_2 / TiO_2 .

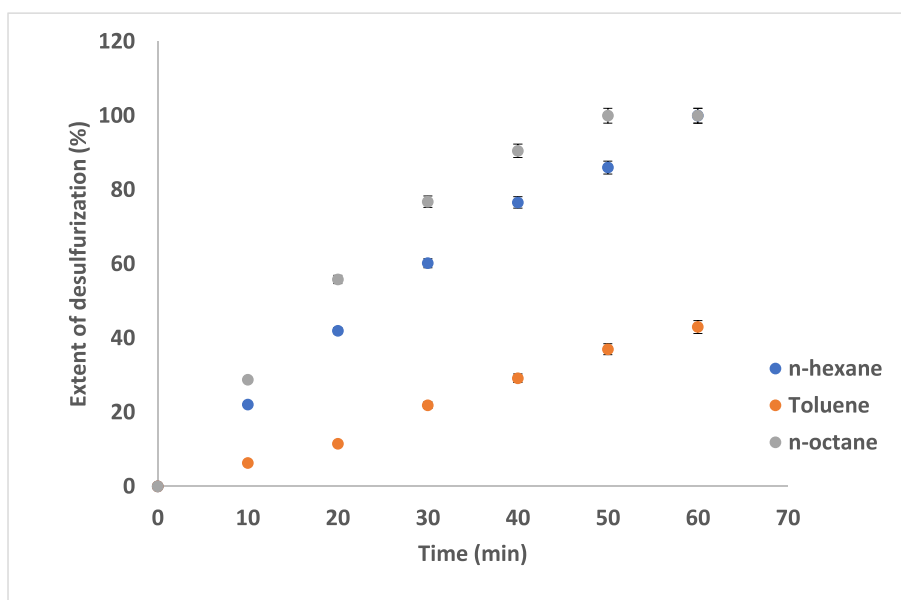


Fig. 12. Effect of solvent on extent of desulfurization of thiophene using US/UV/ H_2O_2 / TiO_2 .

present in solvent.

3.6. Kinetic analysis

The kinetic analysis was also performed on the basis of integral approach for different individual and combinational approaches using toluene as key diesel compound. The comparative kinetic analysis was also performed for the best approach of desulfurization (US/UV/ TiO_2 / H_2O_2) using different solvents as representative diesel compound. The graph of $\ln(C_{A0}/C_A)$ v/s time for the first order fitting has been represented in Figs. 13 and 14. It was observed that good fitting was indeed observed for the all the approaches and for all the solvents used in the work. The results for rate constant, extent of desulfurization and R^2 values for different approaches have been tabulated in Table 1. The results for the combinational approach US/UV/ TiO_2 / H_2O_2 using different solvents have been tabulated in Table 2. The extent of

desulfurization was observed lowest for the individual approaches of sonication and UV irradiation with kinetic rate constant of $7.1 \times 10^{-4} \text{ min}^{-1}$ and $1.7 \times 10^{-3} \text{ min}^{-1}$, respectively. The synergism was observed for the combinational approaches when compared to individual approach of ultrasound and UV irradiation. A marginal difference in desulfurization of thiophene and rate constant (actual values $2.3 \times 10^{-3} \text{ min}^{-1}$ and $2.7 \times 10^{-3} \text{ min}^{-1}$) was observed for the combinational approach of US + UV and US + H_2O_2 + UV thus implying absence of synergism between them. The synergism was observed for combinational approach of US/UV/ TiO_2 / H_2O_2 as the obtained extent of desulfurization (43%) and rate constant ($9.3 \times 10^{-3} \text{ min}^{-1}$) were significant higher than all other approaches. The application of ultrasound in this combination approach is responsible for the generation of enhanced quantum of hydroxyl radicals based on the dissociation of H_2O_2 , and also for enhanced micro mixing, deagglomeration of catalyst particles and generation of local hot spots of high pressure and temperature

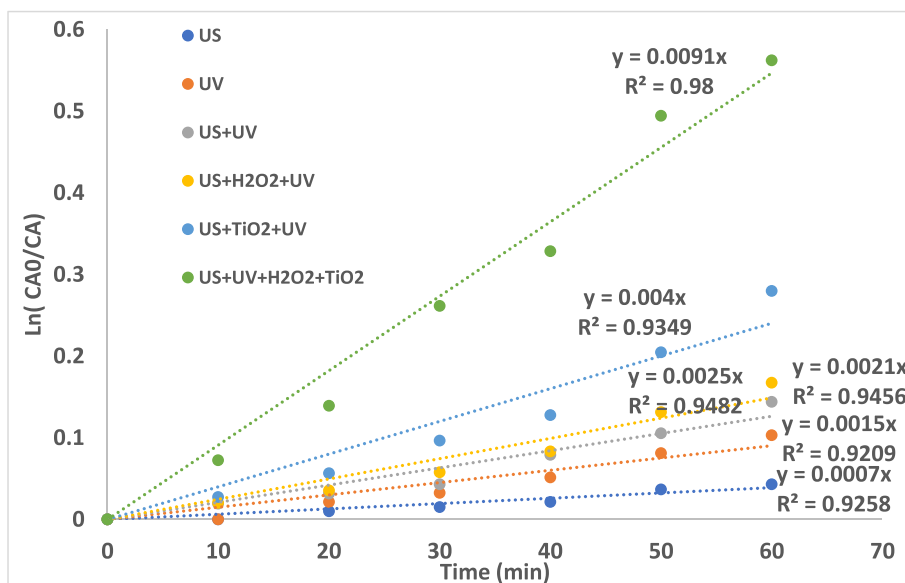


Fig. 13. Plot of pseudo first order kinetics for the desulfurization of thiophene using different approaches.

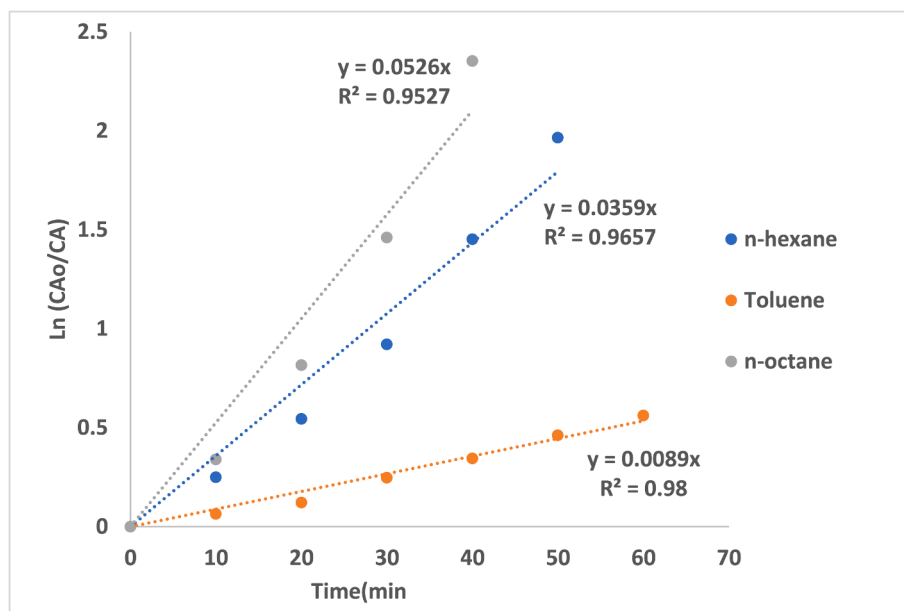


Fig. 14. Plot of pseudo first order kinetics for the desulfurization of thiophene for combinational approach of US/UV/ $\text{H}_2\text{O}_2/\text{TiO}_2$ using different solvents.

Table 1

Kinetic rate constants and the extent of thiophene desulfurization using different approaches of desulfurization with toluene as key diesel compound.

Schemes (toluene as key diesel compound)	Extent of desulfurization(%)	Rate constant K (min^{-1})	R^2
US	4.21	7.1×10^{-4}	0.9682
UV	9.8	1.7×10^{-3}	0.9652
US + UV	13.4	2.3×10^{-3}	0.9791
US + H_2O_2 + UV	15.41	2.7×10^{-3}	0.98
US + TiO_2 + UV	24.41	4.6×10^{-3}	0.9739
US + UV + H_2O_2 + TiO_2	43	9.3×10^{-3}	0.9928

leading to enhanced kinetic rate constants. All these phenomenon together enhances the rate of oxidation in desulfurization process.

In terms of different solvents used in the study for the combinational approach of US/UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$, lowest kinetic rate constant of 9.3×10^{-4}

Table 2

Kinetic rate constants and the extent of thiophene desulfurization using US/UV/ $\text{H}_2\text{O}_2/\text{TiO}_2$ approach for different solvents.

Solvent/Key diesel compound	Extent of desulfurization(%)	Time (min)	Rate constant K(min^{-1})	R^2
Toluene	43	60	9.3×10^{-3}	0.9928
n-hexane	100	60	3.9×10^{-2}	0.9867
n-octane	100	50	5.8×10^{-2}	0.9803

3 min^{-1} was found for toluene and significantly higher rate constants were observed for the other two solvents. Specifically, 100% desulfurization of thiophene was obtained for n-hexane and n-octane solvents using combinational approach of US/UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ with a kinetic rate constant of $3.9 \times 10^{-2} \text{ min}^{-1}$ and $5.8 \times 10^{-2} \text{ min}^{-1}$, respectively. Hence, it can be concluded that solvent can dramatically affect the

desulfurization process. It is worthwhile to compare the results for the kinetics of thiophene desulfurization with literature. Alhaddad et al. [49] investigated the photooxidative desulfurization of thiophene dissolved in acetonitrile using 1.2 g/L of MoS₂@rGO catalyst and reported that pseudo first order reaction kinetics was found to explain the data well with a rate constant of 0.0047 min⁻¹ and complete sulfur removal efficiency. Zhen et al. [50] reported that photocatalytic desulfurization of thiophene dissolved in n-octane followed pseudo first order reaction kinetics with 98.4% desulfurization and 0.0246 min⁻¹ as the rate constant for 1.5 g/L loading of 5% Ag/α-MoO₃ photocatalyst. More and Gogate [42] also reported that thiophene desulfurization followed pseudo first order reaction kinetics for a combinational approach of ultrasound, UV light and additives and reported a rate constant of 5.9 × 10⁻² min⁻¹ with 98.9% of thiophene removal.

4. Conclusions

The present work demonstrated an improved method to synthesize TiO₂ catalyst in the presence of CTAB and ultrasound. Ultrasonically synthesized TiO₂ was observed to give the lowest particle size of 222 nm at optimized 0.091 g CTAB loading, 110 W US power and 45 min US time whereas conventionally treated TiO₂ gave 987 nm as the particle size at same conditions. SEM analysis revealed a smoother and less aggregated TiO₂ particle for ultrasonically prepared catalyst as compared to conventionally prepared TiO₂ thus establishing the effectiveness of sonication in enhancing the morphological characteristics and particle size reduction. The catalyst activity was investigated for desulfurization of thiophene using different approaches of ultrasound, ultraviolet, oxidant and catalyst. The best approach of thiophene desulfurization was observed to be US/UV/TiO₂/H₂O₂ giving maximum extent of desulfurization. A comparative analysis of ultrasonically and conventionally synthesised TiO₂ was also evaluated to demonstrate the efficacy for extent of thiophene desulfurization. At the lower particle size of TiO₂ (ultrasonically synthesized TiO₂), the extent of desulfurization was found to be 43% while for conventionally synthesized TiO₂ it was found to be 29% only. Enhanced extent of desulfurization was observed when the solvent was changed from toluene to n-hexane and n-octane. 100% desulfurization was observed in 60 min of reaction time for n-hexane and in 50 min reaction time for n-octane as a solvent. The order of reactivity and thiophene removal efficiency was found to be Toluene < n-hexane < n-octane. The combinational approach of US/UV/H₂O₂/TiO₂ and also the other combination or individual approaches were demonstrated to follow pseudo first order kinetics. Overall, the results obtained in the present work demonstrated the feasibility of ultrasonically synthesized catalyst and US/UV/H₂O₂/TiO₂ combinational approach for intensified desulfurization of thiophene.

CRedit authorship contribution statement

Ashlesha Tiple: Methodology, Investigation, Writing - original draft. **Pankaj S. Sinhmar:** Methodology, Investigation, Writing - review & editing. **Parag R. Gogate:** Supervision, Writing - review & editing, Project administration.

Declaration of 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.

Acknowledgement

Authors would like to acknowledge the support of Institute of Chemical Technology for supporting the summer internship of AT and M/s Mangalam Organics for supporting the PhD fellowship for PS.

References

- [1] F. Lin, Z. Jiang, N. Tang, C. Zhang, Z. Chen, T. Liu, B. Dong, Photocatalytic oxidation of thiophene on RuO₂/SO₄²⁻-TiO₂: Insights for cocatalyst and solid-acid, *Appl. Catal. B Environ.* 188 (2016) 253–258.
- [2] G. Colón, M.C. Hidalgo, G. Munuera, I. Ferino, M.G. Cutrufello, J.A. Navío, Structural and surface approach to the enhanced photocatalytic activity of sulfated TiO₂ photocatalyst, *Appl. Catal. B Environ.* 63 (1–2) (2006) 45–59.
- [3] S. Bagheri, N. Muhd Julkapli, S. Bee Abd Hamid, Titanium dioxide as a catalyst support in heterogeneous catalysis, *Sci. World J.* 2014 (2014) 727496.
- [4] Q. Chen, F. Ji, T. Liu, P. Yan, W. Guan, X. Xu, Synergistic effect of bifunctional Co-TiO₂ catalyst on degradation of Rhodamine B: Fenton-photo hybrid process, *Chem. Eng. J.* 229 (2013) 57–65.
- [5] R.S. Dubey, K.V. Krishnamurthy, S. Singh, Experimental studies of TiO₂ nanoparticles synthesized by sol-gel and solvothermal routes for DSSCs application, *Results Phys.* 14 (2019), 102390.
- [6] T. Löffler, J. Clausmeyer, P. Wilde, K. Tschulik, W. Schuhmann, E. Ventosa, Single entity electrochemistry for the elucidation of lithiation kinetics of TiO₂ particles in non-aqueous batteries, *Nano Energy* 57 (2019) 827–834.
- [7] N. Fajariah, W.A.E. Prabowo, F. Fathurrahman, A. Melati, H.K. Dipojono, The investigation of electronic structure of transition metal doped TiO₂ for diluted magnetic semiconductor applications: a first principle study, *Procedia Eng.* 170 (2017) 141–147.
- [8] R. Ambati, P.R. Gogate, Ultrasound assisted synthesis of iron doped TiO₂ catalyst, *Ultrason. Sonochem.* 40 (2018) 91–100.
- [9] G. Li, K.A. Gray, The solid-solid interface: explaining the high and unique photocatalytic reactivity of TiO₂-based nanocomposite materials, *Chem. Phys.* 339 (2007) 173–187.
- [10] Z. Ding, G.Q. Lu, P.F. Greenfield, Role of the crystallite phase of TiO₂ in heterogeneous photocatalysis for phenol oxidation in water, *J. Phys. Chem. B* 104 (19) (2000) 4815–4820.
- [11] C. Canevali, S. Polizzi, A. Testino, I.R. Bellobono, V. Buscaglia, Optimizing the photocatalytic properties of hydrothermal TiO₂ by the control of phase composition and particle, *J. Am. Chem. Soc.* 129 (2017) 3564–75.
- [12] S. Abbad, K. Guergouri, S. Gazaoui, S. Djebabra, A. Zertal, R. Barille, M. Zaabat, Effect of silver doping on the photocatalytic activity of TiO₂ nanopowders synthesized by the sol-gel route, *J. Environ. Chem. Eng.* 8 (2020), 103718.
- [13] S.B. Wategaonkar, R.P. Pawar, V.G. Parale, D.P. Nade, B.M. Sargar, R.K. Mane, Synthesis of rutile TiO₂ nanostructures by single step hydrothermal route and its characterization, *Mater. Today Proc.* 23 (2020) 444–451.
- [14] Z. Wang, S. Liu, X. Cao, S. Wu, C. Liu, G. Li, W. Jiang, H. Wang, N. Wang, W. Ding, Preparation and characterization of TiO₂ nanoparticles by two different precipitation methods, *Ceram. Int.* 46 (10) (2020) 15333–15341.
- [15] D. Huang, Y.J. Wang, Y.C. Cui, G.S. Luo, Direct synthesis of mesoporous TiO₂ and its catalytic performance in DBT oxidative desulfurization, *Microporous Mesoporous Mater.* 116 (1–3) (2008) 378–385.
- [16] J. Jiu, S. Isoda, F. Wang, M. Adachi, Dye-sensitized solar cells based on a single-crystalline TiO₂ nanorod film, *J. Phys. Chem. B* 110 (5) (2006) 2087–2092.
- [17] Y. Qu, W. Wang, L. Jing, S. Song, X. Shi, L. Xue, H. Fu, Surface modification of nanocrystalline anatase with CTAB in the acidic condition and its effects on photocatalytic activity and preferential growth of TiO₂, *Appl. Surf. Sci.* 257 (1) (2010) 151–156.
- [18] S. Anandan, M. Ashokkumar, Sonochemical synthesis of Au-TiO₂ nanoparticles for the sonophotocatalytic degradation of organic pollutants in aqueous environment, *Ultrason. Sonochem.* 16 (2009) 316–320.
- [19] B. Neppolian, Q. Wang, H. Jung, H. Choi, Ultrasonic-assisted sol-gel method of preparation of TiO₂ nano-particles: characterization, properties and 4-chlorophenol removal application, *Ultrason. Sonochem.* 15 (2008) 649–658.
- [20] S.R. Shirsath, D.V. Pinjari, P.R. Gogate, S.H. Sonawane, A.B. Pandit, Ultrasound assisted synthesis of doped TiO₂ nano-particles: characterization and comparison of effectiveness for photocatalytic oxidation of dyestuff effluent, *Ultrason. Sonochem.* 20 (2013) 277–286.
- [21] N. Ghows, M.H. Entezari, Ultrasound with low intensity assisted the synthesis of nanocrystalline TiO₂ without calcination, *Ultrason. Sonochem.* 17 (5) (2010) 878–883.
- [22] A.M.A. Abdel-Wahab, A.E.A.M. Gaber, TiO₂-photocatalytic oxidation of selected heterocyclic sulfur compounds, *J. Photochem. Photobiol. A Chem.* 114 (3) (1998) 213–218.
- [23] S. Matsuzawa, J. Tanaka, S. Sato, T. Ibusuki, Photocatalytic oxidation of dibenzothiophenes in acetonitrile using TiO₂: effect of hydrogen peroxide and ultrasound irradiation, *J. Photochem. Photobiol. A Chem.* 149 (1–3) (2002) 183–189.
- [24] G. Dedual, M.J. Macdonald, A. Alshareef, Z. Wu, D.C.W. Tsang, A.C.K. Yip, Requirements for effective photocatalytic oxidative desulfurization of a thiophene-containing solution using TiO₂, *J. Environ. Chem. Eng.* 2 (4) (2014) 1947–1955.
- [25] K. Keynejad, M. Nikazar, B. Dabir, Diesel desulfurization using a UV-photocatalytic process, *Pet. Sci. Technol.* 35 (9) (2017) 813–819.
- [26] X.J. Wang, F.T. Li, J.X. Liu, C.G. Kou, Y. Zhao, Y.J. Hao, D. Zhao, Preparation of TiO₂ in ionic liquid via microwave radiation and in situ photocatalytic oxidative desulfurization of diesel oil, *Energy and Fuels.* 26 (11) (2012) 6777–6782.
- [27] W. Zhu, Y. Xu, H. Li, B. Dai, H. Xu, C. Wang, Y. Chao, H. Liu, Photocatalytic oxidative desulfurization of dibenzothiophene catalyzed by amorphous TiO₂ in ionic liquid, *Korean J. Chem. Eng.* 31 (2) (2014) 211–217.
- [28] D. Zheng, W. Zhu, S. Xun, M. Zhou, M. Zhang, W. Jiang, Y. Qin, H. Li, Deep oxidative desulfurization of dibenzothiophene using low-temperature-mediated titanium dioxide catalyst in ionic liquids, *Fuel.* 159 (2015) 446–453.

- [29] F.T. Li, R.H. Liu, Z.M. Sun, D.S. Zhao, Photocatalytic oxidation kinetics of thiophene with Nano-TiO₂ as photocatalyst, 2nd Int. Conf. Bioinforma. Biomed. Eng. ICBBE 2008 (2008) 3887–3890.
- [30] A. Hassanjani-Roshan, S.M. Kazemzadeh, M.R. Vaezi, A. Shokuhfar, The effect of sonication power on the sonochemical synthesis of titania nanoparticles, *J. Ceram. Process. Res.* 12 (2011) 299–303.
- [31] S.S. Sabnis, P.R. Gogate, Ultrasound assisted size reduction of DADPS based on recrystallization, *Ultrason. Sonochem.* 54 (2019) 198–209.
- [32] Y. Kitamura, H. Okawa, T. Kato, K. Sugawara, Effect of ultrasound intensity on the size and morphology of synthesized scorodite particles, *Adv. Powder Technol.* 27 (3) (2016) 891–897.
- [33] J.B. Zhong, J.Z. Li, F.M. Feng, S.T. Huang, J. Zeng, CTAB-assisted fabrication of TiO₂ with improved photocatalytic performance, *Mater. Lett.* 100 (2013) 195–197.
- [34] Y. Xie, X. Zhao, Y. Li, Q. Zhao, X. Zhou, Q. Yuan, CTAB-assisted synthesis of mesoporous F-N-codoped TiO₂ powders with high visible-light-driven catalytic activity and adsorption capacity, *J. Solid State Chem.* 181 (8) (2008) 1936–1942.
- [35] H. Li, C.P. Tripp, Spectroscopic identification and dynamics of adsorbed cetyltrimethylammonium bromide structures on TiO₂ surfaces, *Langmuir* 18 (24) (2002) 9441–9446.
- [36] A. Kathiravan, R. Renganathan, Photosensitization of colloidal TiO₂ nanoparticles with phycocyanin pigment, *J. Colloid Interface Sci.* 335 (2) (2009) 196–202.
- [37] K. Lv, H. Zuo, J. Sun, K. Deng, S. Liu, X. Li, D. Wang, (Bi, C and N) codoped TiO₂ nanoparticles, *J. Hazard. Mater.* 161 (1) (2009) 396–401.
- [38] M. Rashidzadeh, Synthesis of high-thermal stable titanium dioxide nanoparticles, *Int. J. Photoenergy.* 2008 (2008), 245981.
- [39] P. Praveen, G. Viruthagiri, S. Mugundan, N. Shanmugam, Structural, optical and morphological analyses of pristine titanium di-oxide nanoparticles – Synthesized via sol-gel route, *Spectrochim. Acta – Part A Mol. Biomol. Spectrosc.* 117 (2014) 622–629.
- [40] J. Payromhorm, S. Chuangchote, N. Laosiripojana, CTAB-assisted sol-microwave method for fast synthesis of mesoporous TiO₂ photocatalysts for photocatalytic conversion of glucose to value-added sugars, *Mater. Res. Bull.* 95 (2017) 546–555.
- [41] L. Wang, Y. Chen, L. Du, S. Li, H. Cai, W. Liu, Nickel-heteropolyacids supported on silica gel for ultra-deep desulfurization assisted by Ultrasound and Ultraviolet, *Fuel.* 105 (2013) 353–357.
- [42] N.S. More, P.R. Gogate, Intensified desulfurization of simulated crude diesel containing thiophene using ultrasound and ultraviolet irradiation, *Ultrason. Sonochem.* 58 (2019), 104612.
- [43] P.S. Sinhar, P.R. Gogate, Ultrasound assisted oxidative deep-desulfurization of dimethyl disulphide from turpentine, *Ultrason. Sonochem.* 63 (2020), 104925.
- [44] A.J. Haider, R.H. Al-Anbari, G.R. Kadhim, C.T. Salame, Exploring potential Environmental applications of TiO₂ Nanoparticles, *Energy Procedia.* 119 (2017) 332–345.
- [45] N.B. Suryawanshi, V.M. Bhandari, L.G. Sorokhaibam, V.V. Ranade, Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation, *Fuel.* 210 (2017) 482–490.
- [46] N.B. Suryawanshi, V.M. Bhandari, L.G. Sorokhaibam, V.V. Ranade, A non-catalytic deep desulphurization process using hydrodynamic cavitation, *Sci. Rep.* 6 (2016) 1–8.
- [47] L. Jaimes, H. de Lasa, Catalytic conversion of thiophene under mild conditions over a ZSM-5 catalyst. A kinetic model, *Ind. Eng. Chem. Res.* 48 (16) (2009) 7505–7516.
- [48] L. Jaimes, M. Badillo, H. De Lasa, FCC gasoline desulfurization using a ZSM-5 catalyst: Interactive effects of sulfur containing species and gasoline components, *Fuel.* 90 (2011) 2016–2025.
- [49] M. Alhaddad, A. Shawky, Superior photooxidative desulfurization of thiophene by reduced graphene oxide-supported MoS₂ nanoflakes under visible light, *Fuel Process. Technol.* 205 (2020), 106453.
- [50] Y.Z. Zhen, J. Wang, J. Li, M. Fu, F. Fu, Y.Z. Zhang, J.H. Feng, Enhanced photocatalytic degradation for thiophene by Ag/ α -MoO₃ heterojunction under visible-light irradiation, *J. Mater. Sci. Mater. Electron.* 29 (5) (2018) 3672–3681.