Experimental and theoretical study of deep oxidative desulfurization of Dibenzothiophene using Oxalate-Based catalyst

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ABSTRACT

The present study reports the experimental and theoretical investigation for production of ultra-low sulfur liquid fuels through estimation of various reactive species formed during the reaction with the help of simulation. All the experiments were performed using an ultrasound bath which operates at a frequency of 37 kHz and a theoretical power of 95 W. The presented oxalate-based technique is found to be more efficient with > 93% DBT oxidation within 15 min of reaction time at 25 °C due to formation of reactive species like Fe(C_2O_4) and Fe(C_2O_4)_2^- which accelerate the reaction kinetics. Moreover, we have also investigated the influence of process parameters such as molar ratio of C_2O_4^2^-/Fe^{3+}, oxidant concentration, volume ratio of organic to aqueous phase, sulfur concentration, and activation methods of oxidant. The results revealed that catalyst can be reused for several runs without decrease in catalytic activity. The experimental and simulation of cavitation bubble dynamics results revealed that sonochemical effect assists to accelerate the reaction kinetics through formation of free radicals (^1O_2, ^1H, ^1OH and HO_2) and other reactive species like O_3 and H_2O_2 generated during transient cavitation. The sono-physical effects of cavitation help to create a fine emulsion in the liquid–liquid heterogeneous system leading to enhanced mass transfer rate by providing more interfacial surface area for occurring chemical reaction.

1. Introduction

The sulfur-containing aromatic hydrocarbons are the primary source of emission of SO_x gases from the vehicles. It has resulted in increased pollution and its abatement remains a challenge. Environment protection regulations have issued stringent measures to fight the vehicular emissions. These rules particularly limit the sulfur content of transportation fuels. The US Environmental Protection Agency has mandated that the maximum sulfur content of diesel and gasoline be 15 and 30 ppm, respectively [1]. Several techniques have been introduced to address this issue. The conventional procedure for the removal of sulfur compounds as employed by the petroleum refineries is catalytic hydro-desulfurization or hydro-treatment method. These processes are highly energy-intensive and require extreme conditions of temperature (>600 K) and pressures (>3 MPa) to achieve the desired target. Moreover, they also suffer from ineffective removal of the targeted organo-sulfur compounds such as thiophenes [2]. A significant amount of research effort is being put into developing more sustainable technologies for deep desulfurization of liquid fuels. The oxidative desulfurization (ODS) technique has been steadily gaining attraction for producing ultra-low sulfur content fuels [3-6]. In this process, the sulfur compounds are oxidized to their respective sulfones, which then can be extracted via a suitable solvent. One of the limitations of this process is that it is essentially a liquid–liquid heterogeneous system. The main drawback of such a process is the limitation by mass transfer, and hence achieving the ultra-low sulfur content fuel is difficult. Recently, microwave technique is introduced to enhance the mass transfer for investigation in oxidative desulfurization process. However, the energy requirement is comparatively high. For example, 94.5% and 93% of desulfurization was achieved at microwave power of 600 W and 540 W, respectively [7,8]. The application of microwave enhances the mass transfer rate through the temperature-induced diffusion phenomenon, in which the process of transport is driven by the temperature gradients in addition to the concentration [9]. In microwave heating, much faster temperature increase can be observed due to the mass heating effect depending on the microwave power. Also, the generation of heat by microwave technique in the system requires the presence of dielectric properties in the materials that causes friction due to the rotation of the dipoles in an...
alternating field leading to the generation of heat. However, the heating in microwave system is not homogeneous due to non-uniform distribution of microwave field. As a result, the dissipation of energy is not homogeneous in the system, and “hot-spots” occurs only if the generation of heat is faster than the heat transfer [10]. The other methods such as ionic liquids based oxidants [11], metal–organic frameworks as adsorbents [12], bi-metallic nanoparticles [13] as reactive catalysts have been reported for desulfurization of liquid fuels efficiently. As the desulfurization process is a liquid–liquid heterogeneous system, it is limited to a certain value of the mass transfer coefficient. Thus, there is always a challenge for conventional oxidative desulfurization processes. To overcome the mass transfer limitations, the application of ultrasound has been found to be very effective and efficient for the removal of sulfur compounds from liquid fuels. The ODS The principle behind this is the cavitation phenomenon, which enhances the reaction kinetics and yields in the ODS process by increasing the overall mass transfer rate in the medium [14-16]. The sono-hybrid ODS techniques have been found to be very useful, highly efficient and easy to implement for ODS [5,16,17]. The application of ultrasound in such heterogeneous processes always helps to increase the reaction kinetics by enhancing the interfacial surface area, thus increases the mass transfer rate across the liquid–liquid inter-phases. The ultrasound and its secondary effect cavitation provide the physical and chemical effects that are responsible for enhanced kinetics. The dissipation of energy during the application of ultrasound is also uniform compared to microwave-assisted mass transferred technique as the ultrasound induces intense physical mixing in the system generated by cavitation [18,19]. In sonolysis process, the liquid medium is subjected to irradiation under ultrasound waves, and during this process the nucleation, growth and vibrant collapse of microbubbles occur if the acoustic pressure is significantly high. This phenomenon can be explained on the basis of “hot-spots” produced during the cavitation that leads to a generation of extremely high temperature and pressure inside the cavitation bubbles during the last nearly adiabatic compression which happens just before the collapse. During this process, the heating and cooling rate is greater than 10^6 K s^-1 [20]. This causes the breakage of molecular bonds and formation of several species including reactive radicals, which is known as chemical effects of cavitation [10,20,21]. While the physical effects of cavitation enhance the kinetics through the generation of microstreaming, microturbulence, and microjet in the medium [22].

A thorough review of the recent literature revealed that no study has yet been undertaken to investigate the desulfurization process of liquid fuels by oxalate-based catalyst system. In the present study, several hybrid techniques have been investigated for desulfurization under different experimental conditions, viz. ferrioxalate (FeOX), sono-ferrioxalate(SFeOX), sono-Fenton (SF), sono-Fenton-ferrioxalate (SFFeOX) systems, for obtaining ultra-low sulfur liquid fuels. The FeOX or SFeOX system is environmentally benign as it doesn’t use any hazardous chemicals. Interestingly, unlike other ODS systems (Fe/H_2O_2, peracetic acid/H_2O_2, etc.) in-situ generated H_2O_2 through the FeOX and SFeOX pathways acts as an oxidant during the reaction [23-25], thereby reducing overall cost and making it a continuous operation. Moreover, most studies investigating the oxidation of sulfur compounds in liquid fuels have mainly looked into the chemistry of the processes; thus, there is a need to gain mechanistic insights into the ODS process. This study is the first attempt of mechanistic investigation into the desulfurization of liquid fuels using the ferrioxalate process. Therefore, it would provide helpful inputs into the ferrioxalate system and its subsequent scale-up as and when required.

2. Materials and methods

2.1. Materials

Dibenzothiophene, 5,5-Dimethyl-1-pyrroline N-oxide and Dibenzo-thiophene sulfone were procured from Sigma Aldrich. Toluene (Analytical Grade), H_2O_2 (30% v/v), FeSO_4·7H_2O, NaOH, HCl, Oxalic acid were purchased from Merck India Ltd. and FeCl_3 was procured from RANKEM Chemicals. All the chemicals have been used without any further purification. MilliQ water (resistivity ≥ 18 MΩ cm at 25 °C) was obtained from a Millipore synthesis unit (Millipore®, USA) to prepare the solutions used in the experiments.

2.2. Methodology

The experiments were carried out in a 100 mL borosilicate glass beaker with an initial dibenzothiophene (DBT) concentration of 100–1000 ppm. Toluene was used as the model liquid fuel for all experiments. The total volume of the organic phase was 20 mL. An appropriate amount of pre-decided H_2O_2, Fe(II) and oxalate have been added to the DBT solution just before the reaction commences. The pH of the reaction mixture was maintained at ~ 2 by adding a few drops of concentrated HCl. Then the beaker containing the reaction mixture is placed in an ultrasound bath (Make: Elmasonic, Model: S15-H) with a theoretical power output of 95 W and a frequency of 37 kHz. The ultrasound bath was filled with water which acted as the propagating medium for the ultrasound waves. Precautions have been taken to ensure that the position of the beaker is fixed at the center of the bath to avoid any spatial variations in the intensity of ultrasound. The temperature rise of the water due to the application of ultrasound was maintained at 25 ± 2 °C.

For the experiments with UV light sources, the ultrasound bath, along with the reaction mixture, was placed in a dark box. Two types of UV irradiation have been used with maximum emission at 254 nm (9 W) and 365 nm (11 W). The UV light source was placed precisely at the top of the beaker mouth with a distance of ~14 cm in between the light source and the reaction mixture. The tube was kept on to allow the light for proper diffusion in the chamber prior to each experiment. The concentration of DBT was monitored by withdrawing aliquots of samples from the organic layer at regular time intervals of 15 min. Based on the study of the desulfurization reaction, the reaction time was fixed for 60 min with samples being drawn in each 5 min for the first 15 min and then 15 min for the remaining 45 min of reaction. To the aliquots withdrawn from the reaction mixture a few drops of NaOH (1.0 mol L^-1) solution was added to raise the pH of the mixture to ~7 to terminate the Fenton like reaction (if any). Then, the samples have been centrifuged and filtered through a 0.45 μm Whatman® filter paper to remove the solid particle, if any, and analyzed for DBT concentration.

Analytical technique: The extent of desulfurization is analyzed with the help of a Gas-Chromatograph (Make: Agilent, Model: 7820A) equipped with a flame ionization detector and a capillary column (HP-5, 30 m × 0.320 mm × 0.25 μm). The method used to detect the DBT concentration is as follows [26]: injector temperature at 280 °C, detector at 280 °C, column temperature at 200 °C held for 2 min and then increased up to 280 °C at a ramping rate of 10 °C per min which was held for 15 min, the carrier gas was nitrogen at a flow rate of 1.5 mL/min and the sample injection volume was 1.0 μL. The oxidation of DBT is confirmed by performing the FTIR analysis of the oxidation product.

3. Numerical simulation and estimation of cavitation effects

The application of ultrasound is a well-known practice for enhancing the reaction kinetics of the processes through the phenomenon of cavitation. During the transient collapse of micro-bubbles, hot-spot is generated, leading to the formation of various reactive species like *H, *O, *OH, H_2O_2, which are responsible for enhancing the reaction kinetics [27,28]. In the present study, the numerical simulation of a mathematical model for bubble dynamics has been performed to estimate the magnitude of the effects due to cavitation. The cavitation bubble dynamic model in liquid is based on the gas content of the liquid medium and it provides nuclei for cavitation in the medium. During the transient collapse, the wall of the cavitation bubble achieves the sonic speed...
leading to formation of hot-spot in the medium. At this moment, the
temperature and pressure inside the bubbles reach extreme conditions
(approximately 5000 K of temperature and 500 bar of pressure) [27]. As
the collapse of the bubble occurs within a few tens of nanoseconds, the
transient cavitation phenomenon generates concentric energy on
extremely temporal scale and small spatial.

The estimation of the physical and chemical effects of cavitation has
been analyzed using a diffusion-limited ordinary differential equation
(ODE) model proposed by Toegel et al. [29]. This model uses boundary
layer approximation based on the partial differential equation (PDE)
model proposed by Storey and Szeri [30]. The model assumed that the
vapor is entrapped inside the cavitation bubble that leads to the for-
mation of radicals as described above and is essentially a diffusion-
limited process. The details of the model are described in our previous
paper [5,27,28,31]. The mathematical equations and the relevant
boundary conditions are given in Table S1 in the supplementary infor-
mation. The main component of this diffusion-limited cavitation bubble
dynamics model consists of three equations: (1) radial motion equation
of the bubble; (2) diffusive flux equation of liquid vapor across the
bubble wall; (3) heat conduction equation across the bubble wall; and
(4) overall energy balance.

The Chapman-Enskog theory which is based on the Lennard-Jones
12-6 potential has been used to determine the transport parameters
for heat and mass transfer (i.e. thermal conductivity and diffusion co-
efficient) in the medium at bulk temperature. Dimensional analysis has
been adopted to estimate the thermal and diffusive depths. As the
diffusion time scale of the gas (typically in millisecond) is much greater
than the time scale for the radial motion of the bubble which is in
the order of micro-second, the diffusion of gas through the bubble inter-
face has been ignored in this model. The four ODEs of the cavitation bubble
dynamic model are solved simultaneously using Runge-Kutta adaptive
step-size method [32]. The air bubble has been considered as the source
of cavitation nuclei. The condition for transient collapse of the cavita-
tion bubble is taken the first compression after its initial expansion. The
details of the model are described in our previous paper [5,27,28,31].

The sonochemical effect has been estimated assuming that the bub-
ble is thermodynamically at equilibrium condition [33,34]. The simu-
lation results provide the information about the vapor content of the
bubble with time along with the composition of the bubble content at
transient collapse of the cavitation bubble. The equilibrium molar frac-
tion inside the bubble is estimated using online FactSage software [35]
under the conditions of temperature and pressure of the first compres-
sion of the cavitation bubble using the Gibbs free-energy minimization
 technique which is same as proposed by Eriksson [36]. The other ther-
modynamic parameters used for simulation of the diffusion-limited
model for cavitation bubble dynamic are listed in Table S2 [37-42].

4. Results and discussion

Experiments have been carried out in two stages. In the first stage, the
influence of process parameter on desulfurization process has been
investigated and in the second stage, the experiments have been con-
ducted under different experimental conditions to identify the synergy
between the individual and hybrid processes including the effect of
oxidative desulfurization techniques. The process parameters such as
the molar ratio of iron to oxalate ions, iron concentration, effect of H₂O₂
addition, effect of organic to aqueous phase volume ratio, concentration
of sulfur compounds, activation methods of oxidant and reaction time
have been investigated. Finally, the oxidation of DBT has been per-
formed under different hybrid processes at optimum conditions and the
results are explained as below.

4.1. Influence of oxalate ion concentration and molar ratio of Fe(II) to
oxalate

The influence of oxalate ions (C₂O₄²⁻) and the effect of molar ratio of
iron to oxalate on desulfurization of DBT with a constant Fe²⁺ amount of
0.5 mol L⁻¹ and 2 mL of H₂O₂ (corresponds to 9.8 mol L⁻¹ in the aqueous
phase) was investigated and the results are depicted in Fig. 1(a-c). In
order to investigate the mechanistic insight of the activation method of
Fe(II)-oxalate, three techniques have been adopted (viz. ultrasound,
UVA and UVC). The results revealed that the presence of oxalate ions in
the reaction mixture increases the reaction kinetics significantly in all
three activation method. From the experimental results it can be seen
that with increasing the oxalate ion concentration the efficiency of
desulfurization increases and the maximum DBT content decrease was
achieved for the oxalate ion concentration of 1.5 M, i.e. 1:3 M ratio of
iron to oxalate ions. This essentially indicates that the layer fraction of
Fe²⁺ present in the bulk solution combines with oxalate and produces
more Fe(II)-oxalate complexes in the reaction mixture [43,44].

\[
\text{Fe}^{2+} + C_2O_4^{2-} \rightarrow \text{Fe}^{4+}(C_2O_4) \quad (1)
\]

At a constant concentration of Fe²⁺ ions, addition of more oxalate in
the reaction mixture increases the Fe⁴⁺(C₂O₄)²⁻ complex which is more
reactive thermodynamically than the Fe⁴⁺(C₂O₄) species. Additionally,
increasing the oxalate concentration in the reaction mixture decreases
the potential value of ferrous-oxalate species. As a result, the reaction
kinetic is increased by accelerating the reduction of oxygen in the system
[45]. Hence, the desulfurization efficiency increases with increasing the
oxalate concentration in the reaction mixture.

The maximum desulfurization efficiency was achieved approx.
91.5% at the optimum oxalate concentration of 1.5 mol L⁻¹ (cor-
responds to the molar ratio of 1:3 with Fe⁴⁺). However, the reaction kin-
etics during the desulfurization process reduces as the ratio of
C₂O₄²⁻/Fe²⁺ increases above the optimum molar ratio of 3. This is
because at the higher molar concentration of C₂O₄²⁻ in the reaction
mixture, the unreacted C₂O₄²⁻ remains in the bulk solution. As a result,
*OH radical are scavenged by C₂O₄²⁻ through the following reaction
[25,46]:

\[
\text{C}_2\text{O}_4^{2-} + \text{OH} \rightarrow \text{CO}_2 + \text{CO}_2^- + \text{OH}^- \quad (3)
\]

\[
\text{HC}_2\text{O}_4^- + \text{OH} \rightarrow \text{CO}_2 + \text{CO}_2^- + \text{H}_2\text{O} \quad (4)
\]

Therefore, the efficiency of desulfurization process for oxidation of
DBT was decreased as shown in the Fig. 1. On the other hand, Fe⁴⁺C₂O₄
complex can also undergo dissociation in the presence of ultrasound and
UV light radiation; and generates more *OH radical in the system which
Participates in oxidative desulfurization process through the following
reaction mechanism and further accelerate the reaction kinetics [47]:

\[
\text{Fe}^{4+}(\text{C}_2\text{O}_4) + \text{H}_2\text{O}_2 + h\nu \rightarrow \text{Fe}^{3+}(\text{C}_2\text{O}_4)^+ + \text{OH} + \text{OH}^- \quad (5)
\]

In addition to this, the other species of Fe(III)-oxalate are also highly
light sensitive and can produce other alternative radicals like C₂O₄²⁻,
O₂, HO₂ and finally *OH radicals through Fenton reaction and promote
the desulfurization process in the presence of light irradiation as shown
in the reactions (Eqs. S1-S10), provided in the supplementary infor-
mation [24,43,47].

However, comparing the activation method of FeOX complexes, it
was observed that irradiation of UV light during SFeOX process the desulfurization efficiency in both the cases (UVA and UVC light irradiation) was reduced even at the optimum molar ratio of \( \text{C}_2\text{O}_4^{2-}/\text{Fe}^{2+} \). The results obtained under these categories are depicted in Fig. 1(d). This could be attributed to the scavenging of the excess \( \cdot\text{OH} \) radicals produced during the photo-Fenton-ferrioxalate system in the presence of UV light irradiation through the following reaction [48].

\[
\cdot\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
\]  

As a result, the excess \( \cdot\text{OH} \) radicals generated during the reaction is scavenged by the hydroperoxyl radical (\( \text{HO}_2 \)); and produces molecular oxygen and \( \text{H}_2\text{O} \). This is a loss of oxidation potential; thus the overall desulfurization efficiency of DBT oxidation was decreased when the sono-Fenton-Fe(II)-oxalate system is employed in the presence of ultraviolet light irradiation.

4.2. Influence of Fe(II) concentration in the reaction mixture

The presence of \( \text{Fe}^{2+} \) concentration in the reaction mixture influences the desulfurization efficiency as it is one of the major compounds for FeOX system. In order to investigate, the experiments were conducted at various \( \text{Fe}^{2+} \) ions concentrations with a fixed molar ratio of \( \text{Fe}^{2+} \) to oxalate as 1:3 and the results are shown in Fig. 2. The rate of desulfurization was increased as the concentration of \( \text{Fe}^{2+} \) ion increases. The maximum DBT oxidation of ~ 94% was seen when the \( \text{Fe}^{2+} \) concentration was 0.005 mol L\(^{-1}\). This augmentation is attributed to the greater extent of Fe(II)-oxalate complex formation and decomposes to generate free radicals. There was no effect on the overall desulfurization efficiency till the \( \text{Fe}^{2+} \) concentration of 0.25 mol L\(^{-1}\). This is due to the increase of the concentration of Fe(II)-oxalate complexes, \( \text{Fe}^{II}(\text{C}_2\text{O}_4) \) and \( \text{Fe}^{II}(\text{C}_2\text{O}_4)^2_2 \). Therefore, the production of radicals also increases resulting in enhanced desulfurization efficiency.

Further increasing the \( \text{Fe}^{2+} \) concentration the reaction kinetic was reduced significantly when the \( \text{Fe}^{2+} \) ion concentration was increased from 0.005 to 0.75 mol L\(^{-1}\). This could be attributed to the less production of more reactive species \( \text{Fe}^{II}(\text{C}_2\text{O}_4)^2_2 \) as the concentration of \( \text{Fe}^{2+} \) is increased at a constant amount of oxalate. But the Fe(II)-oxalate system is critically dependent on the molar ratio of \( \text{Fe}^{2+} \) to \( \text{C}_2\text{O}_4^{2-} \) ions. On the other hand, there is also a scavenging effect of \( \cdot\text{OH} \) radicals by the excess \( \text{Fe}^{2+} \) ions; thus, the desulfurization efficiency decreases [5,49]. The scavenging reactions of \( \cdot\text{OH} \) radical are given by Eqs. 7–9.

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**Fig. 1.** Influence of oxalate ions concentration on desulfurization of DBT under (a) sonolysis process, (b) sono-photo-FeOX system conducted under UVA light, (c) sono-photo-FeOX system conducted under UVC light, and (d) effect of activation method of FeOX on overall DBT oxidation performed at optimum ratio of \( \text{Fe}^{II} \) to oxalate ions concentration. Experimental composition: \([\text{Fe}^{2+}] = 0.5 \text{ mol L}^{-1}, \text{H}_2\text{O}_2 (30\% \text{ v/v}) = 2 \text{ mL (9.8 \text{ mol L}^{-1} \text{ in aqueous phase}), [DBT] = 100 ppm.} \)
Fig. 2. (a) Influence of iron concentration on desulfurization process of DBT under sono-Fe(II)-oxalate system, (b) enlarged view of the desulfurization of DBT conducted at different Fe$^{2+}$ concentration. Experimental composition: [DBT] = 100 ppm, Fe$^{2+}$ to oxalate = 1:3, H$_2$O$_2$ (30% v/v) = 2 mL (9.8 mol L$^{-1}$ in aqueous phase).

\[
\begin{align*}
\text{Fe}^{2+} + \text{HO}_2 + \text{C}_2\text{O}_4^{2-} + \text{H}^+ & \rightarrow \text{FeC}_2\text{O}_4^{3+} + \text{H}_2\text{O}_2 \\
\text{Fe}^{2+} + \text{OH} + \text{C}_2\text{O}_4^{2-} & \rightarrow \text{FeC}_2\text{O}_4^{3+} + \text{OH}^{-} \\
\text{Fe}^{2+} + \cdot \text{OH} & \rightarrow \text{Fe}^{3+} + \cdot \text{OH}^{-}
\end{align*}
\]

4.3. Effect of H$_2$O$_2$ concentration and volume ratio of organic to aqueous phase

The influence of H$_2$O$_2$ concentration and the volume ratio of organic to aqueous phase on desulfurization process has been assessed by performing experiments at different operating conditions and the results are depicted in Fig. 3. Addition of H$_2$O$_2$ externally accelerates the Fenton and Fenton-like reactions in the presence of Fe$^{2+}$ and Fe(II)-oxalate as shown below reaction mechanism [50].

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^{-} \\
\text{Fe}^{II}(\text{C}_2\text{O}_4) & + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{III}(\text{C}_2\text{O}_4) + \cdot \text{OH} + \text{OH}^{-}
\end{align*}
\]

Therefore, it promotes the generation of additional *OH radicals in the system and enhanced the desulfurization efficiency. The maximum DBT oxidation of 94% was observed at H$_2$O$_2$ molar concentration of 9.8 mol L$^{-1}$.

However, a significant change in desulfurization efficiency has been observed when the volumetric ratio of organic to aqueous phase was varied. In the present study, the organic phase is toluene that represents the model liquid fuel for gasoline and diesel. In this biphasic reaction mixture, the model sulfur compound DBT is in the organic phase and the oxidizing species are in the aqueous phase. Therefore, the interface between these two phases plays an important role in transferring the oxidant from aqueous phase to organic phase. Hence, formation of proper emulsion is dependent on volumetric ratio of organic to aqueous phase. When the aqueous phase was doubled with the same molar concentration of 9.8 mol L$^{-1}$, the desulfurization rate was reduced from 94% to 55.3%. However, the trend of desulfurization under the same molar concentration of H$_2$O$_2$ remains same even at the higher volumetric ratio of organic to aqueous phase.

4.4. Extend of desulfurization for oxidation of DBT

The maximum removal amount of sulfur compound from the model solvent has been assessed by conducting oxidative desulfurization process with four different concentrations of DBT (viz. 100, 200, 500 and 1000 ppm) and the results are depicted in Fig. 4. Although the percentage of desulfurization for all four concentrations was more or less same, but a significant amount of sulfur compound was left in the solvent at the higher concentration of DBT. This essentially indicates that a longer reaction time is desired for obtaining the same absolute desulfurization in the liquid fuel.

Comparing the desulfurization results obtained under Fenton reaction and Fe(II)-oxalate system, a higher kinetic was observed for the oxalate-based catalytic process for concentrations of DBT. This could be again attributed to the thermodynamically reactive species of Fe(II)-oxalate, Fe$^{II}(\text{C}_2\text{O}_4)$ and Fe$^{III}(\text{C}_2\text{O}_4)$. The reaction of these Fe(II)-oxalate species in the presence of UV and H$_2$O$_2$ for production of radicals that are responsible for oxidation of sulfur compounds is
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comparatively faster than the reaction of free or uncomplexed Fe$^{2+}$ ions [44]. Thus, a faster kinetic has been achieved in the case of Fe(II)-oxalate system.

5. Analysis of desulfurization in sonolysis, Fenton, Photo-Fenton and Fe$^{3+}$-oxalate system

The mechanistic investigation of desulfurization of DBT has been performed by conducting the experiments under different categories and the results are depicted in Fig. 5. The desulfurization experiments were carried out in six categories: (i) Sonolysis alone (US), (ii) MS + H$_2$O$_2$, (iii) US + H$_2$O$_2$, (v) US + H$_2$O$_2$ + Fe$^{2+}$, (v) US + H$_2$O$_2$ + Fe$^{3+}$ + UV, (vi) US + H$_2$O$_2$ + Fe$^{3+}$ + Ox. In all of these categories, the H$_2$O$_2$ was considered as the primary oxidant for generation of *OH radicals which is responsible for deep desulfurization of DBT. The salient features of the experimental results obtained under different categories are as follows:

- Being a weak oxidant, H$_2$O$_2$ ($E^0 = 1.78$ V) with mechanical stirring could not reduce > 1% of DBT concentration in the solvent. While the application of ultrasound (sonolysis process) is well known for in-situ production of *OH and it's expected to obtain significant amount of desulfurization rate. However, only 4.5% of DBT oxidation with rate constant of 0.8 $\times$ $10^{-3}$ sec$^{-1}$ was observed under this category. The addition of H$_2$O$_2$ externally during the sonolysis process, an increased kinetic of desulfurization of 1.05 $\times$ $10^{-3}$ sec$^{-1}$ was seen with a total DBT oxidation of 6%. The marginal enhancement of sulfur compound removal is due to the direct decomposition of H$_2$O$_2$ in the cavitation bubble and generates *OH radicals through the following reaction mechanism [28]. The formation of these radicals is also detected in simulation result which is discussed in the next section.

\[
\text{H}_2\text{O} \xrightarrow{10} \text{HO}^- + \text{H}^+ \quad (12)
\]

\[
\text{H}^+ + \text{O}_2 \rightleftharpoons \text{HO}_2^- \quad (13)
\]

\[
\cdot\text{OH} + \text{O}_2 \rightleftharpoons \text{HO}_2^- + \text{O}^- \quad (14)
\]

\[
\text{O}^- + \text{O}_2 \rightarrow \text{O}_3 \quad (15)
\]

\[
\text{2 HO}_2^- \rightleftharpoons \text{H}_2\text{O}_2^2^- + \text{O}_2 \quad (16)
\]

\[
\text{H}_2\text{O}_2 \xrightarrow{10} 2 \text{OH} \quad (17)
\]

However, the addition of H$_2$O$_2$ externally during sonolysis process (i.e., US + H$_2$O$_2$) does not show significant efficiency in the overall desulfurization of DBT. This could be due to the low vapor pressure of H$_2$O$_2$ that limits the diffusion into the transient cavitation bubble and unable to produce reactive *OH radicals [48,51].

- In the third category where Fe$^{2+}$ was added externally into the (US + H$_2$O$_2$) reaction system to enhance the desulfurization by generating promote the *OH radical generation, a higher extend of desulfurization was seen with the maximum desulfurization efficiency of ~ 93%. This augmentation in desulfurization efficiency is due to the promotion of Fenton reaction (Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + OH$^-$ + OH$^-$). In this case, the oxidation process of sulfur compound is initiated by the Fe$^{3+}$-oxalate system.

- Comparing the desulfurization results between the systems (US + H$_2$O$_2$ + Fe$^{3+}$ + Ox) and (US + H$_2$O$_2$ + Fe$^{3+}$), no significant enhancement in the overall desulfurization was seen. However, a faster reaction kinetic was observed for the desulfurization system of (US + H$_2$O$_2$ + Fe$^{3+}$ + Ox). This is due to the reactive species, Fe$^{0}$(C$_2$O$_4$)$_2$andFe$^{3+}$(C$_2$O$_4$)$_2^{-}$, formed in the oxalate-based system.

Fig. 4. Influence of sulfur compound concentration during desulfurization process under (a) sono-Fenton technique and (b) sono-ferrioxalate technique. Experimental composition: [DBT] = 0.005 mol L$^{-1}$, Fe$^{2+}$ to oxalate = 1:3, H$_2$O$_2$ (30% v/v) = 2 mL (9.8 mol L$^{-1}$ in aqueous phase).

Fig. 5. Desulfurization under different experimental techniques, viz. sonolysis, sono-Fenton, Sono-photo-Fenton performed under UVA and UVC lights irradiation. Experimental composition: [DBT] = 100 ppm, [Fe$^{2+}$] = 0.005 mol L$^{-1}$, Fe$^{2+}$ to oxalate = 1:3, H$_2$O$_2$ (30% v/v) = 2 mL (9.8 mol L$^{-1}$ in aqueous phase).
These Fe(II)-oxalate complexes are highly reactive and showed faster kinetics compared to the uncomplexed Fe$^{2+}$ or Fe$^{3+}$ ions [44].

- Irradiation of ultra violet light during the desulfurization processes of (US + H$_2$O$_2$ + Fe$^{2+}$+Ox) and (US + H$_2$O$_2$ + Fe$^{2+}$) is expected to achieve a higher extent of desulfurization efficiency. But it showed a contradictory result for both the cases. This results can be explained as follows:

In the Fenton reaction, H$_2$O$_2$ is activated by Fe$^{2+}$ ions through electron transfer and generates *OH radicals along with Fe$^{3+}$ ions. According to Haber and Weiss catalytic cycle, Fe$^{3+}$ can be reduced to Fe$^{2+}$ ions by H$_2$O$_2$ but it is the rate determining step of the reaction [52]. Therefore, to generate the reactive *OH radicals at the same rate in the system, Fe$^{2+}$ ions must be available to react with H$_2$O$_2$. The regeneration of Fe$^{3+}$ from Fe$^{2+}$ can be increased in the reaction mixture by applying UV light though photo-reduction of the dissolved Fe(III) species [53].

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \quad (18)$$

$$\text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{OH} \quad (19)$$

On the other hand, H$_2$O$_2$ can also absorb UV irradiation and decomposes directly to produce additional *OH radicals through photolysis process. As a result, the excess *OH radicals can either recombine to form molecular species or be scavenged by the un-reacted H$_2$O$_2$ as shown below [54]; thus desulfurization efficiency of DBT is reduced under the UV light irradiation.

$$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{HO}_2^- \quad (20)$$

$$\cdot\text{OH} + \cdot\text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (6)$$

### 6. Stability and reusability of catalyst

In order to reduce the operational cost of any catalytic process, it is essential to determine the stability and reusability of the catalyst. Therefore, the catalyst has been collected, re-generated, and used for desulfurization reaction. The results of desulfurization obtained in different runs are depicted in Fig. 6. There was no major loss observed in catalyst activity after the first and second run of the reaction. Only 1.33% and 1.56% reduction in catalyst activity was seen after the first and second runs, respectively. However, a reduced reaction kinetic was observed for every recycle. The major decrease in catalyst activity was happened after the third run, i.e. in the fourth time of reaction, and ~46.5% catalyst activity was decreased. This reduction in catalytic activity could be due to the oxidation of the catalyst. Also, few amounts of iron or oxalate may be lost during recycling, leading to an imbalance in the molar ratio of Fe and oxalate. As a result, the desulfurization efficiency was reduced to 49% only.

### 7. Analysis of simulation results

The simulation results of the cavitation bubble dynamic model are presented in Fig. 7 and Table 1. The results showed the (i) time history of the bubble radius, (ii) the peaks of the temperature and pressure reached inside the bubble at the time of first collapse, (iii) the number of the nitrogen, oxygen, toluene and hydrogen peroxide molecules present in the bubble, (iv) equilibrium composition of the species generated at the time of first collapse of the bubble resulted from the thermal dissociation of liquid molecules (viz., toluene and hydrogen peroxide). From the results, it has been observed that most of the species generated are from the dissociation of O$_2$ and N$_2$ in both the medium. The simulation results can be summarized as follows:

(i) The predominant radicals generated in the aqueous medium are *OH, *O and HO$_2^-$ in the order of $\sim10^{-3}$–$10^{-4}$, while other oxidizing species H* and H$_2$O$_2$ are also estimated in the magnitude order of $\sim10^{-5}$–$10^{-6}$. In the case of the organic phase, the major contribution in oxidative desulfurization was from *O with a magnitude of $\sim10^{-2}$. A trace amount of H$_2$O formation was also observed in organic phase along with other nitrogen oxides like NO and NO$_2$. The formation of radicals like *OH, *O, H* and HO$_2^-$ in the organic phase was minimal and it was in the range of $\sim10^{-6}$–$10^{-7}$. However, no formation of H$_2$O$_2$ was seen in the organic phase, unlike the aqueous phase.

(ii) Due to the low vapor pressure, the evaporation of toluene molecules inside the bubble was almost insignificant (~$10^{-6}$). As a result, the formation equilibrium species is mainly from the thermal dissociation of N$_2$ and O$_2$ under the temperature peak of 4663 K; whereas, the temperature peak in aqueous medium was only 2726 K.

(iii) The physical effect of cavitation was very strong in both cases that results from the generation of micro-turbulence and shockwaves. Therefore, the application of ultrasound in a liquid–liquid heterogeneous oxidative desulfurization process creates an appropriate emulsion in the system as shown in Fig. 8 that enhances the mass transfer rate by providing more interfacial surface area for occurring chemical reaction. Also, the application of ultrasound increases the transportation of free radicals from aqueous phase to organic phase (i.e. DBT-Toluene solution). In order to corroborate this hypothesis, the DMPO-trapped electron paramagnetic resonance (EPR) technique has been performed and the results are depicted in Fig. 9. The EPR results revealed that the samples collected from the organic phase of ultrasound-assisted ODS systems showed a high intensity peak. While almost no *OH radical was detected for the sample collected from the organic phase in the reaction system that is performed without ultrasound.

(iv) The simulation and the experimental results of desulfurization help to identify the mechanistic physical insight of the DBT oxidation under sono-Fenton-oxalate based system. The formation radicals such as *OH, *O, H* and HO$_2^-$ in the liquid mediums play important roles in the overall chemistry for enhancing the oxidative desulfurization process of DBT oxidation.

### 8. Conclusions

The present study has reported a new technique for obtaining ultra-low sulfur fuel through sono-hybrid oxalate-based oxidation desulfurization process. The maximum desulfurization efficiency was observed for the Fe-oxalate system under the experimental condition of 0.05 mol L$^{-1}$ Fe$^{2+}$, 0.15 mol L$^{-1}$ oxalate, 10:1 vol ratio of organic to aqueous phase, oxidant concentration of 9.74 mol L$^{-1}$. The experimental results
revealed that a faster desulfurization kinetics can be achieved under the sono-Fenton-oxalate based system compared to sono-Fenton process due to the formation of reactive species of $\text{Fe}^{2+}(\text{C}_2\text{O}_4)^2-$ and $\text{Fe}^{2+}(\text{C}_2\text{O}_4)$

The catalyst reusability experiments showed that there is no significant loss of catalyst activity till 3rd run of desulfurization reaction. However, ~49% of desulfurization efficiency was reduced in the fourth run due to either self oxidation of the catalyst or loss of iron and/or oxalate during the recycle that led to the imbalance in the molar ratio of $\text{Fe}^{2+}$ and oxalate ions. On the other hand, the radicals such as $\cdot\text{OH}$, $\cdot\text{O}$, $\cdot\text{H}$ and $\text{HO}_2$ generated during the transient collapse of cavitation bubbles through the thermal dissociation of the vapor molecules of $\text{H}_2\text{O}_2$ and $\text{C}_7\text{H}_8$ in the presence of air play an important role in the overall chemistry. The physical effect of cavitation helps in the formation of fine emulsion in the liquid–liquid heterogeneous system that accelerates the reaction kinetics by enhancing the mass transfer through an increased interfacial area where the main desulfurization reaction occurs.

Fig. 7. Simulation results of radial motion of a 5 µm air bubble in organic phase and aqueous phase. Time history of (A) the radius of the air bubble; (B) peak temperature inside the bubble; (C) evaporation of water vapor in the bubble; (D) pressure inside the bubble; (E) microturbulence generated during oscillation of the bubble; (F) the acoustic waves emitted by the bubble.
Table 1

| Physical conditions and composition inside the bubble at the first collapse |
|-----------------------------------------------|
| **Aqueous Phase**                          |
| Parameters for simulation                   |
| \( P_a = 5 \, \mu \text{m}, P_s = 100 \, \text{kPa} \) | \( P_a = 5 \, \mu \text{m}, P_s = 100 \, \text{kPa} \) |
| \( P_s = 150 \, \text{kPa}, f = 37 \, \text{kHz} \) | \( P_s = 150 \, \text{kPa}, f = 37 \, \text{kHz} \) |
| **Organic Phase**                           |
| **Physical conditions of the bubble at the first collapse** |
| \( T_{\text{max}} = 2726 \, \text{K}, P_{\text{max}} = 277.7 \, \text{MPa} \) | \( T_{\text{max}} = 4663 \, \text{K}, P_{\text{max}} = 9605 \, \text{bar} \) |
| \( V_{\text{max}} = 0.222 \, \text{m/s}, P_{\text{AW}} = 0.082 \, \text{MPa} \) | \( V_{\text{max}} = 0.123 \, \text{m/s}, P_{\text{AW}} = 246.2 \, \text{bar} \) |
| \( x_{\text{H}_2} = 0.723, x_{\text{O}_2} = 0.192 \) | \( x_{\text{H}_2} = 0.79, x_{\text{O}_2} = 0.21 \) |
| \( x_{\text{H}_{2}\text{O}_2} = 0.084 \) | \( x_{\text{O}} = 2.75 \times 10^{-6} \) |
| Equilibrium composition of species generated at the time of first collapse |
| **Species** | Hydrogen Peroxide (30%) | Toluene |
| \( N_2 \) | \( 7.08 \times 10^{-6} \) | \( 7.21 \times 10^{-6} \) |
| \( O_2 \) | \( 2.17 \times 10^{-5} \) | \( 1.32 \times 10^{-5} \) |
| \( H_2O \) | \( 8.24 \times 10^{-8} \) | \( 9.55 \times 10^{-10} \) |
| \( OH \) | \( 2.74 \times 10^{-8} \) | \( 4.81 \times 10^{-9} \) |
| \( O \) | \( 2.37 \times 10^{-9} \) | \( 1.72 \times 10^{-9} \) |
| \( H \) | \( 5.03 \times 10^{-10} \) | \( 3.13 \times 10^{-9} \) |
| \( O^3 \) | \( 2.20 \times 10^{-9} \) | \( 3.49 \times 10^{-9} \) |
| \( HO \) | \( 2.13 \times 10^{-9} \) | \( 2.63 \times 10^{-9} \) |
| \( HOO \) | \( 1.76 \times 10^{-9} \) | \( - \) |
| \( H_2 \) | \( 3.68 \times 10^{-9} \) | \( - \) |
| \( HONO \) | \( 1.23 \times 10^{-9} \) | \( 6.96 \times 10^{-10} \) |
| \( HNO \) | \( 3.99 \times 10^{-10} \) | \( 4.48 \times 10^{-9} \) |
| \( HONO_2 \) | \( 7.21 \times 10^{-9} \) | \( 2.46 \times 10^{-9} \) |
| \( N \) | \( 1.46 \times 10^{-9} \) | \( 1.27 \times 10^{-9} \) |
| \( N_2 \) | \( 2.30 \times 10^{-10} \) | \( 2.52 \times 10^{-10} \) |
| \( NO \) | \( 2.87 \times 10^{-10} \) | \( 1.34 \times 10^{-9} \) |
| \( NO_2 \) | \( 7.02 \times 10^{-10} \) | \( 6.81 \times 10^{-10} \) |
| \( NO_3 \) | \( 1.66 \times 10^{-9} \) | \( 2.27 \times 10^{-9} \) |
| \( NO_2 \) | \( 1.68 \times 10^{-9} \) | \( 1.54 \times 10^{-9} \) |
| \( N_2O_3 \) | \( 4.37 \times 10^{-9} \) | \( 1.03 \times 10^{-9} \) |
| \( N_2O_5 \) | \( 1 \) | \( 1.30 \times 10^{-10} \) |
| \( NH \) | \( 1.84 \times 10^{-9} \) | \( 4.02 \times 10^{-9} \) |
| \( NH_2 \) | \( 2.19 \times 10^{-9} \) | \( - \) |
| \( NH_3 \) | \( 4.77 \times 10^{-9} \) | \( - \) |
| \( N_2O_4 \) | \( 1.73 \times 10^{-10} \) | \( 2.20 \times 10^{-9} \) |

Fig. 8. Reaction mechanism and formation of fine emulsion due to physical effects of cavitation in liquid-liquid heterogeneous system.

CRediT authorship contribution statement

Satadru Chakrabarty: Writing - original draft, Data curation, Investigation, Methodology. Prachi Upadhyay: Writing - original draft, Data curation, Investigation, Methodology. Sankar Chakma: Writing - review & editing.

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.

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Appendix A. Supplementary data

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