



Heterogeneous Fenton-like oxidative desulfurization of fuel using iron-modified lignin/S-g-C₃N₄ nanocomposite: Optimization via Box-Behnken design

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ABSTRACT

Oxidative desulfurization (ODS) is an effective technology for achieving ultra-low sulfur levels in fuels to meet stringent environmental regulations. This study evaluates the effectiveness of an Fe@KL/S-g-C₃N₄ (Fe-doped Kraft lignin coupled with S-g-C₃N₄) nanocomposite for the oxidative desulfurization of dibenzothiophene (DBT) from model fuel. The synthesis and electronic structure of the composite were confirmed using FTIR, Raman spectroscopy, PL, UV-visible spectroscopy, XRD, FE-SEM, EDX, and XPS analyses, which confirmed that Fe-modified lignin was successfully coordinated with the S-g-C₃N₄ framework. The incorporation of iron and lignin improved Fe³⁺ redox cycling and •OH generation, increased active site accessibility, and lowered the optical band gap to 1.85 eV, which enhanced Fenton-like radical generation. The Box-Behnken Design (BBD) optimization identified the optimum reaction conditions as 0.3 g of catalyst, 32.5 min reaction time, and 60 °C. With H₂O₂ used as a green oxidant, a maximum sulfur removal of 98.37% was achieved. This study demonstrates that Fe@KL/S-g-C₃N₄ is a high-performance, economical and sustainable heterogeneous catalyst for ultra-low sulfur fuel production, while exhibiting high structural stability and reusability over multiple cycles.

1. Introduction

The world is still overwhelmingly dependent on petroleum energy products and fossil fuel energy products account for nearly 80% of global energy consumption [1]. The sulfur content of crude oils is mainly in the form of organosulfur compounds, usually ranging from 0.5 to 5 wt %, depending on the crude source. These compounds, upon combustion, create sulfur oxides (SO_x) which play a major role in atmospheric pollution, acid rain, and respiratory health problems in humans [2–4]. The production of ultra-low sulfur fuels (sulfur below 10 ppm) is now required under strict global regulations to overcome these environmental dangers. Oxidative desulfurization (ODS) is a process that selectively oxidizes sulfur-containing compounds to polar sulfoxides or sulfones using an oxidant like hydrogen peroxide (H₂O₂), and then extracts the oxidized compounds from the fuel phase via solvent extraction. Reactive oxygen species (ROS) are generated to oxidize sulfur compounds to sulfoxides, and then to sulfones. These polar compounds can be easily separated from the organic phase [5]. An efficient ODS

system requires the engineering of green, cost-effective, and recyclable catalysts capable of high sulfur removal under mild conditions. So far, heterogeneous catalysts have become significantly interesting when it comes to using them in ODS as they are reusable, chemically stable, and environmentally friendly. Graphitic carbon nitride is considered a highly promising heterogeneous catalyst because of its visible-light responsiveness, tunable electronic structure, and low cost [6].

Several studies have explored doping and hybridization of g-C₃N₄ to improve its catalytic and redox properties for oxidative applications. Non-metal doping, particularly sulfur, is a feasible method to surmount these drawbacks [7,8]. Partial replacement of nitrogen by sulfur in the g-C₃N₄ matrix also forms mid-gap energy states which promote absorption in the visible spectrum and boost the redox potential [9,10]. The S-doped g-C₃N₄ tends to agglomerate, which decreases the number of active sites and the overall catalytic efficiency [11]. Considerable interest has emerged in the use of another abundant biomass material, the biopolymer lignin, with rich functional groups (-OH, -COOH, -OCH₃) that can improve the properties of nanoparticles [12,13]. Lignin acts as

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both a stabilizing agent, and a structural modifier, thus improving the surface area and charge transfer in g-C₃N₄ [14,15]. Despite these advantages, lignin-based materials have not been employed in oxidative desulfurization, especially in combination with transition metals. Iron is an excellent catalyst as it is readily available, non-toxic, and has versatile redox chemistry (Fe³⁺) [16]. Introducing iron into the lignin matrix has the potential to enhance active sites and prevent agglomeration of metal nanoparticles.

In this study, a novel Fe@KL/S-g-C₃N₄ nanocomposite is proposed that contains three synergistic components: (i) Fe³⁺ centers anchored on Kraft lignin (KL), which enable Fenton catalytic activity and also function as electron traps to suppress charge recombination; (ii) sulfur-doped g-C₃N₄ (S-g-C₃N₄), which provides visible-light driven generation of electron-hole pairs through a narrowed band gap; and (iii) KL, derived from biomass, which acts as a structural scaffold to prevent the nanoparticles from agglomerating, increase the surface area, and act as a structural mediator through its quinone/hydroquinone functionality. No previous study has incorporated these three components into a composite for catalytic ODS.

The combination of the catalytic activity of iron, the tunable electronic properties of S-g-C₃N₄, and the stable structure of lignin forms this multi-component system. The oxidative desulfurization of the model fuel, involving the conversion of dibenzothiophene (DBT) to dibenzothiophene sulfone (DBTO₂), was used to evaluate the catalytic activity of the Fe@KL/S-g-C₃N₄ composite, with hydrogen peroxide (H₂O₂) as an oxidant. Optimization of the reaction conditions and statistical validation of sulfur removal were carried out by Box-Behnken Design (BBD) under Response Surface Methodology (RSM). The synthesized catalyst was also evaluated for structural stability and reusability over several cycles. The study offers a viable, economical, scalable, and green pathway for the synthesis of biomass-derived catalysts, which can be employed for the generation of cleaner fuels. Testing under more complex and realistic fuel conditions is proposed as essential future work.

2. Experimental section

2.1. Materials

Lignocellulosic biomass (bagasse) was obtained from the local market of Pakistan. Iron (III) nitrate nonahydrate [Fe (NO₃)₃·9H₂O], hydrogen peroxide (H₂O₂, 30%), concentrated sulfuric acid (H₂SO₄), hydrochloric acid (HCl), melamine (C₃H₆N₆), sodium hydroxide (NaOH), sodium sulfate (Na₂SO₄), thiourea (CH₄N₂S), ethanol, methanol, and distilled water were sourced from Sigma-Aldrich, and used as received, with all reagents being of analytical grade.

2.2. Methodology

2.2.1. Extraction of Kraft Lignin (KL)

Sugarcane bagasse was used to extract Kraft lignin following an established protocol. An acidic pretreatment (1.66 mL HCl in 200 mL water) was applied to 20 g of bagasse and kept at ambient temperature for 24 h. Next, the filtered residue was treated with an alkaline-peroxide solution (3 g NaOH and 3 mL of 30% H₂O₂ in 100 mL water) at 80 °C for 30 min. The lignin was then precipitated from the filtrate by a second filtration.

2.2.2. Synthesis of Iron-doped Lignin Nanoparticles

The preparation of Fe@KL nanoparticles involved the addition of 5.55 mg of Fe (NO₃)₃·9H₂O and 50 mg of extracted Kraft lignin to 10 mL and 50 mL of distilled water, respectively. After sonication followed by 2 h of stirring of the lignin dispersion, the iron nitrate solution was introduced dropwise, and a molar ratio of 1:20 was maintained. The mixture was stirred for an additional 2 h and was then aged at room temperature for 24 h to enable coordination between iron ions and lignin functional groups and was finally dried at 60 °C [17].

2.2.3. Synthesis of S-g-C₃N₄

A precursor mixture containing thiourea and melamine in a 3:1 M ratio underwent solid-state polycondensation to synthesize S-g-C₃N₄. The precursors were thoroughly mixed in a covered alumina crucible and heated to 550 °C in a muffle furnace. This mixture was maintained at this temperature in ambient air for 5 h to allow the incorporation of sulfur within the g-C₃N₄ structure. The resulting yellow product was ground and stored in a container after allowing it to cool naturally.

2.2.4. Synthesis of Nanocomposite

Fe@KL/S-g-C₃N₄ nanocomposite was prepared through a modified dispersion process. The Fe@KL and S-g-C₃N₄ (1:11 M ratio) were dispersed in 40 mL of methanol and then mixed by ultrasonication for 30 min to facilitate interfacial contact. The resulting mixture was then refluxed at 80 °C while stirring for 1 h. This material was then cooled to room temperature, centrifuged and washed with ethanol to remove impurities. The pellets were dried at 110 °C to obtain the Fe@KL/S-g-C₃N₄ nanocomposite and ground to a fine powder [18].

2.3. Desulfurization of model fuel via oxidation

The heterogeneous Fenton catalyst Fe@KL/S-g-C₃N₄ was used in the ODS process, with H₂O₂ as the oxidant and acetonitrile as the extracting solvent. A 200 ppm solution of dibenzothiophene (DBT) in n-hexane was used as a model fuel. The volume of simulated fuel used in the reaction was 10 mL, and the amount of nanocomposite catalyst added was 0.3 g. This mixture was shaken in a round bottom flask in the presence of 1 mL of H₂O₂ for 32.5 min at 60 °C. The reaction was conducted under thermal activation at 60 °C without dependence on external light irradiation consistent with Fenton like activation of H₂O. The reaction mixture was then transferred to a separating funnel, to which 6 mL of acetonitrile was added. The system was allowed to stand at room temperature for 15 min to allow phase separation. After separation of the various layers, the organic layer on top was separated from the underlying aqueous layer and the DBT concentration in the organic layer was determined by UV-Vis spectroscopy at 325 nm. Concentration values were determined from the measurements via the formula provided in Eq. (1):

$$\% \text{conversion} = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

where C_i denotes the initial concentration of DBT in the model fuel, while C_o is the concentration of DBT in the fuel sample after oxidation. Note that this UV-Vis method measures DBT disappearance (conversion), not the distribution of oxidation products.

2.4. Characterization

The representative physicochemical characteristics of KL, Fe@KL nanoparticles, S-g-C₃N₄, and Fe@KL/S-g-C₃N₄ were studied using several analytical techniques. The optical absorption properties were analyzed in the 200–800 nm range with the help of a spectrophotometer (PerkinElmer Lambda 750). Fourier Transform Infrared Spectroscopy (Nicolet iS50 FTIR) was employed to characterize functional groups in the 400–4000 cm⁻¹ range. The crystal structures of the samples were investigated by powder X-ray diffraction (Rigaku miniFlex600-C) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of 10° to 80° Raman spectroscopy (Renishaw Raman UK) was performed with a 532 nm laser source to examine the structural defects. Scanning Electron Microscopy (FE-SEM), together with Energy Dispersive X-ray Spectroscopy (Thermo Fisher Scientific Apreo) was used to examine the morphological and elemental characteristics of the samples. Surface chemical states and elemental oxidation states were examined using an X-ray Photoelectron Spectrometer (Thermo Scientific K-Alpha). The DBT oxidation products were confirmed by gas chromatography–mass spectrometry (GC-MS;

Agilent 7890B GC coupled to an HP-5MS capillary column and an electron-impact ionization (70 eV) mass-selective detector) with helium as the carrier gas. A potentiostat electrochemical workstation (Metrohm Autolab PGSTAT204) equipped with a three-electrode setup (catalyst-coated ITO working electrode, Pt-wire counter electrode, and Ag/AgCl reference electrode), was used to carry out EIS and Mott–Schottky analyses in 0.1 M Na₂SO₄ electrolyte with a 10 mV AC amplitude over the frequency range of 0.1 Hz to 100 kHz.

3. Results and discussions

3.1. FTIR studies

The functional groups and chemical interactions of Kraft lignin, S-g-C₃N₄, Fe@KL, and Fe@KL/S-g-C₃N₄ were investigated using FTIR in the 4000–400 cm^{−1} range as indicated in Fig. 1 and Table S1. The FTIR spectrum of Fe@KL/S-g-C₃N₄ provides direct evidence of the functional groups responsible for Fenton-like (PF) catalytic activity. The wide absorption band at 3400–3500 cm^{−1} shows N–H stretching modes and surface-adsorbed moisture [19]. The persistence of lignin-derived hydroxyl (O–H, 3400 cm^{−1}) and carboxyl (C=O, 1720 cm^{−1}) groups in the composite confirms that the iron is chelated onto the lignin scaffold through these oxygen-containing functionalities. Such Fe–O–C coordination environments are known to stabilize dispersed Fe³⁺ species and facilitate the Fe³⁺/Fe²⁺ redox cycle critical for H₂O₂ activation. This anchoring, through lignin oxygen groups is expected to enhance iron dispersion and reduce leaching, thereby maintaining catalytic activity across multiple reaction cycles [20,21].

3.2. Raman analysis

To investigate the structural defects of Kraft lignin, Fe@KL, S-g-C₃N₄, and the Fe@KL/S-g-C₃N₄ composite, the Raman spectroscopy was

employed, as shown in Fig. 2. The in-plane bending of the heptazine motif and N–H vibrations at ~973 cm^{−1} and 1153 cm^{−1}, respectively, are indicative of the polymeric structure of S-g-C₃N₄. The Fe@KL/S-g-C₃N₄ Raman spectrum exhibits a higher D/G band intensity ratio than that of pristine S-g-C₃N₄, reflecting the higher proportion of structural defects created by the incorporation of iron and functionalization of lignin.

In heterogeneous Fenton-like catalysis, lattice defects and surface irregularities serve as preferential sites for H₂O₂ adsorption and decomposition, thereby increasing the local •OH generation rate. This correlation between Raman-derived defect density and catalytic

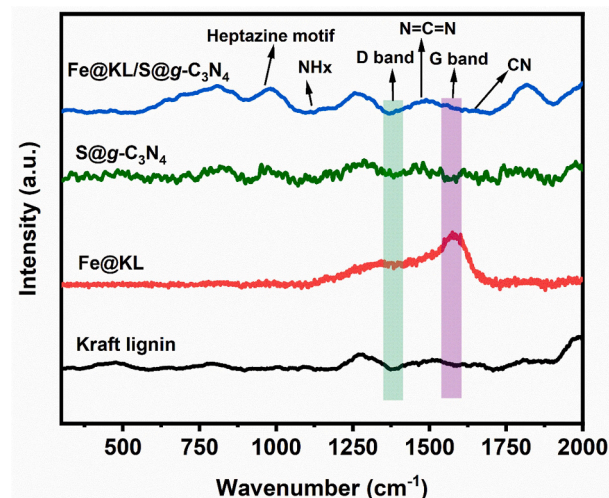


Fig. 2. Comparison of Raman spectra of KL, Fe@KL, S-g-C₃N₄ and Fe@KL/S-g-C₃N₄.

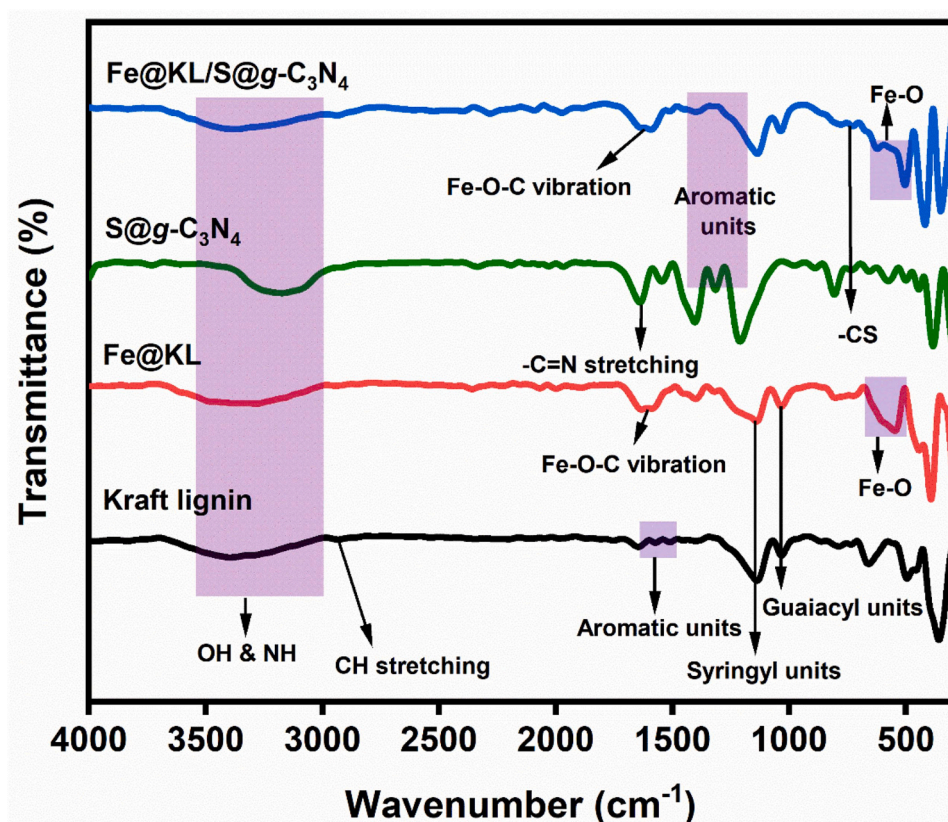


Fig. 1. Comparison of FTIR spectra of KL, Fe@KL, S-g-C₃N₄, and Fe@KL/S-g-C₃N₄.

performance has been documented in iron-modified carbon nitride systems [22]. The enhanced disorder also implies a greater number of accessible edge sites and coordinatively unsaturated iron centers, both of which are established descriptors of Fenton-like activity in Fe/g-C₃N₄ composites.

3.3. UV-visible analysis

The spectral characteristics of Kraft lignin, Fe@KL, S-g-C₃N₄ and the nanocomposite were observed in the 200–800 nm region, indicative of their electronic structures (Fig. 3). The UV-Vis spectra show λ_{max} at 290 nm for Kraft lignin, 310 nm for Fe@KL, 320 nm for S-g-C₃N₄ and 330 nm for the nanocomposite. The graphitic structure doped with sulfur exhibits a red shift, due to heteroatom incorporation that changes the heptazine structure, improving π - π^* and n - π^* transitions [23].

Further alterations in the electronic properties and electron adsorption behaviors were studied with the help of Eq. (2).

$$\alpha h\nu = A (h\nu - E_{\text{opt}})^n \quad (2)$$

where h , ν , and A represent Planck's constant, photon frequency and absorbance. The optical band gaps were calculated using Tauc plots $(\alpha h\nu)^2 = 0$ [24]. The band gap values extracted from the Tauc plots (g-C₃N₄: 2.65 eV; S-g-C₃N₄: 2.38 eV; Fe@KL/S-g-C₃N₄: 1.85 eV) are consistent with the stepwise electronic structure modifications introduced by S-doping (+S), Fe-coordination (+Fe-N), and lignin π -conjugation (+KL).

As shown in Fig. S1, Kraft lignin has a band gap of 3.57 eV, which reduces to 3.09 eV after Fe doping. Similarly, the S-g-C₃N₄ band gap, which is approximately 2.38 eV, reduces to 1.85 eV in the nanocomposite. The observed band gap reduction from 2.38 to 1.85 eV can be attributed to iron incorporation, which introduces localized electronic states within the band gap and enhances visible-light absorption. These effects are associated with Fe 3d orbital contributions and charge-transfer interactions within the Fe-coordinated g-C₃N₄ structure, as reported for analogous Fe-modified systems [25]. Second, the π -conjugated system of S-g-C₃N₄ is extended, and the absorption onset is red-shifted into the visible region, as a result of hybridization with the aromatic chromophores of Kraft lignin, such as phenolic, conjugated carbonyl groups, and the cinnamyl-type. Third, the higher Raman D/G ratio of the material results in an Urbach energy tail which widens the optical absorption edge and leads to the apparent narrowing of the band gap. Combined, these three effects give a composite with broad absorption across the visible range of the spectrum (400–700 nm), which makes it well suited for catalysis using solar radiation.

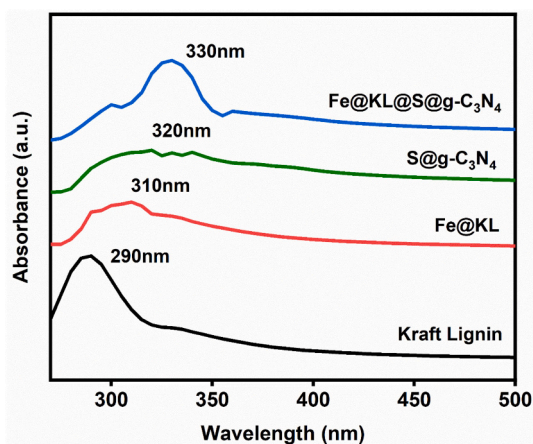


Fig. 3. Comparison of UV-Visible spectrum of KL, Fe@KL, S-g-C₃N₄, and Fe@KL/S-g-C₃N₄.

3.4. X-ray diffraction (XRD)

The XRD patterns of Kraft lignin, Fe@KL, S-g-C₃N₄, and the nanocomposite demonstrate progressive structural modification upon hybridization, as shown in Fig. 4. Kraft lignin has a strong diffraction halo at 18.9°, which indicates that it is mainly amorphous [5,26]. Fe@KL exhibits distinct peaks at 32°, 34°, and 48.9° after iron incorporation, which are the characteristic peaks of crystalline hematite (α -Fe₂O₃) species, implying that iron oxide is dispersed throughout the lignin matrix [27]. The distinctive peaks of S-g-C₃N₄ are located at 13.3° and 27°, which correspond to the (100) in-plane packing and (002) inter-layer stacking of graphitic carbon nitride. In the Fe@KL/S-g-C₃N₄ composite, the dominant ~27° peak is retained, with its diffraction pattern closely resembling, that of S-g-C₃N₄, which confirms that the addition of Fe@KL does not disrupt the crystal structure of the g-C₃N₄ framework. Overall, the XRD patterns verify the amorphous lignin matrix and the effective synthesis of the Fe@KL/S-g-C₃N₄ nanocomposite.

3.5. FE-SEM/EDX studies

Scanning Electron Microscopy (SEM) shows that Kraft lignin (KL) consists of irregular and fragmented particles with rough surfaces and a broad size distribution, typical of industrial lignin, as shown in Fig. 5a [5]. EDX analysis (Fig. 5f) identifies C and O as the dominant elements, with residual S from the Kraft pulping process. The elemental mapping (Fig. 5b–e) further confirms the homogeneous dispersion of the expected elements (C, O, and S) throughout the matrix. Fe@KL is roughened and textured after Fe incorporation, suggesting that the surface functional groups anchor Fe species to the lignin matrix, as shown in Fig. 6a. The incorporation of iron is confirmed by EDX (Fig. 6g) and the elemental maps (Fig. 6b–f) reveal a uniform distribution of Fe throughout the lignin matrix. The morphology of S-g-C₃N₄ is nanosheet-like with wrinkling [1] (Fig. 7a). The constituent elements S, C, and N are confirmed by elemental mapping (Fig. 7b–f) and EDX, which shows sulfur doping to be effective (Fig. 7g). The Fe@KL/S-g-C₃N₄ composite consists of Fe-modified lignin particles embedded within the S-g-C₃N₄ sheets, creating a hierarchical heterostructure with abundant interfaces, as shown in Fig. 8a. In the composite EDX image (Fig. 8h), all three components are successfully integrated, as all constituent elements (C, N, O, S, and Fe) are shown in the elemental maps (Fig. 8b–g) [28].

3.6. XPS analysis

X-ray Photoelectron Spectroscopy was applied to determine the surface chemistry and elemental oxidation states of the resulting Fe@KL/S-g-C₃N₄ nanocomposite. The survey scan indicates the

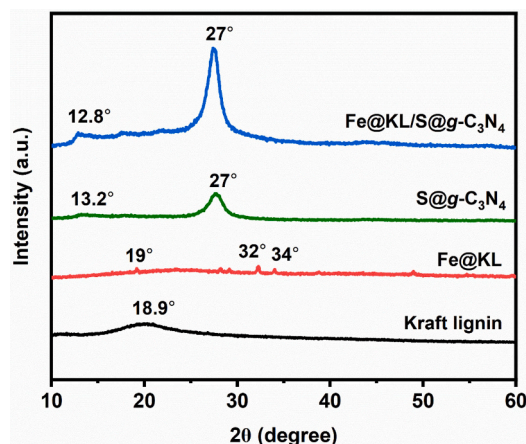


Fig. 4. Comparison of XRD patterns of KL, Fe@KL, S-g-C₃N₄ and Fe@KL/S-g-C₃N₄.

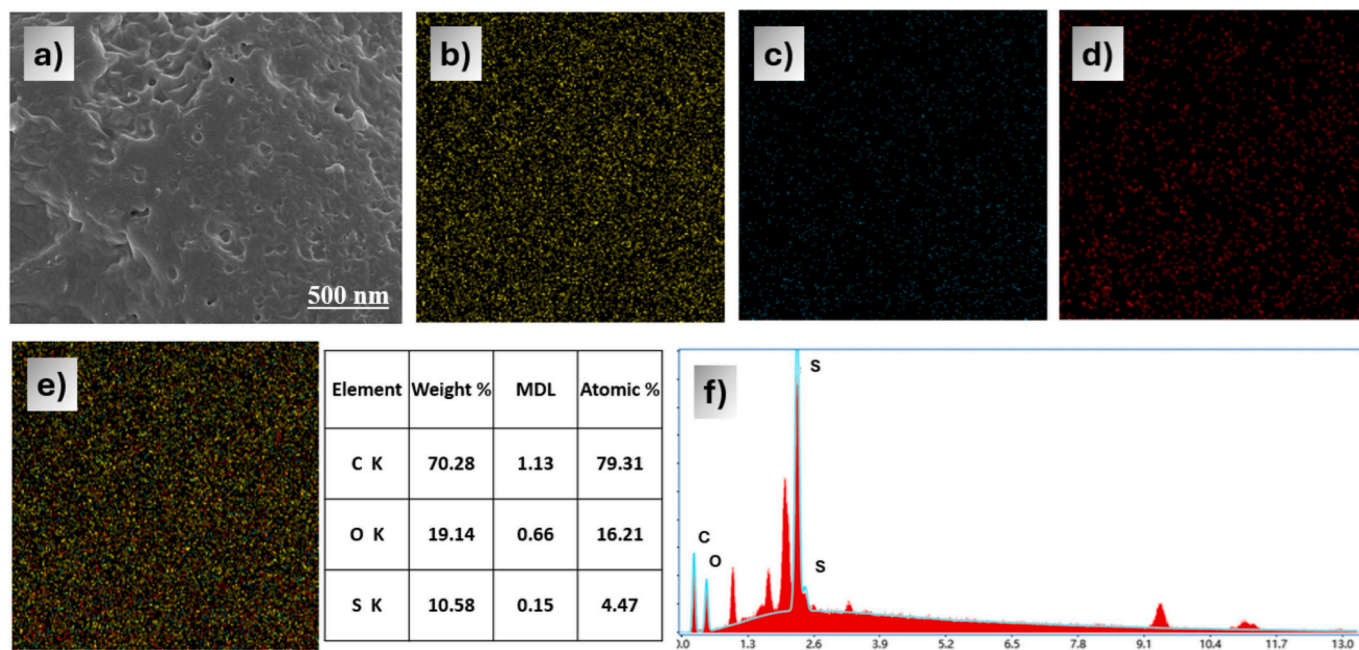


Fig. 5. SEM-EDX characterization of raw KL: a) SEM micrograph showing the surface morphology; b–d) individual elemental mapping for sulfur (S), oxygen (O), carbon (C), and e) combined elemental overlay map; and f) EDX spectrum.

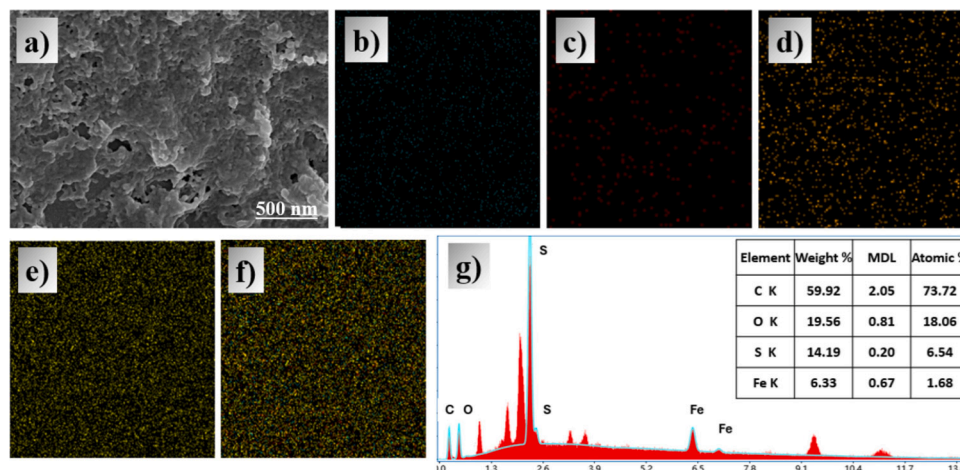


Fig. 6. SEM-EDX characterization of iron-modified Kraft lignin: a) SEM micrograph showing the surface morphology; b–e) individual elemental mapping for oxygen (O), carbon (C), iron (Fe), and sulfur (S); f) combined elemental overlay map; and g) EDX spectrum.

existence of C (C 1s), N (N 1s), O (O 1s), S (S 2p), and Fe (Fe 2p) in the material (Fig. 9A). The high-resolution C 1s scan shows that carbon in the triazine rings and lignin framework is present in the form of carbon-carbon single bonds (C–C) and sp^2 -hybridized carbon in N–C=N environments, together with carbonyl (C=O) and ester linkages (O–C=O), corresponding to binding energies of 284.8 eV and 288.4 eV respectively (Fig. 9B). As Fig. 9C shows, the core-level scan of N 1s is deconvoluted into two major components of 398.8 eV and 400.1 eV, which are related to the C=N–C aromatic nitrogen and N–(C)₃ tertiary nitrogen, respectively, present in the graphitic carbon nitride structure [29]. The Fe 2p spectrum (Fig. 9D) reveals the coexistence of Fe^{2+} and Fe^{3+} oxidation states. The $Fe\ 2p_{3/2}$ region is deconvoluted into peaks at 710.8 and 713.4 eV assigned to Fe^{2+} and Fe^{3+} , respectively. The $Fe\ 2p_{1/2}$ region consists of peaks at 724.8 and 727.3 eV related to Fe^{2+} and Fe^{3+} . In addition to this, shake-up satellite peaks further confirm the presence of high-spin iron species. The coexistence of Fe^{2+}/Fe^{3+} redox couples is

beneficial for the Fenton-like catalytic reactions, as it enables electron transfer and continuous production of ROS during oxidative desulfurization [47]. The O 1s spectrum (Fig. 9E) is centered around 532.5 eV, and is attributed to oxygen-containing functional groups, such as –OH, C–O and C=O species, originating from lignin and surface adsorbed oxygen species [30]. Most importantly, the S 2p spectrum (Fig. 9F) resolves four components in two regions of binding energy: the peaks at 163.3 eV and 164.9 eV are assigned to thiophenic C–S–C reduced sulfur incorporated into aromatic rings, and the peaks at 167.5 eV and 169.1 eV are assigned to sulfonate (C–SO₃[–]) and sulfate-type (–SO₄^{2–}) oxidized sulfur species, respectively [31]. The coexistence of both reduced thiophenic and oxidized sulfonate/sulfate sulfur environments confirms that sulfur undergoes partial oxidation during the 550 °C polycondensation of the thiourea precursor, with the oxidized species modifying the local electron density around adjacent nitrogen atoms in the heptazine framework and enhancing charge separation efficiency [49].

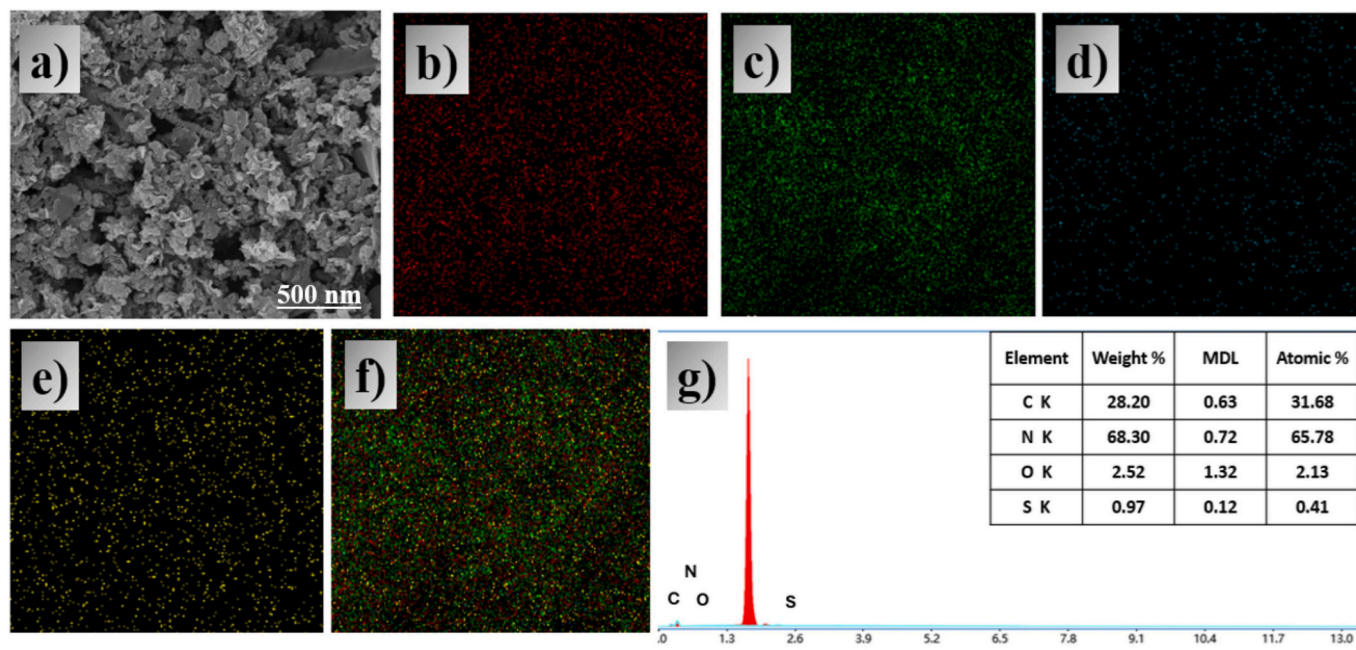


Fig. 7. SEM-EDX characterization of S-g-C₃N₄: a) SEM micrograph showing the surface morphology and porous structure; b-e) individual elemental mapping for carbon (C), nitrogen (N), oxygen (O), and sulfur (S); f) combined elemental overlay map; and h) EDX spectrum.

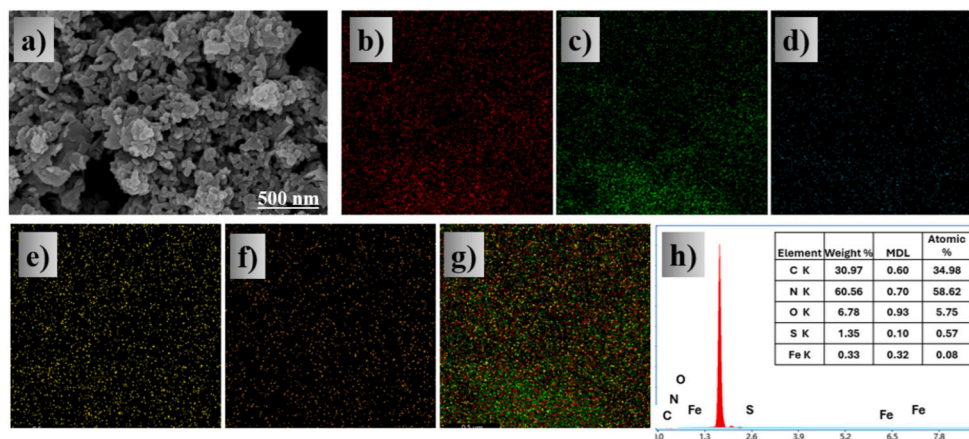


Fig. 8. SEM-EDX characterization of the nanocomposite: a) SEM micrograph showing the surface morphology and granular structure; b-f) individual elemental mapping for carbon (C), nitrogen (N), oxygen (O), sulfur (S), and iron (Fe); g) combined elemental overlay map; and h) EDX spectrum.

3.7. Photoelectrochemical characterization

3.7.1. Mott-Schottky analysis

To explore the semiconductor properties, flat band potential (V_{fb}), and donor density (ND) of Kraft lignin and the Fe@KL/S-g-C₃N₄ catalyst (Fig. 10B and 10C), the Mott-Schottky (MS) analysis was carried out. The positive slopes of both materials in the plots of $1/C^2$ vs. potential indicate that the materials are n-type semiconductors with electrons being the majority charge carriers, which is consistent with the behavior of g-C₃N₄-based materials [32]. The values of V_{fb} obtained from the extrapolation of the linear fit to the x-intercept were 0.132 V vs. Ag/AgCl for Kraft lignin and 0.094 V vs. Ag/AgCl for Fe@KL/S-g-C₃N₄. The cathodic shift of the flat-band potential indicates a more negative conduction band edge, as the flat-band potential of n-type semiconductors is close to the conduction band minimum. This change should increase the thermodynamic driving force for reduction reactions, due to an increase in the reduction potential of the electrons [33].

3.7.2. Electrochemical impedance spectroscopy (EIS)

Comparative EIS analysis (Fig. 10C) reveals that the Fe@KL/S-g-C₃N₄ catalyst exhibits a substantially lower charge-transfer resistance (R_{ct} = 21.93 Ω) than Kraft lignin (R_{ct} = 51.31 Ω), indicating faster interfacial charge-transfer kinetics and superior electrocatalytic activity. The solution resistance (R_s) is also lower for the catalyst sample (31.39 Ω) than Kraft lignin (43.50 Ω) which also indicates reduced electrolyte resistance. On the other hand, the Warburg diffusion coefficient for the composite sample is higher (32.83×10^{-3} S·s^{1/2}) than that for the Kraft lignin (14.91×10^{-3} S·s^{1/2}), indicating that the composite sample's impedance response has a higher diffusion-limited contribution. Overall, the composite appears to be the more kinetically favorable catalyst. The lower R_{ct} indicates good electron transport at the interface, which can promote fast Fe³⁺/Fe²⁺ redox cycling in the Fe-O-C coordination network. The PL spectrum (Fig. S2) also supports this, showing that the Fe@KL/S-g-C₃N₄ composite has a significantly lower emission intensity than S-g-C₃N₄, which indicates improved electronic properties upon incorporation of Fe and lignin. It, in turn, stimulates ongoing activation

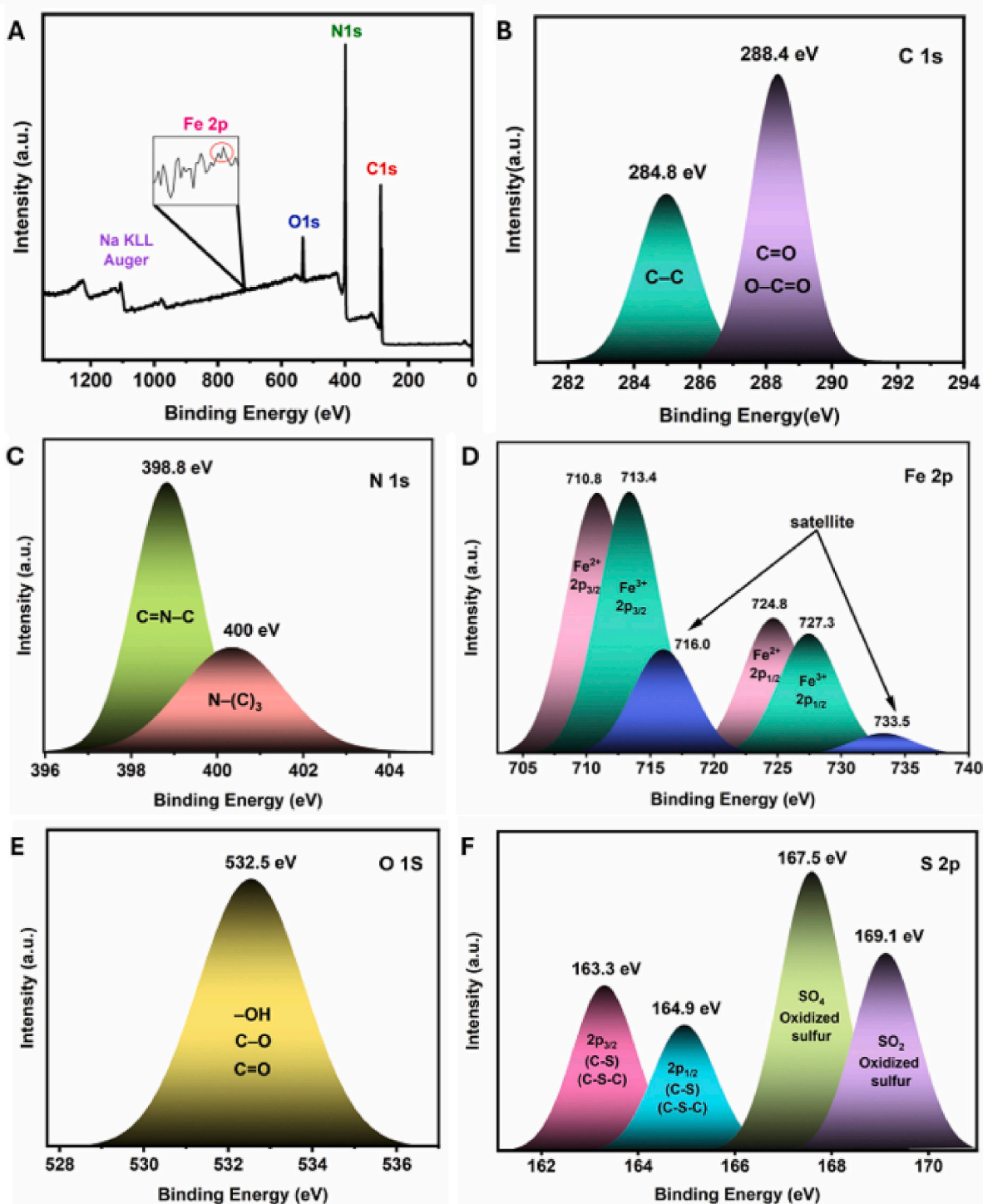


Fig. 9. XPS analysis of the catalyst: (A) survey spectrum and deconvoluted high-resolution spectra of (B) C 1s, (C) N 1s, (D) Fe 2p, (E) O 1s, and (F) S 2p.

of H_2O_2 and ROS formation, therefore being a key player in the Fenton-like oxidative desulfurization pathway [34].

4. Strategies for optimizing DBT conversion in fuel

To evaluate the catalytic behavior of the synthesized $\text{Fe@KL/S-g-C}_3\text{N}_4$ nanocomposite, various reaction parameters were optimized to evaluate their effect on the oxidation of DBT in model fuel. The variables selected were catalyst dosage, temperature and reaction time. The usual reagent combination included 10 mL of model fuel (200 ppm DBT

solution in *n*-hexane), 1 mL of 30% H_2O_2 as the oxidant, and 6 mL of acetonitrile as an extraction solvent. Varying amounts of catalyst (0.1–0.3 g) were added to the reaction medium and stirred at varying temperatures (25–60 °C) for varying times (15–50 min). Control experiments confirmed the necessity of both the catalyst and H_2O_2 , as the blank reaction showed negligible DBT conversion, while the H_2O_2 -only system achieved only 7% conversion, compared with over 98% conversion for the complete $\text{Fe@KL/S-g-C}_3\text{N}_4/\text{H}_2\text{O}_2$ system under the optimized conditions (Fig. S3). The catalyst achieved a maximum DBT conversion exceeding 98% under optimized conditions (0.3 g catalyst,

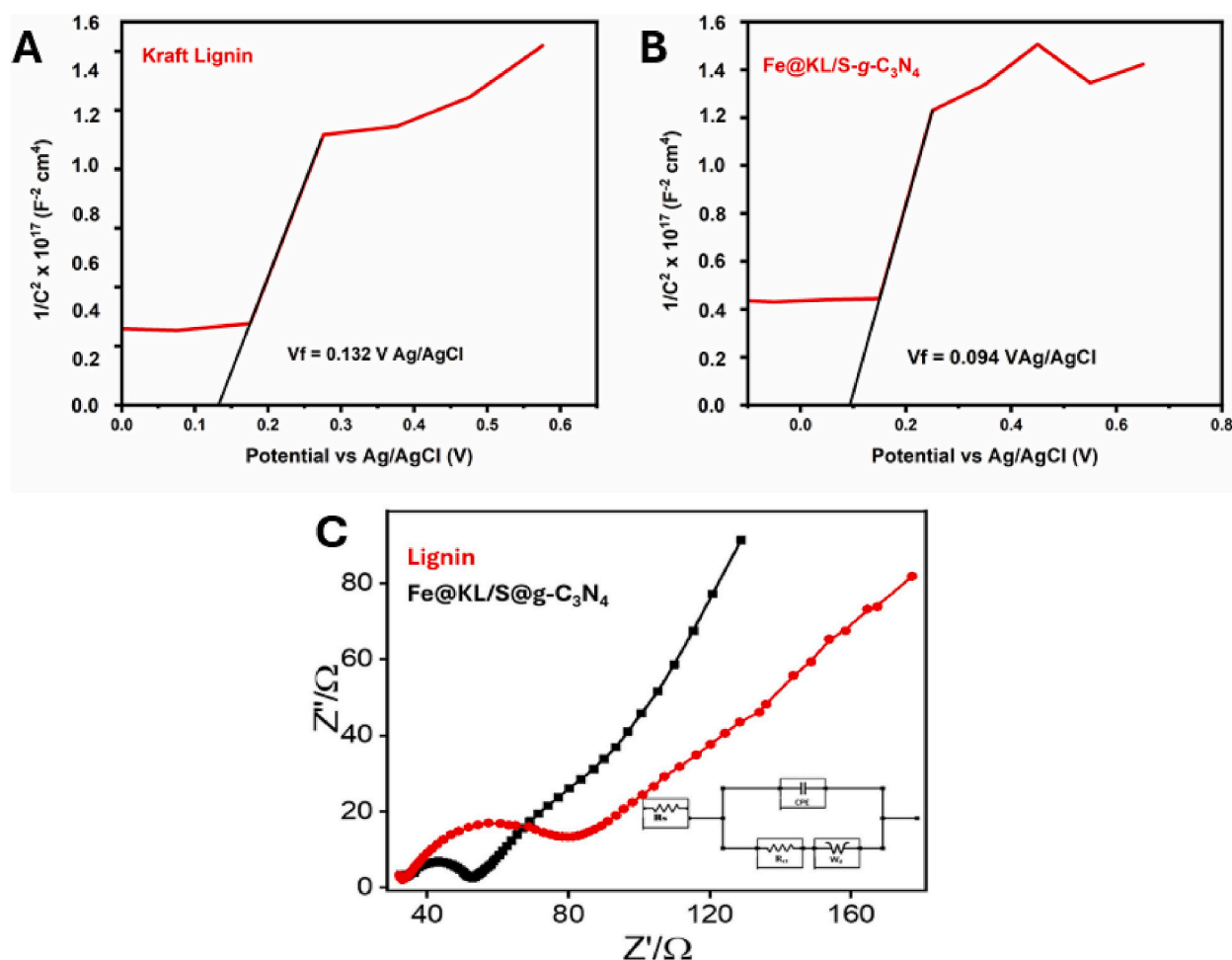


Fig. 10. Mott-Schottky plots of (A) kraft lignin, (B) Fe@KL/S-g-C₃N₄, and (C) Nyquist impedance spectra comparing the charge-transfer characteristics of lignin and Fe@KL/S-g-C₃N₄.

60 °C, 32.5 min). GC-MS analysis of the reaction mixture (Fig. S4) further confirmed the formation of dibenzothiophene sulfoxide (DBTO) and dibenzothiophene sulfone (DBTO₂), together with residual DBT fragments, corroborating the oxidative desulfurization pathway. The oxidation process at low temperatures was rate-limited by the activation of reactive oxygen species (ROS) and the rate of oxidation rose with temperature to reach a maximum at 60 °C. Hydrogen peroxide served as the primary oxidant, generating reactive oxygen intermediates that converted DBT sequentially to dibenzothiophene sulfoxide (DBTO) and then to dibenzothiophene sulfone (DBTO₂), as proposed in the mechanism section below and consistent with the established ODS literature [35].

4.1. Box-Behnken design in response surface methodology

Response Surface Methodology (RSM) combined with a Box-Behnken Design (BBD) was employed to systematically optimize the key operational parameters governing the Fenton-like oxidative desulfurization (ODS) of dibenzothiophene (DBT) over Fe@KL/S-g-C₃N₄. The hydroxyl radical (•OH) generation rate and the oxidation of DBT to dibenzothiophene sulfone (DBTO₂) are critically dependent on the interplay between catalyst dosage, reaction temperature and contact time. It is recognized that these variables have interdependent, nonlinear relationships, which are not well represented by one factor at a time (OFAT) approaches. BBD was therefore chosen as an efficient three-level, three-factor design (as shown in Table 1), which estimated

Table 1

Variables and their respective ranges and levels that impacted the desulfurization process.

Parameters	Range and Levels		
	−1	0	1
Catalyst dosage (g)	0.1	0.2	0.3
Reaction temperature (°C)	25	42.5	60
Reaction time (min)	15	32.5	50

the quadratic interaction effects of heterogeneous Fenton-like catalysis while requiring the minimum number of experimental runs. Recent studies using BBD have validated the use of this model for Fenton-like oxidative desulfurization systems where both substrate diffusion and the availability of the active site control the performance of the system [5].

Table 2 shows the responses of oxidative desulfurization (ODS). The ratio of 1.62 indicates that there is no need for additional modifications, with values ranging from 60.67 to 98.37.

4.2. Effects of parameters on dibenzothiophene conversion in model fuel

A second order polynomial equation (Eq. (3)) was used to establish the relationship between the selected variables and the response through regression analysis.

Table 2

Experimental matrix and observed desulfurization responses.

Run	Factor (i) A: Catalyst loading (g)	Factor (ii) B: Reaction temperature (°C)	Factor (iii) C: Reaction time (min)	Predicted values	Actual values R1
1	0.2	42.5	32.5	83.77	85.07
2	0.2	60	15	96.61	96.88
3	0.1	60	32.5	86.13	85.9
4	0.3	42.5	50	78.42	78.45
5	0.2	60	50	92.75	91.97
6	0.1	25	32.5	65.88	65.13
7	0.2	25	50	68.36	68.1
8	0.2	25	15	79.00	79.79
9	0.1	42.5	50	59.65	60.67
10	0.3	42.5	15	77.63	76.61
11	0.3	25	32.5	75.86	76.1
12	0.2	42.5	32.5	83.77	83.11
13	0.1	42.5	15	74.96	74.94
14	0.2	42.5	32.5	83.77	85.25
15	0.2	42.5	32.5	83.77	81.2
16	0.2	42.5	32.5	83.77	84.22
17	0.3	60	32.5	97.61	98.37

$$\text{Response (R)} = 83.77 + 5.36A + 10.50B - 3.63C + 37.50AB + 4.03AC + 1.70BC - 6.96A^2 + 4.56B^2 - 4.15C^2 \quad (3)$$

Multiple models, including linear, 2FI, cubic, and quadratic, were tested using Design Expert, with the quadratic model showing the best agreement with experimental results. F-tests confirmed model precision, and the absence of significant lack of fit was verified (Table S2). The quadratic model, having the highest polynomial order and R^2 value, was selected as the most reliable, while the aliased model was excluded (Table S3).

4.3. Variance analysis for quadratic model

Analysis of variance (ANOVA) calculated the mean square values for each model term given in Table 3, by using response surface methodology. It determined the corresponding degrees of freedom and sums of the squares of independent variables.

The predictive ability of the quadratic model was assessed by comparing the predicted and experimental values of DBT conversion using regression coefficient (R^2). The results of the model are in good agreement with the experimental results, as seen in Fig. S5a. The normal probability plot of the externally studentized residuals, shown in Fig. S5b, is close to the line, indicating that the residuals are approximately normally distributed.

The externally studentized residuals are plotted against the predicted

DBT conversion in Fig. S6a. Random residuals around the zero line suggest constant error variance, no systematic error. The residuals plotted against the run number Fig. S6b indicate that the observations are independent of each other and that there are no significant outliers.

4.4. Analysis of 3D graphs and surface contour plots

The three-dimensional RSM surface plots in Fig. 11 reveal that catalyst dosage and reaction temperature exert the strongest combined influence on DBT conversion efficiency, consistent with the Fenton-like mechanistic model. Increasing catalyst dosage augments the surface density of Fe^{3+} active sites available to decompose H_2O_2 into $\bullet\text{OH}$ radicals via the reaction: $\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HOO}\bullet$, followed by $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$. This redox cycle is promoted by higher temperature, but at higher temperatures ($>60^\circ\text{C}$) this process competes with the decomposition of H_2O_2 into H_2O and O_2 , leading to a decrease in the conversion. The quadratic model was found to be a very good fit with the experimental data ($R^2 = 0.98$, $p < 0.0001$ for the model; $p > 0.05$ for lack-of-fit) and it was reliable for prediction in the experimental parameter range studied. The statistical significance of all three main effects and two-way interaction terms are confirmed by the ANOVA results. The BBD model is thus presented here as a practical optimization tool underpinned by the Fenton reaction chemistry rather than an end in itself.

4.5. Optimization of experimental conditions

The process optimization was done to find out the optimum condition for removing dibenzothiophene (DBT) from the oxidative desulfurization system. Box–Behnken Design (BBD) methodology was used to consider the interaction effect of important variables (catalyst dosage, reaction time, and temperature) and to determine the optimum operating conditions shown in Fig. S7. It must be noted that the overall difference between the experimental matrix (Run 17: 0.3 g, 60°C , 32.5 min, 98.37% efficiency) and the optimum conditions (0.16 g, 29.28°C , 43.01 min, 70.24% efficiency) is apparent, and the reason is that the desulfurization efficiency falls as the reaction progresses. These two values do not contradict each other, they are addressing different questions. The highest 98.37 % conversion of DBT found experimentally in the BBD design space corresponds to the maximum dose of the catalyst, maximum temperature, and mid-level time. The 70.24 % is the result of the optimization of the desirability function, which was set up with the aim of finding a compromise operating point between high desulfurization efficiency and practical and economical factors, namely lower catalyst dosage (to reduce the cost of the material) and lower temperature (to reduce the energy consumption). The desirability ramps for ODS optimization show optimal catalyst dosage (0.3 g), temperature (60°C), and reaction time (32.5 min), achieving a predicted

Table 3

Assumptions for ANOVA in the context of the Quadratic Model.

Source	Sum of squares	Degrees of freedom	Mean square	Fisher value (F)	Probability value (p)	
Model	1649.84	9	183.32	81.07	< 0.0001	Significant
A-Catalyst Dosage	229.94	1	229.94	101.69	< 0.0001	
B-Temperature	882.00	1	882.00	390.07	< 0.0001	
C-Time	105.34	1	105.34	46.59	0.0002	
AB	0.5625	1	0.5625	0.2488	0.6332	
AC	64.88	1	64.88	28.70	0.0011	
BC	11.49	1	11.49	5.08	0.0588	
A ²	203.74	1	203.74	90.11	< 0.0001	
B ²	87.60	1	87.60	38.74	0.0004	
C ²	72.38	1	72.38	32.01	0.0008	
Residual	15.83	7	2.26			
Lack of Fit	4.70	3	1.57	0.5639	0.6671	
Pure Error	11.12	4	2.78			
Cor Total	1665.66	16				Not significant

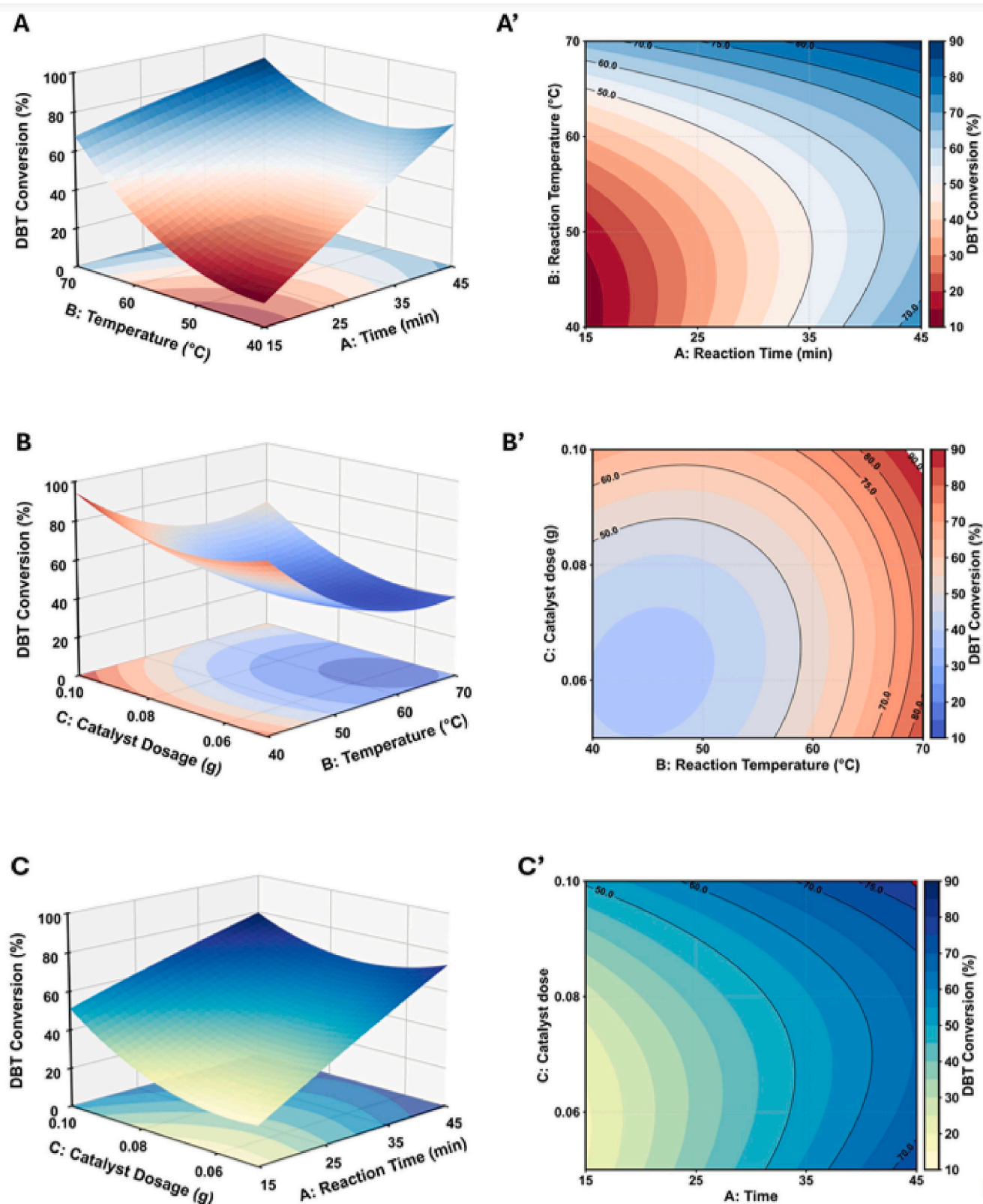


Fig. 11. 3D response surface plots with corresponding 2D contours demonstrating the combined influence of reaction time (C), temperature (B), and catalyst dosage (A) on response R1: (A, A') A vs. B; (B, B') B vs. C; (C, C') A vs. C.

desulfurization of 97.8% and an experimentally confirmed value of 98.37%. The close agreement between predicted and experimental values at both points validates the BBD model [36].

4.6. Mechanistic studies

The Fe@KL/S-g-C₃N₄ nanocomposite possesses abundant heterogeneous Fenton active sites, which are formed by Fe–O–C coordination

environments as evident from FTIR analysis. The coexistence of Fe^{2+} and Fe^{3+} species is confirmed by XPS, and the decreased optical band gap suggests that the electronic structure is modulated after Fe incorporation and lignin coupling. These results, combined with the cathodic shift in the flat-band potential and the decrease in charge transfer resistance obtained from Mott–Schottky and Nyquist plots, indicate improved electron transfer properties, which enable efficient $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycling and the continuous activation of H_2O_2 (Eqs. (4) & (5)) [34].



The natural presence of phenolic hydroxyl groups and quinone/hydroquinone redox pairs in Kraft lignin further facilitate the reduction of Fe^{3+} to Fe^{2+} , which can be attributed to the electron shuttle effect, thereby continuing the heterogeneous Fenton cycle [37].

Radical scavenging and hot filtration experiments were also carried out to confirm the reaction mechanism. The effect of adding isopropanol (IPA), a hydroxyl radical ($\bullet\text{OH}$) scavenger, resulted in a reduction of around 65% in the DBT conversion, thus supporting the fact that $\bullet\text{OH}$ radicals are the key Reactive Oxygen Species (ROS) involved in the oxidation of DBT, as previously reported in heterogeneous Fenton-like oxidation processes [38]. Moreover, during the hot filtration test, the catalyst was removed after 15 min of reaction, when the desulfurization efficiency was 11.3%. At the end of the total reaction time of 32.5 min, the catalyst-free filtrate was then found to have only 16% DBT conversion, which suggests negligible catalytic activity in the absence of the solid catalyst. These results confirm that the oxidation proceeds through a heterogeneous catalytic pathway with no significant contribution from leached iron species. The resulting ROS sequentially oxidize dibenzothiophene (DBT) to dibenzothiophene sulfoxide (DBTO) and then to dibenzothiophene sulfone (DBTO₂) as shown in Eqs. (7) and (8), respectively. DBTO₂ is more polar and can be easily extracted into the acetonitrile phase.



The regenerated Fe^{3+} species can repeatedly participate in the next heterogeneous Fenton-like oxidation cycles to remove the sulfur efficiently. Overall, the structural (FTIR and XPS) and electrochemical (Mott–Schottky and EIS) results are consistent, showing that Fe incorporation into the lignin/S-g-C₃N₄ framework improves electron-transfer properties and $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycling, enabling efficient activation of

Table 4

Comparison of the current catalytic system with previously reported systems.

Catalyst	Initial sulfur (ppm)	Conditions	Removal (%)	Ref
Ni-WO ₃ @g-C ₃ N ₄	100	0.1 g, 60 min, 40 °C, H ₂ O ₂	97	[35]
PW/TiO ₂ /g-C ₃ N ₄	500/1900	0.03 g, 200 min, 80 °C, H ₂ O ₂	29.6/34.7	[39]
Mo@g-C ₃ N ₄	500	1 g, 120 min, 80 °C, H ₂ O ₂	98	[40]
Z-scheme TiO ₂ -ZnO@O-g-C ₃ N ₄	200	0.05 g, 90 min, 50 °C, H ₂ O ₂	95.2	[41]
Fe ₃ O ₄ /g-C ₃ N ₄ (Z-scheme)	300	0.2 g, 60 min, 55 °C, H ₂ O ₂	94.8	[42]
Phosphotungstic acid IL/g-C ₃ N ₄	500	0.05 g, 60 min, 60 °C, H ₂ O ₂	>99	[43]
Fe@KL/S-g-C ₃ N ₄ (This study)	200	0.3 g, 32.5 min, 60 °C, H ₂ O ₂ , Xe lamp $\lambda > 420$ nm	98.37	–

H_2O_2 and enhancing heterogeneous Fenton-like oxidative desulfurization performance. The detailed redox pathway for DBT oxidation is shown in Fig. 12.

As shown in Table 4, earlier studies generally required elevated temperatures and extended reaction times to reach sulfur removal efficiencies exceeding 90%. In contrast, the Fe@KL/S-g-C₃N₄ catalyst achieved 98.31% conversion at 60 °C within 32.5 min, indicating superior catalytic efficiency and improved reaction performance relative to conventional systems.

The Fe@KL/S-g-C₃N₄ composite is as efficient as the other reported ODS systems based on g-C₃N₄ regarding removal efficiency, and it has the benefit of incorporating the renewable biomass material, Kraft lignin (KL) from sugarcane bagasse. The mass-specific DBT removal rate was estimated to be about 6.6 mg DBT g^{−1} catalyst, and the sulfur capacity was estimated to be about 1.1 mg S g^{−1} catalyst, based on the experimental data (200 ppm DBT, 10 mL, 98.37% conversion, 0.3 g catalyst).

5. Reusability and stability studies

To evaluate the stability of the catalyst, recycling experiments were performed. The test procedure was similar to the Fenton-like ODS reactions with a slight modification to the final step. The used catalyst was reused after the DBT was converted into DBTO₂ for a new sample of model fuel under the same conditions. As shown in Fig. 13, the catalyst exhibits gradual but limited deactivation over ten cycles, retaining

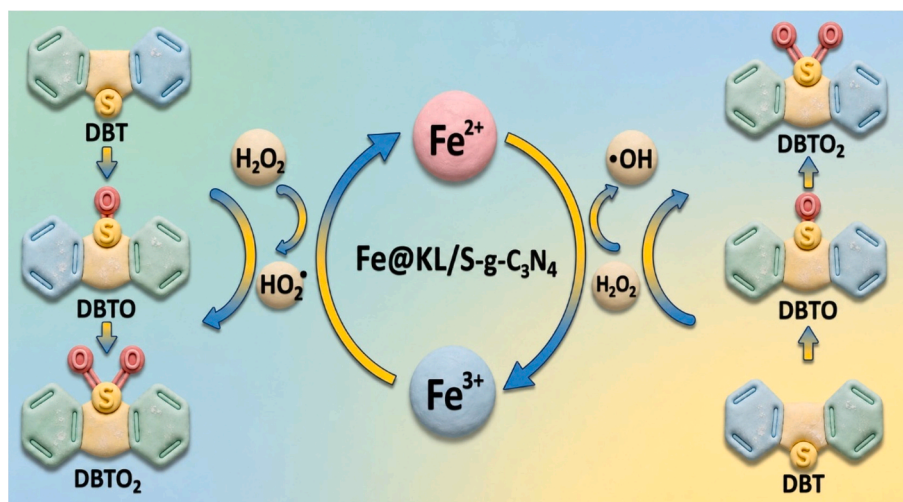


Fig. 12. Proposed mechanistic pathway for heterogeneous Fenton-like oxidative desulfurization with Fe@KL/S-g-C₃N₄.

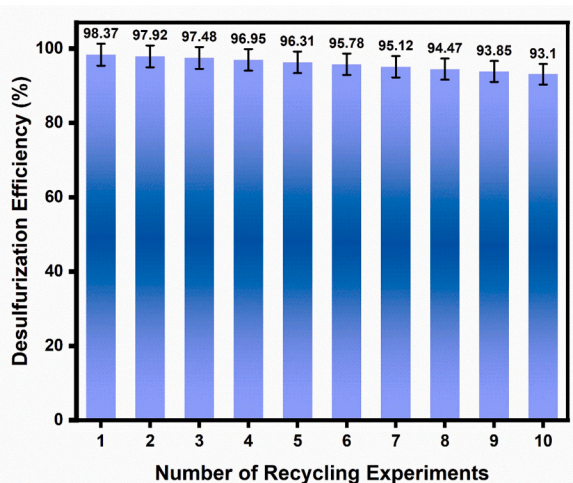


Fig. 13. Reusability of the catalyst under optimum conditions.

approximately 93% of its initial activity after the tenth cycle, indicating excellent operational stability and resistance to structural degradation. Post-reaction FTIR analysis (Fig. S8) confirms the retention of characteristic vibrational bands, further supporting the structural integrity of the catalyst after repeated use [44].

6. Conclusion

A Fe@KL/S-g-C₃N₄ nanocomposite with high catalytic activity was synthesized for use in the Fenton-like oxidative desulfurization of model fuel in this study. The band gap was reduced from 3.57 eV in Kraft lignin to 1.85 eV in the composite, which is attributed to the presence of Fe 3d sub-gap states and S-derived mid-gap levels that enable the Fe³⁺/Fe²⁺ Fenton redox cycle at mild temperatures. This improvement resulted in more efficient charge transfer, improving the availability of active sites, which in turn enabled 98.37% sulfur removal efficiency with H₂O₂ as a green oxidant. The Box-Behnken Design (BBD) optimization determined the optimum reaction conditions as 0.3 g of catalyst, a 32.5 min reaction time and a temperature of 60 °C. ANOVA validation of these results showed that the model was reliable with a high regression coefficient ($R^2 = 0.9905$) and that the lack of fit was not significant ($p = 0.6671$). In conclusion, the Fe@KL/S-g-C₃N₄ catalyst offers a stable and highly reusable route to the production of ultra-low sulfur fuels using biomass-derived materials.

CRedit authorship contribution statement

Saba Iqbal: Writing – original draft, Visualization, Software, Methodology, Investigation, Conceptualization. **Hina Murtaza:** Writing – review & editing, Software. **Shahid Nazir:** Writing – review & editing, Resources. **Syed Irfan:** Writing – review & editing. **Fiaz Hussain:** Writing – review & editing. **Sadaf Ul Hassan:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used Google Gemini to assist with language editing and improving clarity. After using this tool, the authors reviewed and edited the content as needed. The authors take full responsibility for the content of the published article.

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

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijbiomac.2026.153813>.

Data availability

Data will be made available on request.

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