

Schiff's base of Fe_3O_4 @chitosan with 4,4'-diselenobisbenzaldehyde: Preparation, characterization and its catalytic activity for oxidation of sulphides

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ABSTRACT

We have synthesized Schiff's base of Fe_3O_4 @chitosan with 4,4'-diselenobisbenzaldehyde (Fe_3O_4 @CSSe) composite and used it as a catalyst for the oxidation of sulfides, having some advantageous properties such as eco-friendly, cost-effective and highly efficient magnetic biocatalyst of selenium. The synthesized schiff's base was characterized by different physical characterization techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Vibrating sample magnetometer (VSM) and Dynamic light scattering (DLS). Further, we used the resulting schiff's base as a catalyst in the presence of a green oxidant (H_2O_2) to oxidize sulfides to corresponding sulfoxides at room temperature. It has been found that yield of sulfoxides depend on the amount of H_2O_2 , loading catalyst and various solvents condition. Besides, more efficiently oxidation of dibutyl sulfide observed in the solvent-free condition with the yield of 94 per cent in the presence of 20mg Fe_3O_4 @CSSe and 0.5 mL H_2O_2 . Thus, the magnetic schiff's base catalyst applied to oxidation of a broad range of sulfides. This may help enrich and develop future research on organic synthesis.

KEYWORDS: Oxidation, Sulfide, Sulfoxide, Hydrogen peroxide, Chitosan, Magnetic catalyst.

INTRODUCTION

Organoselenium compounds are widely used in different application fields such as medicinal chemistry, biochemistry, organic synthesis,

coordination chemistry and materials chemistry. These are used extensively in the fields mentioned earlier due to the chemical reactivity, operational simplicity, remarkable

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structural diversity and easy availability^[1-6]. In addition, these compounds show high pharmaceutical and biological activities including antioxidant^[7], antimicrobial^[8], anticancer^[9], antihypertensive^[10], antiviral^[11], antiaging^[12], antithyroid^[13] and anti-HIV^[14] properties. In the beginning, several synthetically important organoselenium reagents were successfully achieved. Various synthetic transformations have been developed using these reagents, such as selenenylations, selenocyclizations, selenoxide eliminations, and 2,3-sigmatropic rearrangements^[15].

Recently, the chemistry of organoselenium reagents has drawn considerable attention of the researcher towards its advantages over transition metal catalysts and its green synthesis methods^[16-18]. Moreover, the utilization of organoselenium catalysts under benign and neutral conditions with green procedures provide the opportunity to develop a novel green and synthetic method^[13,19,20].

Selenium is a well-known abundant element that is nontoxic in the elemental form, but it is highly toxic in hydrogen selenide. Thus, hydrogen selenide (reagents or evolved) should be avoided in the reactions, or reactions should do with precautions^[21].

Selenium compounds such as diphenyl diselenide, are neseleninic acids, selenium (IV)oxide, selenic (VI) and selenic (IV) acids have low volatility and odourless properties but may be moderately toxic and may cause skin irritation when absorbed. On the other hand, according to known rule, some organoselenium compounds should be of low toxicity, while the toxicity remains unknown for most organoselenium compounds^[21,22].

Chitosan (CS) is an amino polysaccharide having deacetylated unit and an acetylated unit. These units attached into linear chains through β -(1-4) connections (β -(1 \rightarrow 4)-linked D-glucosamine unit attached with N-acetyl-D-glucosamine unit) (Figure-A).

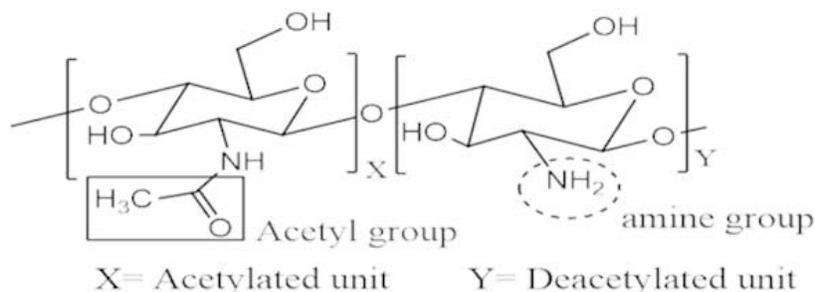


Figure A: Structure of chitosan

CS is the second most abundant natural polysaccharides after cellulose which is nontoxic biodegradable, biocompatible, inexpensive, renewable amino-polysaccharides. CS is a deacetylated form of chitin, marine waste materials mainly obtained from

crustaceans waste and shrimp shells^[23,24]. Both the polymers (chitin and chitosan) have a wide range of applications in water chemistry, food production, drug delivery, fuel cells, biomedical and chemical engineering^[25-27].

Despite that, CS has also been used as metal carriers and drug carriers due to its excellent chelating and mechanical properties, high hydrophilicity, insolubility in organic solvents, large amino and hydroxyl groups, unique three dimensional and flexible structure^[28-32]. Amine and hydroxyl groups present on the surface of CS provide coordination sites to the metals and make it more versatile for chemical modification^[23]. Magnetic materials with chitosan has several advantages: good thermal stability and easy to separate by applying an external magnetic field from the reaction mixture without requiring centrifugation, filtration, or any other tedious workup processes^[33].

It is well known that there are numerous advantages of sulfoxides derivatives as valuable and useful synthetic intermediates in organic chemistry, having a large number of applications in the field of industrial, medicinal and chemical industries^[34]. Herein, chemical oxidation for the transformation of sulfides into sulfoxides used with the help of inexpensive, greener and sustainable heterogeneous catalyst. There are several catalysts available for the transformation of sulfides to sulfoxide such as silica sulphuric acid/sodium nitrate^[35], zirconium tetrachloride^[36], glycol/O₂^[37], H₃BO₃^[38], Fe(sal)Cl/UHP^[31], Ti-complex/MCM-41^[39], DABCO Fe(eta)Cl₂^[40], tribromide^[41], VO₂F(dmpz)₂^[42], etc^[43]. These reported work have some disadvantages: the formation of side product as toxic waste, poor yields, expensive reagents, long reaction time, and tedious workup processes like centrifugation, filtration, etc. So there is a demand for a new catalyst to prevail all these challenges.

Selenium compounds have proven to be valuable reagents and catalysts for organic synthesis

in the past several decades. Several reports on the advantages of selenium compounds such as hydroperoxide/selenium (IV) oxide and hydroperoxide/organoselenium catalyst systems are used as green reagents for oxidation in organic synthesis. For example, Narender et al. have studied SeMCM-41 as a catalyst for the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone with hydrogen peroxide^[44].

Also, epoxidation, ring contraction of cycloalkanones, halomethyl conversion, α -oxyfunctionalization of alkenes, formyl groups from active methylene groups, carboxylic acids from carbonyl groups, sulfoxides from sulfides, nitrones from secondary amines are successfully obtained by using selenium compounds (selenides, diselenides, selenium(IV) oxide, etc.). Also, some reactions of selenium (IV) oxide or organoselenium compounds are used for the active carbon-carbon bond cleavage, bromolactonization, dehydrogenation and aromatization and oxidative amidation^[22].

Mlochowski et al. have investigated that Selenenamides (2-phenyl-1,2-benzisoselenazol-3(2H)-one (ebselen) and its analogues) are efficient and selective oxidation catalysts^[21]. Joshi et al. have reported Fe₃O₄@SiO₂@SePh@Ru(OH)_x nanoparticles for one-pot conversion of nitriles, aldehydes, and benzylamine to primary amides in water without using any organic solvents^[45].

This research paper has reported the synthesis of magnetic Schiff's base Fe₃O₄@CS/Se composite and using it for organic synthesis of sulfoxide from sulfide via an efficient and mild oxidation process. Hence, in our knowledge,

this new magnetic organoselenium Schiff's base ($\text{Fe}_3\text{O}_4@\text{CSSe}$) for the chemical oxidation of sulfide to sulfoxide, may help the enrichment and development of future research on organic synthesis.

EXPERIMENTAL

Materials and methods

4-aminobenzaldehyde, sodium nitrite (NaNO_2), selenium powder, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Ammonium acetate, Chitosan (75-85 % degree of deacetylated), glacial acetic acid (CH_3COOH), Ethanol (EtOH), Sodium sulphate (Na_2SO_4), Hydrochloric acid (HCl), 30% Hydrogenperoxide (H_2O_2) solution and different sulfides were purchased from SRL, Merck and Sigma-Aldrich chemical companies.

Preparation

Preparation of 4,4'-diselenobisbenzaldehyde: A 0.9 g of 4-aminobenzaldehyde was taken in the HCl solution: H_2O (1:7) and this solution is allowed to cool with an ice bath. Subsequently, 8 mL of an aqueous solution of NaNO_2 (0.5 g) was slowly added to the above reaction mixture with continuous stirring and allowed to stir for 40 min. Further, the resulting solution of diazonium salt was added drop by drop to the aqueous solution of Na_2Se_2 (as prepared according to literature procedure^[46]). With continuous stirring for 1 h at r.t. and after 1 h the solution was allowed to warm up to 100°C (scheme-1), next cooled to r.t. and filtered, washed with methanol and dried in vacuum.

Preparation of $\text{Fe}_3\text{O}_4@\text{CS}$: The preparation of magnetic nanoparticles performed according to a literature protocol^[47]. It is performed by using the chemical co-precipitation method. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 100 mL distilled water and this solution, kept under a nitrogen atmosphere, taken in a round bottom flask fitted with a condenser. Then, 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added vigorously, and the compound was collected by centrifugation and filtration. Subsequently, 1g of CS was dissolved in 2% glacial acetic acid (25 mL) and added in a 100 mL flask fitted with a condenser with a mixture of magnetic

nanoparticles and sodium sulphate under continuous stirring for 2 h to obtain the aqueous suspension of $\text{Fe}_3\text{O}_4@\text{CS}$ (scheme-1). Then, the suspension of $\text{Fe}_3\text{O}_4@\text{CS}$ was collected by using an external magnet and washed with EtOH several times and dried under vacuum.

Preparation of $\text{Fe}_3\text{O}_4@\text{CSSe}$: 4, 4'-diselenobisbenzaldehyde (0.5 g) and $\text{Fe}_3\text{O}_4@\text{CS}$ (1 g) were dispersed in ethanol (20 mL), and this mixture was stirred for 30 h at 70°C (scheme-1). Then, the resulting product was filtered, washed with EtOH several times and dried in air.

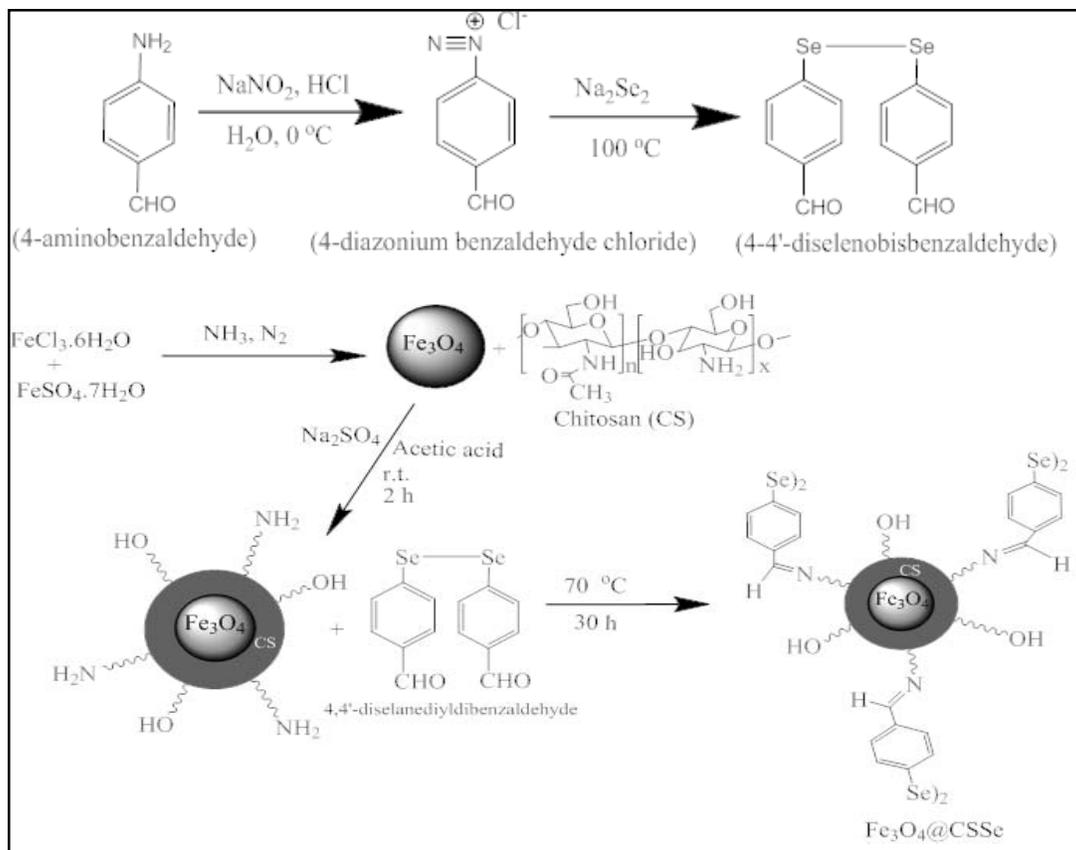
Characterization

Nicolet 170 SXFT-IR spectrophotometer was used for FTIR spectra. IR-spectra was recorded on KBr pellets in the operating range $500\text{--}4000\text{ cm}^{-1}$ with a resolution of 8 cm^{-1} . Rigaku Smart lab diffractometer was used for X-ray diffraction (XRD) analysis operating in the range of $10^\circ\text{--}80^\circ$ and 4°min^{-1} scan rate. Quantum design versa Lab-3 tesla was used for VSM analysis and operating in the range of magnetic field from -20000 Oe to $+20000\text{ Oe}$ at r.t.

RESULTS AND DISCUSSION

FTIR

In FTIR spectra (Fig. 1), the characteristic absorption peak was observed at 538 cm^{-1} , indicating Fe-O bond in Fe_3O_4 ^[26]. Other absorption peaks were observed at around 1020 cm^{-1} , 1390 cm^{-1} , 1560 cm^{-1} , 1635 cm^{-1} , and 3395 cm^{-1} which are related to stretching frequency of the bonds C-O-C, C-O (primary alcohol), C=O (amide group) and O-H, N-H (alcohol and amine groups), respectively, of the CS in $\text{Fe}_3\text{O}_4@\text{CS}$ (Fig. 1b, 1c). However, some new characteristic peaks at around 2928 cm^{-1} , 2860 cm^{-1} , 1397 cm^{-1} , 1660 cm^{-1} were observed in Fig. 1c, attributed to C-H asymmetric and symmetric stretching vibration of CH_2 (methylene) groups, C-N bond and C=N bonds (imine bonds), respectively. Thus, the



Scheme-1: Preparation of $\text{Fe}_3\text{O}_4@CSSe$

appearance of these new characteristic peaks may confirm the formation of the imine bond between 4,42 -diselenobisbenzaldehyde and $\text{Fe}_3\text{O}_4@CS$.

XRD

The XRD patterns of CS, Fe_3O_4 and $\text{Fe}_3\text{O}_4@CSSe$ are shown in Fig 2. The sharp characteristic diffraction peak of CS is around $2\theta = 20^\circ$ indicates the crystalline nature of CS (Fig. 2a) and other six distinct diffraction peaks at about $2\theta = 30^\circ, 36^\circ, 43^\circ, 53^\circ, 57^\circ,$ and 63° corresponding to the (220), (311), (400),

(422), (511), and (440) can be observed for Fe_3O_4 nanoparticles (Fig. 2b). However, these six characteristic diffraction peaks of Fe_3O_4 nanoparticle were also observed with a reduction in the intensity of peaks in the final product, presumably due to the grafting of 4,42 -diselenobisbenzaldehyde on $\text{Fe}_3\text{O}_4@CS$. Despite that, some new characteristic diffraction peaks were observed ranging from $2\theta = 16$ to $2\theta = 28$ (Fig. 3c), which may confirm the presence of chitosan and 4,42 -diselenobisbenzaldehyde.

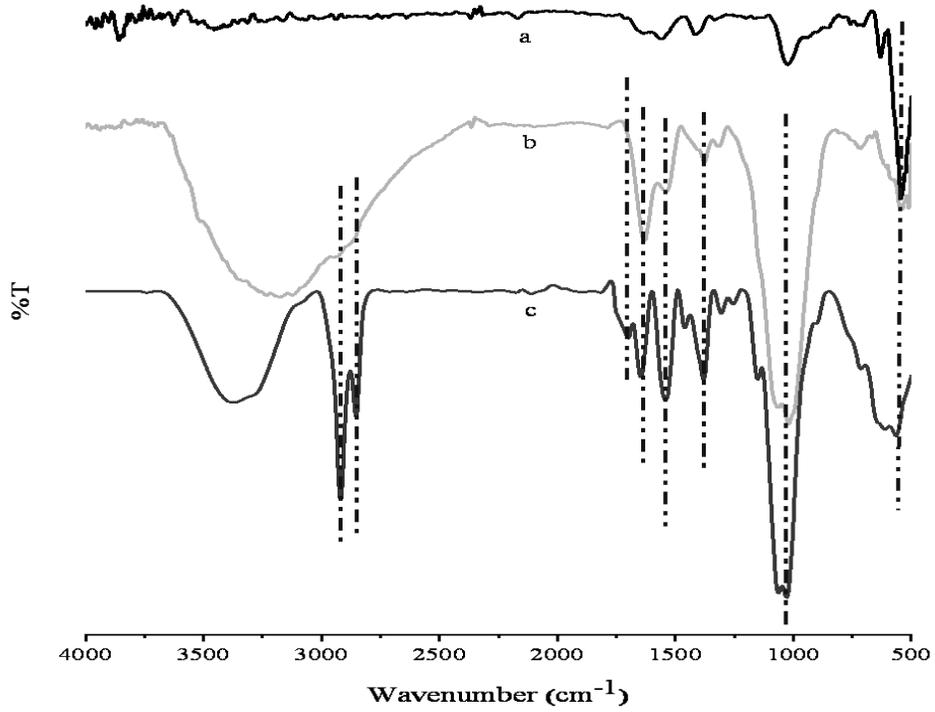


Figure 1: FTIR spectra of (a) Fe₃O₄, (b) Fe₃O₄@CS, (c) Fe₃O₄@CSSe

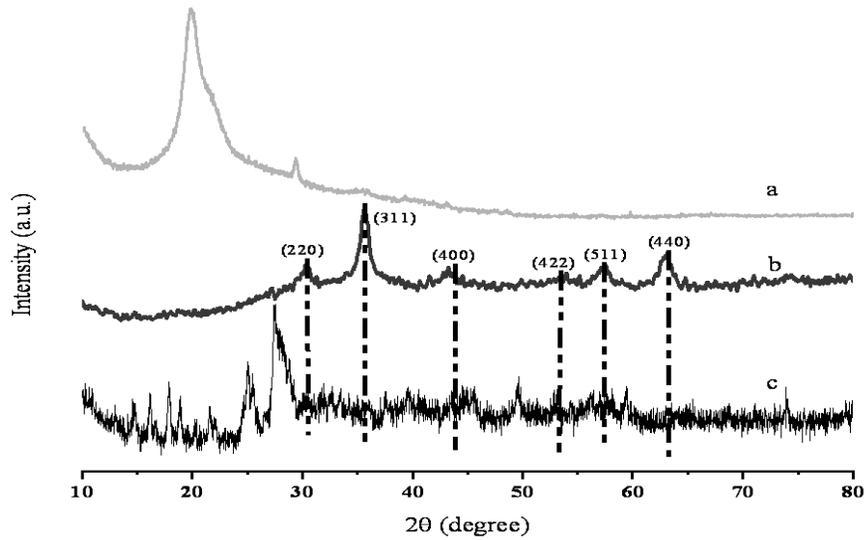


Figure 2: The XRD patterns of (a) CS, (b) Fe₃O₄, (c) Fe₃O₄@CSSe

VSM

The magnetization curves of Fe_3O_4 and Fe_3O_4 @CSSe are shown in Fig. 3, which examined by using VSM analysis in the range of magnetic field from -20000 Oe to +20000 Oe at r.t. The saturation magnetization value (Ms) of Fe_3O_4 and Fe_3O_4 @CSSe was observed at 60.15 emu/g (Fig.3a) and 26.30 emu/g (Fig.3b), respectively. Therefore, decrease in magnetization value for Fe_3O_4 @CSSe may be

attributed to the grafting of 4,4'-diselenobisbenzaldehyde on Fe_3O_4 @CS via the formation of imine bonds. However, it is seen that Ms Value of Fe_3O_4 @CSSe is sufficient for magnetic separation from the reaction mixture by applying external magnetic fields and quickly recovering for further use and recycling.

DLS

DLS technique was used for the determination of particles size distribution. Particle size

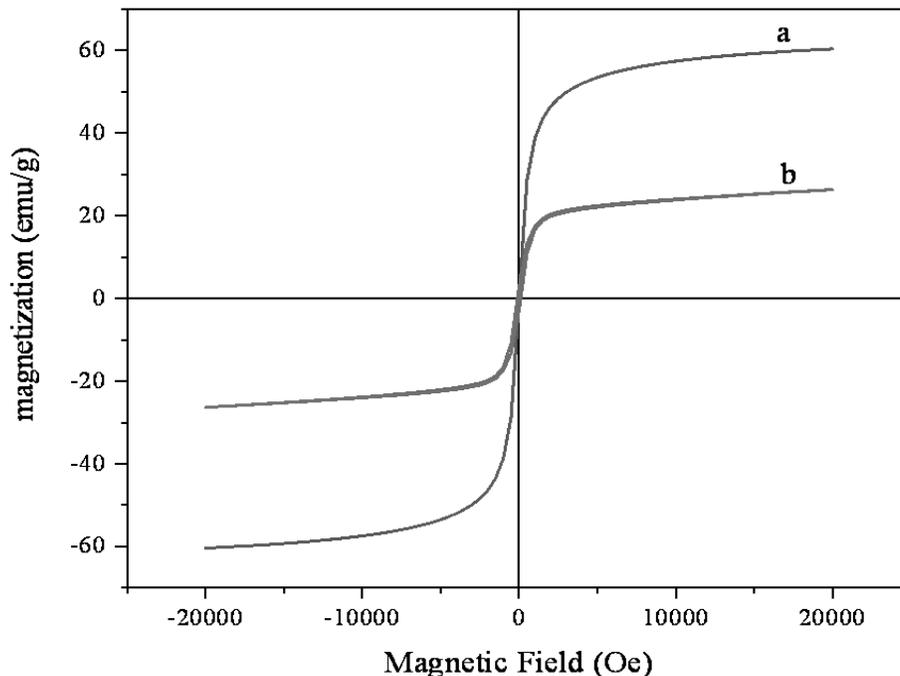


Figure 3: saturation magnetization value (Ms) of (a) Fe_3O_4 and (b) Fe_3O_4 @CSSe

determination was done by using nano Microtrac total solution based on quasi-elastic light scattering. For the determination of particle size, scattered light from the suspension was measured when its intensity

changes randomly. It was found that nanoparticles of Fe_3O_4 @CS and Fe_3O_4 @CSSe are almost uniformly distributed, having a diameter of 700 nm and 1100 nm, respectively (Fig.4a, 4b). Therefore, the particle size of

$\text{Fe}_3\text{O}_4@CS\text{Se}$ is larger than $\text{Fe}_3\text{O}_4@CS$ due to the grafting of diselenobisbenzaldehyde on $\text{Fe}_3\text{O}_4@CS$ via the formation of imine bonds.

Oxidation study of sulfides to sulfoxides by using $\text{Fe}_3\text{O}_4@CS\text{Se}$ as a catalyst

Reaction condition for the oxidation of sulfides

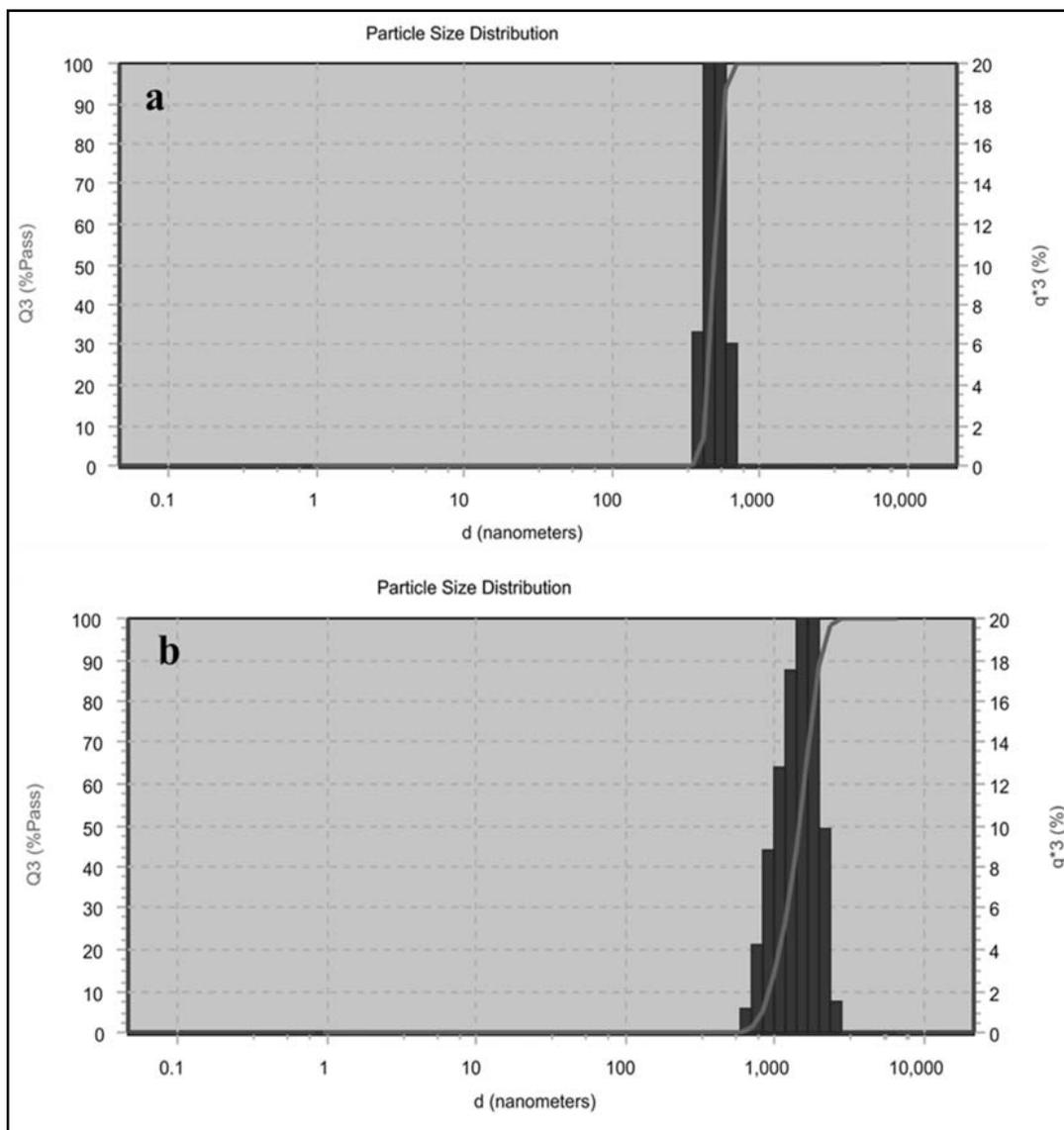


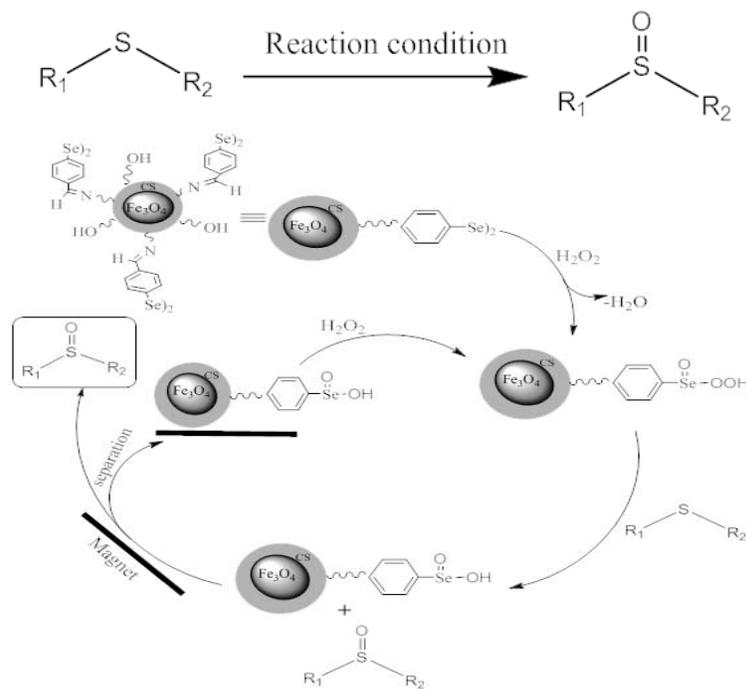
Figure 4: Particle size distribution by DLS histogram of (a) $\text{Fe}_3\text{O}_4@CS$ and (b) $\text{Fe}_3\text{O}_4@CS\text{Se}$

Sulfide (1 mmol), 30% H₂O₂ (0.5 mL) and catalyst (20 mg Fe₃O₄@CSSe) were taken in the 25 mL of round bottom flask under continuous stirring for a specific time at room temperature and thin layer chromatography (n-hexane: EtOAc, 9:1) was used for a monitor of improvement in the reaction. After completing the reaction, the catalyst was separated by applying an external magnetic field (permanent magnet), washed with ethanol, acetone and dried for another run. Hence, extraction of the product was done using Et₂O (15 mL), dried over Na₂SO₄, and finally, we got pure products after the evaporation of organic solvents.

A plausible reaction mechanism for the oxidation of sulfides to sulfoxides shown in

scheme-2^[43]. Initially, peroxoseleninic acid was generated in situ by using H₂O₂ and Fe₃O₄@CSSe and has active oxygen donors. Then, this peroxoseleninic acid has transformed the sulfides into sulfoxides. Chu et al. suggested that oxidation of sulfide into sulfoxides occur by the metal-oxygen shift mechanism. Also, in the present reaction, we believe that metal-oxygen shift mechanism was involved for the oxidation of sulfides and in which nucleophilic attack by sulfide to O-O bond of peroxoseleninic acid leads to the formation of corresponding sulfides, thus helping the regeneration of the catalyst^[48].

To demonstrate the catalytic activity of Fe₃O₄@CS Semagnetic composite in the



Scheme 2. Plausible reaction mechanism for the synthesis of sulfoxides.

presence of H_2O_2 as a green oxidant for the oxidation of sulfide to sulfoxide and different factors were investigated, such as the amount of oxidant, catalyst loading and types of organic solvents for the oxidation of aliphatic/aromatic sulfides to the corresponding sulfoxide. Initially, oxidation of dibutylsulfide as a probe reaction was taken for optimization study. The optimization results of the dibutylsulfide are given in table 1, which were examined under different reaction condition with changes in the amount of oxidant and loading catalyst. During the optimization study, it has also been

observed that the oxidation reaction is not detectable in the absence of oxidant (H_2O_2) and catalyst (Table 1, Entry-7, 8). Hence, the amount of oxidant and catalyst played an essential role in the oxidation of sulfide to the corresponding sulfoxide as we have examined the decrease in the amount of oxidant, a product of sulfoxide was also decreases and variation of loading catalyst affect the yield of the sulfoxide (Table 1, Entry-1, 2, 5, and 6).

Therefore, a solvent-free condition having 20 mg catalyst $\text{Fe}_3\text{O}_4@\text{CSSe}$ and 0.5 mL oxidant

Table 1: Optimization study for the oxidation of dibutyl sulfide (1 mmol) to the corresponding sulfoxide by using $\text{Fe}_3\text{O}_4@\text{CSSe}$ in solvent-free condition.



Entry	H_2O_2 (mL)	Catalyst (mg)	Time(min)	Yield (%)
1	0.5	10	45	85
2	0.5	15	30	88
3	0.5	20	20	94
4	0.5	25	20	94
5	0.4	25	25	86
6	0.3	25	25	65
7	-	25	50	-
8	0.5	-	25	-

H_2O_2 obtained to be the best optimum condition for the oxidation of dibutyl sulfide to the corresponding sulfoxide.

Besides, the reaction with the parameter mentioned earlier (20 mg catalyst and 0.5 ml H_2O_2) was also carried out using different organic solvents condition. It has been observed that less polar solvents such as diethyl

ether, acetone, and ethyl acetate are immiscible with aqueous H_2O_2 (Table 2, Entry 2,3 and 4). Therefore, the interaction between sulfide and H_2O_2 decreases in less polar solvent conditions and hence, these solvents were not effective for the oxidation of sulfide. On the other hand, polar solvents such as ethanol and acetonitrile were miscible with aqueous H_2O_2

and hence, efficient for the oxidation of sulfides into corresponding sulfoxides (Table 2, Entry 1 and 5)^[49]. Thus, the best results obtained in EtOH among other organic solvents (Table 2, Entry 1). Hence, there is a comparison between organic solvents and solvent-free conditions; therefore, the reaction proceeded more

efficiently in solvent-free conditions than with organic solvents condition, possibly attributed to the synergistic interaction between sulfides and catalysts.

Hussain et al. have reported that the hydrophobic alkyl chain length of the sulfur

Table 2: Optimization study for the oxidation of dibutyl sulfide (1 mmol) to the corresponding sulfoxide by using Fe₃O₄@CSSe (cat., 20 mg), H₂O₂ (0.5mL) in various solvents condition

Entry	Solvents	Time (min)	Yield (%)
1	ethanol	35	90
2	Diethyl ether	45	82
3	acetone	80	88
4	ethyl acetate	50	80
5	acetonitrile	40	85

atom may decrease the reaction rate. Furthermore, the hydrophobic alkyl chain orientation around the sulphur atom may inhibit the availability of a lone pair of electrons present on the sulphur atom and reduce its nucleophilicity. In addition, the electron-withdrawing group present on the sulphur atom also reduces its nucleophilicity and hence lower the yield of the product^[42].

It has been noted that the longer alkyl chain present on sulphur atom reduces the rate of reaction due to hydrophobic alkyl chain orientation around the sulphur atom (Table 3, Entry 1, 2 and 3). Also, the electron-withdrawing group present on the benzene ring, which reduces electron density on the sulphur atom, decreases the reaction rate (Table 3, Entry 6 and 7).

Based on the reaction mentioned above, all the aliphatic and aromatic substituted sulfides

were successfully oxidized in good to high yields in a short reaction time into corresponding sulfoxides without any by-products (Table 3). Thus, this catalyst system is very efficient and specific for the oxidation of a wide range of sulfides to sulfoxides. Since the catalyst system is highly magnetic than other previously reported similar selenium-based catalyst systems, it was easily recovered from the reaction mixture by applying an external magnetic field after completing the reaction. The remaining catalyst washed with EtOH and dried in an oven at 80°C for 4 h, which could again use as a catalyst in the subsequent oxidation reaction.

CONCLUSIONS

This study introduced the magnetic schiff's base Fe₃O₄@CSSe composite as a catalyst for the first time to oxidize sulfides into

Table 3: Oxidation of various sulfide to sulfoxide by using Fe₃O₄@CSSe

Sulfide	Sulfoxide	Time (min)	Yield ^a (%)
		15	91
		15	88
		20	94
		20	95
		60	85
		40	95
		35	95
		55	90
		30	92 ^b

^a isolated yield^b Reaction condition: 20 mg catalyst, 0.5 mL oxidant and 4 mL ethanol solvent

corresponding sulfoxides via an efficient and mild reaction condition. Synthesized magnetic Schiff's base as a nontoxic, inexpensive, biocompatible and shows remarkable catalytic activity for oxidation of sulfides to sulfoxides in the presence of a clean and cheap oxidant (H₂O₂) at room temperature. The yields of sulfoxides depend on H₂O₂, catalyst loading and various solvents condition. Besides, more efficiently oxidation reactions have observed in the solvent-free condition rather than solvents condition. Thus, the magnetic Schiff's base catalyst has been applied to the oxidation of a broad range of sulfides, and this may help future research in organic synthesis.

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