Synthesis of Metal Coordinated Fe_xS_y-alginate Composite at Gel-Liquid Interface for Dye Degradation

M.Sc. Thesis

by

Ayushi Singh 2103131006



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Synthesis of Metal Coordinated Fe_xS_y-alginate Composite at Gel-Liquid Interface for Dye Degradation

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of

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by

Ayushi Singh 2103131006



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis of Metal Coordinated Fe_xS_y-alginate Composite at Gel-Liquid Interface for Dye Degradation**, in the partial fulfilment of the requirements for the award of the degree of **MASTER of SCIENCE** and submitted to the **DEPARTMENT of CHEMISTRY**, **Indian Institute of Technology Indore**, is an authentic record of my work carried out during the period July 2022 to May 2023 under the supervision of **Prof. Apurba K. Das**, Department of Chemistry, Indian Institute of Technology Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the Student

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the M.Sc. Thesis Supervisor

Ayushi Singh has successfully given her M. Sc. oral Examination held on 16/05/2023.

of. Apurba/K.

Signature of supervisor of M. Sc. thesis

5.5

Signature of PSPC Member

Dr. Satya S. Bulusu

Date:

rdostrozz Convener, DPGC 26112023

Signature of PSPC Member Dr. Abhinav Raghuvanshi

Date:

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Ayushi Singh M. Sc. 2nd year Roll No. 2103131006

VII

Dedicated to my Family

ABSTRACT

In recent years, exploring an intermediate gel phase formed between solid and liquid mediums to synthesize nanostructures has gained research momentum. With the pH of the precursor as the driving force, a variety of nanostructures can be synthesized in the gel reaction medium. Therefore, in this work, an eco-friendly and economical sodium alginate is employed to form Fe_xS_y at the gel-liquid interface. The effect of pH of the sulphur source (Na₂S) is varied, and the related changes in the nature of the synthesised compound are investigated. FT-IR and UV-Visible spectroscopic techniques have been done to confirm the presence of functional groups and panchromatic visible light absorption for all the Fe_xS_y -sodium alginate compounds. Further, this synthesized catalyst was used in the photocatalytic degradation of organic effluents.

TABLE OF CONTENT

Nome	enclature Page XV
Acro	nyms Page XVI
List o	f figuresPage XVIII
List o	f tablesPage XIX
Chap	oter 1Page 1-8
1.1 Int	roduction
1.2 Re	eaction scheme
Char	oter 2Page 9-13
2.1	Experimental section
2.1.1	Materials and reagents
2.1.2	Preparation of Fe-SA gel
2.1.3	Synthesis of FeS-SA
2.1.4	Preparation of MB dye solution
2.2	Photocatalytic degradation of MB

Chapter 3	Page 14-23

3.	Instrumentation
3.2	Characterization
3.2.1	Fourier transform infrared spectroscopy
3.2.2	UV-Vis Spectroscopy

3.2.3 Thermogravimetric analysis

3.2.4 BET and BJH plot

Chapter 4.....Page 24-36

- 4.1 Results and Discussion
- **4.1.1** Photocatalytic degradation of MB dye
- **4.1.2** A plausible photocatalytic mechanism
- 4.1.3 Conclusion
- **4.1.4** Future scope
- 4.1.5 References

NOMENCLATURE

°C	Degree Celsius
сс	Centimeter cube
g	Grams
h	Hours
М	Molar
mL	Milliliter
mg	Milligrams
min	Minutes
m	meter
nm	Nanometer
μL	Microlitre
wt%	w/v

ACRONYMS

AgNO ₃	Silver nitrate
AOP	Advanced oxidation process
BJH	Berrett Joyner Halenda
BET	Bruaner Emmett Teller
BQ	Benzoquinone
CR	Congo red
CVD	Chemical vapour deposition
CdS	Cadmium sulphide
CuS	Copper sulphide
DI	Deionised water
DRS	Diffused Reflectance Spectroscopy
e	Electron
EDTA	Ethylene diamine tetraacetate
EtOH	Ethanol
FTIR	Fourier Transform Infrared Spectroscopy
FeS	Iron sulphide
Fe ₂ O ₃	Iron oxide
FeCl ₃	Iron Chloride
h^+	Hole
HCl	Hydrochloric acid
H ₂ O	Water
H_2O_2	Hydrogen peroxide
HER	Hydrogen Evolution Reaction
MB	Methylene Blue
Na ₂ S	Sodium sulphide
NaH ₂ PO ₄	Sodium phosphate monobasic
Na ₂ HPO ₄	Sodium phosphate dibasic
OER	Oxygen Evolution Reaction
PVD	Physical vapour deposition

RhB	Rhodamine B
SA	Sodium alginate
TiO ₂	Titanium oxide
TGA	Thermogravimetric analysis
UV	Ultraviolet
XRD	X-ray diffraction spectroscopy
ZnS	Zinc sulphide

LIST OF FIGURES

- **Figure 1.** The schematics of FeS-SA formation with the help of Na₂S precursor
- **Figure 2.** The development of Fe-alginate gel by altering the buffer solution's pH range from 7.4 to 13
- Figure 3. The formation of Fe-SA gel by varying the concentration of sodium alginate from 1% w/v to 5% w/v as well as the proportion of 0.1 M FeCl₃ solution
- Figure 4. Formation of FeS composite at the gel-liquid interface
- **Figure 5.** Photographs illustrating the formation of the Fe^{y+} -Alginate compound and checked with the inversion tube method
- Figure 6. Rheological experiments for amplitude and frequency sweep
- **Figure 7.** Time-dependent photographs illustrate the formation of the Fe_xS_y coordinated Sodium Alginate (Fe_xS_y-SA) compound after adding Na₂S precursor solution
- Figure 8. FTIR, DRS and Kubelka-Munk plot for all FeS-SA composites
- Figure 9. UV-Vis absorption spectra and thermal stability curve
- Figure 10. The nitrogen adsorption-desorption curve of all three composites, Fe_xS_y-SA#pH7.4, Fe_xS_y-SA#pH10 and Fe_xS_y-SA#pH13, respectively.
- Figure 11. The pore diameter distribution curve of all FeS-SA composites
- **Figure 12.** Photographs illustrating the decolourization of aqueous methylene blue dye solution
- Figure 13. Absorption spectra of all three photocatalysts with MB dye in different conditions
- Figure 14. Ct/C_0 curve of FeS-SA photocatalyst at various pH
- Figure 15. Recyclability and Scavenger test
- Figure 16. A plausible mechanism for the degradation of methylene blue

LIST OF TABLES

- **Table 1.** Optimization of used buffer solution; pH varying fromacidic to the basic medium
- **Table 2.** Optimisation for the concentration of sodium alginate aswell as a proportion for FeCl3:SA solution
- Table 3.
 Tabulation of surface area, pore diameter and pore volume

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Chapter 1

1.1 Introduction

Visible light-catalysed photocatalytic reactions are a type of chemical reaction that uses light energy to drive chemical reactions.¹ Since these reactions are more effective, affordable, and ecologically benign, they are becoming increasingly popular. In the era of rapid industrialisation, lots of organic-inorganic effluents are released that harm the ecosystem and living beings, and it is important to control them.² Visible lightcatalysed reactions play a significant part in this because they effectively combat organic and inorganic contaminants that might harm the environment.³⁻⁶ These chemical reactions are driven by photocatalysis, which includes light energy to perform reactions. Photocatalysis is a common process in which environmentally hazardous organic and inorganic contaminants are broken down into harmless species. TiO2 is the most commonly used photocatalyst in photocatalysed reactions; however, it is generally activated in the presence of ultraviolet light, which restricts its efficiency because it encompasses only a small portion of the solar spectrum.⁷⁻⁹ To address this issue, researchers turned to visible light-catalysed processes. These reactions provide a greater variety of reactions and higher efficiency by activating the photocatalyst with visible light. Numerous processes, such as wastewater treatment, air purification, energy conversion, and photocatalysed organic transformation reactions, can be accelerated by visible light.¹⁰⁻¹²Organic and inorganic effluents, pesticides, etc. that are harmful to the environment can be broken down with the help of visible-light-driven photocatalysed reactions. One of the main advantages of visible lightcatalysed photocatalytic reactions is that they are more efficient than traditional catalytic reactions.¹³ These chemical reactions use light energy to drive the reactions that are more competent than traditional thermal and electro-catalysed reactions. They are more effective than conventional thermal, electro, and biocatalysis because they use light energy to drive the reaction. Furthermore, visible light-catalysed photocatalytic processes produce no byproducts and exclusively degrade certain molecules, making them more selective and effective. Thus, it can be concluded that visible light-catalysed photocatalytic reactions are more efficient, selective, and environmentally friendly than traditional catalytic reactions and may use in various applications.¹⁴⁻¹⁶ As it is well known, organic contaminants have a huge negative impact on our ecology and water quality. The consumption of water has formed a large part of the ecosystem. Apart from this, Water is essential for the existence and survival of all human beings and the ecosystem. However, it must be kept pure as tained water would lead to achieving environmental and health consequences.^{17, 18} Nowadays, it is a great task to provide purified water even though millions of people all over the world are facing the problem of clean water. Groundwater and surface water are getting polluted day by day due to the development of factories, increasing population, unplanned urbanisation, the custom of chemical fertilisers, pesticides, environmental pollution, and many more harmful chemicals that are used in different textile and paint industries. The principal sources of pollution are the discharge of untreated sanitary and toxic industrial wastes, the dumping of industrial effluents, and agricultural runoff.^{19, 20} A large part of organic toxins is being produced all over the world, mainly due to various industries such as textile, painting, petroleum, printing, paints, and pharmaceuticals industry. Most organic pollutants have stable chemical structures, so they cannot be broken down quickly, or they cannot be fully degraded. Organic contaminants can dissolve or become suspended in the water column when they enter water bodies. Due to their non-biodegradability, high toxicity, and carcinogenic effects on humans and aquatic life, these wastages harm the living system. The physical and chemical properties of water, such as pH, dissolved oxygen levels, and nutrient availability, can also be affected by organic pollutants existing in the water. There is so much water consumption in the textile and printing industry, and these industries yield wastewater that, on a large scale, pollutes mainly through organic dyes. Furthermore, organic dye pollution can create serious health problems in humans by interfering with the operation of the central nervous system, the liver, and the brain.

Because of their non-biodegradability and prolonged toxicity, they endanger the health of animals.^{21, 22} The degradation, decomposition, or conversion of organic dyes is very hard. Dye wastage has an extensively undesirable effect on the environment, and most are highly toxic and non-biodegradable. Dyes are those coloured substances that, when applied on a substrate, form a chemical bond with it. Generally, dyes are of two types: first is natural, and second is synthetic dye. Natural dyes are generally derived from natural non-animal sources such as leaves, berries, roots, fungi, plants, minerals, etc., while synthetic dyes are artificial. The twenty-first century is the era of synthetic dyes produced from various petrochemical methods and extracted from insects and minerals. Most synthetic dyes are obtained from this method because of their premium cost, good optical properties, and liability. Synthetic dyes are broadly used in several industries, such as textile manufacturing, food processing, printing, and cosmetics. Though these dyes are nonbiodegradable, their existence in the environment is the origin of serious health and environmental issues.²³ Dyes are the class of organic compounds that have colour mainly due to the presence of two components: (a). Chromophores impart colour to an organic compound by absorbing light from visible regions, e.g., nitro, azo, quinoid, etc. and (b). Auxochromes are substances attached to chromophores to deepen the compound's colour. Some dyes are very dark in colour, and some are light; this is because of the ability of dyes to absorb light from the visible region and also depend upon the excitation of π -electrons in the visible region.²⁴ Synthetic dyes are further classified based on chromophore groups such as azo dyes, anthraquinone, indigoid, phthalocyanine, xanthene, sulphur, azin dyes and triphenylmethane derivatives dyes. Synthetic dyes are further divided into Anionic dyes and Cationic dyes. Anionic dyes are those that dissociate into anions in an aqueous medium. Azo dyes, anthraquinone dyes, heterocyclic dyes, etc., are cationic dyes, e.g., rhodamine B, methylene blue, crystal violet, etc. Cationic dyes can be dissociated into positively charged ions in an aqueous medium. These dyes, particularly cationic and anionic dyes, are carcinogenic and mutagenic, and they can

cause eye irritation, skin irritation, and cyanosis. Furthermore, cationic dyes such as methylene blue (MB) and anionic dyes such as congo red (CR) are the most commonly utilised dyes in industries.²⁵ The textile and printing industry releases organic pollutants on a large scale, mainly different dyes such as methyl orange, rhodamine B, methylene blue, etc., as a form of polluted water that may cause severe non-aesthetic pollution, eutrophication and hazardous for humans as well as aquatic creatures.^{26, 27} Thus, it is very prime to resist the release of these pollutants into the environment. Several methods for degrading synthetic colours include chemical, physical, and biological processes. Various oxidising agents, such as ozone, hypochlorite, hydrogen peroxide, and others, are employed in the chemical technique to break down these colours into smaller, less hazardous components that can be easily removed from the environment. Physical processes like adsorption, reverse osmosis, precipitate, coalescence, and filtering can also degrade these colours. These non-destructive mechanisms merely transmit pollution from one phase to the next. Methylene blue attracts special attention because of its toxins and carcinogenic harmfulness. It is a derivative of phenothiazine and a type of cationic dye that majorly originates in wastewater. It is deep blue, and comments have been made about its existence in wastewater from dyeing, leather, textile, and other industries. Due to high stability, its anti-biodegradability methylene blue degradation is very hard using traditional degrading methods. Taking all these into account, advanced oxidation processes (AOPs) are used as a replacement that can be eco-friendlier and more sustainable as they do not comprise the usage of such harsh reaction conditions. For this instance, photodegradation breaks down the dye molecules into harmless species in exposure to sunlight or ultraviolet (UV) light. In photodegradation, there is a need for a photocatalyst, a catalyst that works in the presence of photons or light. Moreover, it can say that photocatalysts can accelerate the reaction rate by converting light energy, i.e., absorbing from the visible region, into chemical energy. Semiconductor materials generally act as photocatalysts to absorb visible light energy and generate electron-hole pairs. These electron-

hole pairs take part in various chemical reactions and produce a variety of reactive intermediates, including hydroxyl radicals, superoxide radicals, and hydrogen peroxide, among others. The most popular photocatalysts with low bandgap energies include ZnS, Fe₂O₃, CdS, TiO₂, etc., which increase their photocatalytic activity and control their absorption range.²⁸ Various factors can affect photocatalytic activity, involving surface area, crystalline structure, surface chemistry etc. A photocatalyst's activity can be impacted by surface chemistry by changing how reactants and intermediates bind to it. Consequently, photocatalysts may catalyse reactions without extreme circumstances and have several uses in various applications, including water purification, the hydrogen and oxygen revolution, photodegradation, and organic photocatalytic conversion.²⁹⁻³¹ Several previously synthesised photocatalysts require specific conditions and hightemperature procedures, such as solvothermal, hydrothermal, pyrolysis, combustion, co-precipitation, chemical and physical vapour deposition (CVD/PVD), electro-deposition, and so on.^{32, 33} Hence there is a need for a photocatalyst which can be synthesised easily at room temperature, harmless in nature, chemically inert, and reusable without harsh conditions and can efficiently work in mild reaction conditions. So many previously reported photocatalysts of iron sulphide (FeS), such as nanospheres and nanoparticles of FeS, porous sulphide films etc., have numerous applications established in water remediation, OER, HER, photocatalytic organic conversion, and dye degradation. Esmaili et al. developed Fe/FeS nanostructured powder for the photodegradation of toxic organic methylene blue dye. Vala et al. synthesised photocatalytic iron sulphide colloidal dispersion via pulsed laser ablation in liquids used in the photo deterioration of methylene blue. Yong et al. and Peng et al. developed different metal sulphide photocatalysts that can be used in selective oxidation coupling of amines to imines. Iron sulphide is appealing for solar cell applications because it has magnetic semiconducting, magnetic, and photocatalytic properties and is abundant, inexpensive, and non-toxic.³⁴⁻³⁶ Furthermore, research into bio-based polymers with varied functional uses has gained attention. In

this study, for the formation of FeS, a hydrogel is used named sodium alginate. Hydrogels are water-containing gels made from 3D networks of polymers made of repeating units physically twisted and crosslinked by chemical bonds.³⁷ This study focuses on a hydrogel that selfassembles when added to any metal salt solution in a specific ratio. With the help of a self-organising precipitation procedure, there is an establishment of nano and micro-structures in which chemical gardening occurs. This process helps enlarge new methodologies to recognise the non-equilibrium system and progress the different prospective approaches to enhance the future material design, which can contribute to various applications. Chemical grounds were previously hatched from a technique in which a salt seed was immersed in a counterion solution. Good chemical and physical properties are found when the chemical gardens are evolved at the gel-liquid interface.^{38, 39} Many biopolymers exist, such as gelatine, carrageenan, agar, alginate etc. Alginates are the anionic polymer that naturally exists and can be obtained from brown seaweed and have been extensively investigated due to their exclusive possessions such as high-water content, smoothness, flexibility, biocompatibility, low toxicity, relatively low cost, and mild gelation by the addition of bivalent cations such as Cu⁺², Cd⁺² etc.[23] Sodium alginate (SA) is a natural hydrophilic polysaccharide that can be isolated from marine brown algae. Alginates are obtained from alginic acid when a proton is lost, and any alkali balances its negative charge. Alginic acid is a gelling anionic polysaccharide made up of two uronic acids that are β -D-mannuronic acid (M) and C-5 epimer α -L-guluronic acid (G), having 1,4 linkage that represents the constituent of linear biopolymer alginate, which are separated into homopolymer blocks (G- and Mblocks) and heteropolymer blocks (MG- blocks). All the constituents along the above lines are responsible for the stability of sodium alginate biopolymer. Sodium alginate biopolymer was utilised in this investigation because it has good ionic conductivity and biocompatibility in mechanical, electrochemical, and thermal stability. All alginates are soluble in hot water at temperatures above their melting points to yield viscoelastic gel. These hydrogels maintain their shapes when tipped out from containers and retain the vapour pressure and ionic conductivity of the liquid from which they are made. Adding bivalent cations into sodium alginate solution develops a stable physical hydrogel.⁴⁰⁻⁴² As a result, many researchers have incorporated sodium alginate into a system to stabilise the gel and liquid phases through unique interaction and grow chemicals between liquid and gel media. In the previous reports, the Cu⁺²-complexed carrageenan hydrogels convert into CuS-carrageenan nanocomposite using the novel precipitation process at the gel-liquid interface. CuS, as nanoscale particles, particularly covellite-phase CuS nanocrystals, exhibit outstanding structural performance, such as excellent photoelectric properties compared with individual molecules or bulk forms.⁴³

1.2 Reaction Scheme

In the present work, the formation of the FeS-SA photocatalyst is explored at different pH. When Fe^{y+} is coordinated, the hydrogel is allowed to react with the sodium sulphide solution. It acts as a precursor, which initiates the gradual diffusion at the interface of the gel and further enters inside the gel to yield an SA-coordinated FeS photocatalyst. Firstly Fe^{y+} ions, present in an aqueous solution of FeCl₃, were introduced into an aqueous solution of SA and designed a complex gel. After that, sodium sulphide (Na₂S) precursor was added with difficult gel that formed FeS-SA photocatalyst with the help of displacement reaction. Further, the expansion of FeS-SA was studied by varying the pH of the Na₂S precursor solution, i.e., 7.4, 10 and 13. All three corresponding FeS-SA photocatalyst was obtained at the gel-liquid interface, namely as FeS-SA#pH7.4, FeS-SA#pH10, and FeS-SA#pH13 synthesised with the help of Na₂S precursor solution having pH 7.4, 10, and 13, respectively. Figure 1. represents the schematics for designing the FeS-SA photocatalyst, which was further used to decolourise methylene blue dye.



Figure 1 Represents the schematic diagram of FeS-SA formation in which Fe^{y+} ions interact with sodium alginate biopolymer; further addition of Na₂S precursor helps in a composite generation.

CHAPTER 2

2.1 Experimental Section

2.1.1 Materials and Reagents

Sodium alginate (SA) HV extra pure, 1000 cps, 100 mesh, sodium sulphide (Na₂S) flakes extra pure 60%, sodium phosphate monobasic anhydrous (NaH₂PO₄), sodium phosphate dibasic anhydrous (Na₂HPO₄), sodium hydroxide was procured from SRL chemicals. Glycine and methylene blue (MB) dye molecules were purchased from Sigma Aldrich. Hydrochloric acid (HCl, 36%) and ethanol (EtOH, 99.5%) were obtained from Merck. Milli-Q water was assembled from Milli-Q integral, a Millipore Water purifier system. Iron chloride (FeCl₃), hydrogen peroxide (H₂O₂), benzoquinone (BQ), silver nitrate (AgNO₃), ethylenediamine (EDTA), and tertiary butanol were purchased from Merck. All the used chemical reagents are in the purest form.

2.1.2 Preparation of Fe-SA hydrogel

The Fe-alginate gel was prepared by mixing two solutions of (A) a 5% w/v sodium alginate hydrogel and (B) 0.1 M ferric chloride solution.

Solution (A): Hydrogel formation was optimised under four different pH conditions range, varying from acidic medium to basic medium, i.e., (pH#2 to pH#13). 0.1 M buffer solution of glycine-HCl prepared for pH#2, 0.1 M pH#7.4 with the help of phosphate buffer (NaH₂PO₄+Na₂HPO₄), and 0.1 M pH#10 was obtained from a buffer solution of glycine-NaOH, and 0.1 M pH#13 was formed by dissolving NaOH pellets in DI water. It had been observed that pH#7.4 gives good gel. The sodium alginate solution (5% w/v) was prepared by taking 5g sodium alginate powder in 100 mL of milli-Q water followed by continuous stirring at 60 °C using a heating plate until the mixture was well united. All optimisations have been made shown in Figure 2 by varying the sodium alginate concentration. Now, the hydrogel was left to cool down to room temperature.



Figure 2 The figure showing Fe-SA gels by varying the concentration of sodium alginate from 1% w/v to 5% w/v as well as the proportion of 0.1 M FeCl₃ solution, which indicates that FeCl₃:SA::2:8 gives the good gel

Solution (B): 0.1 M Ferric chloride stock solution was prepared by dissolving 243mg of anhydrous FeCl₃ in 15 mL of distilled water, and the mixture was sonicated to achieve complete dissolution. To create a gel with excellent mechanical strength and stability, after optimising the SA gel of multiple pH buffer solutions with varied ferric chloride salt solution ratios, a 2:8 FeCl₃:SA ratio was chosen. For making gel, a 5 mL vial was taken in which 400 μ L of freshly prepared FeCl₃ stock solution was added to 1600 μ L of SA solution, making the overall volume 2 mL, followed by sonication for 30 minutes. The gel mixing was done till the formation of a homogeneous brownish-yellow mixture. Further, an overnight undisturbed vial resulted in the shape of Fe-alginate gel. Figure 3 represents the optimisation conditions.



Figure 3 Representation of the development of Fe-SA gels by altering the pH of the buffer solution ranging from 2 to 13, indicating that 0.1 M phosphate buffer resulted in having higher mechanical strength

2.1.3 Synthesis of FeS-SA photocatalyst of different pH

0.1 M sodium sulphide stock solution of three different pH (7.4, 10, and 13) was prepared by dissolving 117mg of sodium sulphide flakes in 15 mL of relevant buffer solutions. To study the concept of the gel-liquid interface, 2000 µL of Na₂S stock solution was poured into each of three different vials containing Fe-alginate gel of ratio (Solution A: Solution B:: 8:2) as displayed in Figure 4. These three vials were labelled as FeS-SA#pH7.4, FeS-SA#pH pH10, and FeS-SA#pH pH13 with buffers 7.4, 10, and 13, respectively. After adding Na₂S solution, composite growth occurred at the gel-liquid interface within 10 to 15 minutes. These vials were kept undisturbed for the proper development of FeS-SA. The development of FeS-SA was achieved in approximately 24 h. Then the remaining liquid was drained out and discarded without disturbing the assembly. The growth composites were washed with 8:2::ethanol:water thrice, followed by washing with absolute 99.9% ethanol. Then the samples were centrifuged and dried in a vacuum chamber, followed by lyophilisation.



Figure 4 Pictorial representation of the formation of FeS-SA composites at the gel-liquid interface after the addition of Na₂S precursor at pH 7.4, 10, and 13, respectively

2.1.4 Preparation of Methylene Blue dye solution

Methylene Blue is one of the toxic, mutagenic, and carcinogenic cationic dyes majorly produced from organic wastage. It is a heterocyclic aromatic organic compound, a derivative of phenothiazine, having a molecular formula $C_{16}H_{18}N_3SC1$ named 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride. A 10ppm stock solution of methylene blue was prepared by dissolving 10 mg of MB dye in 1000 mL pH 7.4 distilled water.



Methylene Blue

2.1.5 Photocatalytic Degradation of MB dye

The degradation of methylene blue was carried out in the presence of a FeS-SA photocatalyst under the illumination of visible light. Methylene blue was degraded with all three prepared catalysts: FeS-SA #pH7.4, FeS-SA#pH10, and FeS-SA#pH13. For the experiment, in 3.5 mL of the quartz tube, 2.5 mg of the FeS-SA#pH10 photocatalyst was taken with 3 mL of 10 ppm MB dye solution. This quartz tube was placed in a dark box for half an hour for adsorption-desorption. The mixture was magnetically stirred for 30 min in the dark; after that, 10μ L of H₂O₂ was added. Further, this mixture was placed in the visible lamp for 140 min until the dye was completely degraded. Using a Jasco UV-vis spectrophotometer, the absorbance of the reaction mixture at about 669 nm was measured over the course of 140 minutes at 20-minute intervals to examine the photocatalytic degradation of MB. Similarly, the experiment was performed by varying the photocatalyst Fes-SA#pH 7.4 and FeS-SA#pH 13.

CHAPTER 3

3.1 Instrumentation

Various characterisation techniques, namely, Fourier Transform Infrared Spectroscopy (FTIR, Bruker ALPHA II) for analysing the molecular stretching of different functional groups, UV-Visible spectroscopy to study the absorbance range using JASCO V 750 spectrophotometer, Thermogravimetric analysis (TGA, METTLER, TOLEDO Thermal Analyzer) to understand the thermal stability of compounds, X-ray diffraction (XRD) to comprehend the crystallinity, Field Emission Scanning Electron Microscopy (FE-SEM) and High-Resolution Transmission Electron Microscopy (HR-TEM) to investigate the morphological study of grown composites, X-ray photoelectron spectroscopy (XPS) to confirm the oxidation states and Rheology (Anton Paar Physica MCR 301 rheometry) described the mechanical strength of the gel was used.

The gel formation was studied with different concentrations of 5% w/v of sodium alginate hydrogel to understand the formation of metalcoordinated Fe-alginate compound at the gel liquid interface. The sodium alginate and iron chloride salt solution ratios were adjusted. The buffer's pH was changed from an acidic to a primary medium to produce gels with good mechanical strength. Table 1 represents the gel formation with 5% w/v of SA. The optimisation from Table 2 indicates that 5% w/v SA produced excellent gel with a 2:8 ratio of hydrogel and metal salt solution. The optimised concentration, i.e., 5 wt% SA with a 2:8 balance of FeCl₃:SA, was checked with the inversion tube method, as shown in Figure 5. The gel possessed good strength, and the inversion tube method confirmed the formation of Fe-alginate gel.

Sr. no.	Sodium alginate(μl)	FeCl₃ (μl)	Ratio	Gel formation
1	900	100	1:9	No
2	800	200	2:8	Yes
3	700	300	3:7	No
4	600	400	4:6	No
5	500	500	5:5	No
6	400	600	4:6	No
7	300	700	3:7	No
8	200	800	2:8	No
9	100	900	1:9	No

Table 1: Optimisation table for the gel formation by varying theproportion of FeCl3:SA.

5 % w/v SA	Ratio	Condition	
1 %	8:2	Not Formed	
2 %	8:2	Not Formed	
3 %	8:2	Not Formed	
4 %	8:2	Formed	
5 %	8:2	Formed (with good strength)	

Table 1: Optimisation table for the Fe-SA gel formation by varying the concentration of Sodium alginate.



Figure 5 Photographs illustrating the formation of the Fe^{y+} -alginate compound and checked with the inversion tube method.

The mechanical strength of the gel was studied by rheological experiments shown in Figure 6. Given that rheology pertains to the study of material deformation, a series of amplitude and frequency sweep experiments were conducted. The angular sweep strain exhibited a linear increase concerning constant frequency, where G' was more significant than G'' up to a maximum pressure of 17%. A frequency sweep experiment was conducted under a steady 0.5% strain, revealing that the storage modulus of the gel was measured at 3312 Pa. It is observed that G' is consistently greater than G'' across all frequencies. Finally, the

hydrogel with concentration 2:8::FeCl₃:SA made with pH 7.4 buffer was chosen further for forming FeS composites.



Figure 6 (a) Amplitude sweep and (b) Frequency sweep rheological studies for Fe-alginate gel chosen from the optimisation mentioned above, which demonstrates that FeCl₃:SA::2:8 provides the best outcome.

Further, to study the concept of a gel-liquid interface, 0.1 M Na₂S stock solution of three different pH (7.4,10 and 13) was prepared, and 2000µL of this stock solution was poured into each of the three separate vials containing Fe-alginate gel. Following the addition of Na₂S solution to the gel, a greenish-black compound was formed at the gel-liquid interface. The formation of the FeS composite is due to the presence of Fe^{y+} and S^{2-} ions sufficiently present in the gel phase and Na₂S precursor, respectively. After 30 min, there is a distinguishable change in the hydrogel. With time the compound grew downward towards the gel phase, owing to the availability of Fe^{y+} ions in the hydrogel. The complete growth of the FeS-coordinated SA composites at the gel-liquid interface was achieved in 24h, after which the remaining Na₂S solution from all three vials was drained out into a beaker, and the gel was obtained. The obtained FeS-SA gel was washed with ethanol and dried for further use. Figure 7 illustrates the typical synthesis technique and mechanism of forming FeS-SA composites with three different pH values, i.e., FeS-SA#pH7.4, FeS-SA#pH10, and FeS-SA#pH13.



Figure 7 Time-dependent photographs illustrate the formation of the Fe_xS_y coordinated Sodium Alginate (Fe_xS_y -SA) compound after adding Na₂S precursor solution.

3.2. Characterization

Before considering applications, it is crucial to understand some essential properties of the photocatalysts that have been synthesised, such as surface area, band gaps, UV activity, and temperature stability.

3.2.1 Fourier Transform Infrared Spectroscopy

In order to confirm the interaction between sodium alginate biopolymer and iron metal ion, the infrared spectra of FeS-SA were recorded on the FTIR spectrophotometer in the range of 400-4000 cm⁻¹, and it displays numerous stretching vibrations in an assortment of 1600 to 500 cm⁻¹ as shown in Figure 8a, represents the FTIR spectra of powdered samples of bare sodium alginate (SA), sodium sulphide (Na₂S), and FeS-SA composites, i.e. FeS-SA#pH7.4, FeS-SA#pH10, and FeS-SA#pH13. The spectra show a broad stretching at 3252 cm⁻¹ signifying the vibration of O-H groups. The two peaks arise at 1594 and 1405 cm⁻¹ due to the asymmetric and symmetric stretching modes of carboxylate groups (-COO⁻), respectively, present in the SA biopolymer. The band at 1027 cm⁻¹ displays the stretching of the C-O band. Accordingly, the distinctive extension around 669 cm⁻¹ is associated with the extension of FeS bonds because, in the spectra of bare SA, no band is present in the fingerprint region. The rise of this new peak confirms the formation of FeS composites. Since the -COO⁻ stretching modes often exhibit several bands because of coupling, it may be assumed that the interaction

between the FeS and the biopolymer caused these new peaks' appearance.⁴⁴⁻⁴⁷

3.2.2 UV-VIS Spectroscopy

The grown FeS-SA composites were greenish-black in colour and had no absorption peak in the visible region present. Diffused reflectance spectroscopy (DRS) illustrates the optical properties of photocatalysts prepared at various pH ranges. The diffused reflectance spectra display the total reflectance in the visible range for all FeS-SA composites. Though all FeS-SA panchromatic absorption is in the visible range, the relative absorbance of the composites varied independently depending on the precursor pH. However, the FeS-SA#pH13 composite shows lower absorption than other counterparts, as shown in Figure 8b. Further, the Kubelka-Munk function was used to estimate the bandgap of FeS-SA composites, as shown in Figure 8c. With increasing the pH of the Na₂S precursor, the bandgap also increased. The bandgaps of FeS-SA#pH7.4, FeS-SA#pH10, and FeS-SA#pH13 were estimated to be 1.7 eV, 1.6 eV, and 1.9 eV, respectively. FeS-SA#pH10 has the lowest bandgap, i.e., 1.6 eV and shows the highest activity.^{46, 48, 49}



Figure 8 (a) FT-IR spectra of the three grown compounds FeS-SA#pH7.4, FeS-SA#pH10, and FeS-SA#pH13 at the gel-liquid interface. (b) Diffused reflectance spectra and (c) corresponding Kubelka-Munk plot estimating the bandgap of the three grown composites Fe_xS_y -SA#pH7.4, Fe_xS_y -SA#pH10 and Fe_xS_y -SA#pH13 at the gel-liquid interface.

3.2.3. Thermogravimetric analysis

Additionally, TGA was carried out under the nitrogen atmosphere to study the thermal stability of all three FeS photocatalysts. Figure 9a describes the stability curves for the photocatalysts FeS-SA#pH 7.4, FeS-SA#pH 10 and FeS-SA#pH 13, respectively. Further, there is a decrease in the curve, as displayed in the figure, up to 498 °C, 580 °C, and 508 °C. Therefore, it can be concluded that the synthesised FeS-SA composites have excellent thermal stability below 200 °C. Though all FeS-SA composites have high thermal stability, further BET theory was used to examine the nitrogen adsorption-desorption. ⁵⁰



Figure 9 (a) UV-Vis absorption spectra and (b) thermogravimetric analysis of all three composite composites Fe_xS_y -SA#pH7.4, Fe_xS_y -SA#pH10 and Fe_xS_y -SA# pH13, respectively.

3.2.4 Brunauer-Emmett-Teller (BET) analysis

The BET theorem determines the physical adsorption of a gas molecule on a solid surface. The BET method calculated the specific surface area of all three FeS composites of different pH. Surface area is an essential parameter for knowing any compound's porous nature. Once the surface area of the pores has been determined, hazardous gases can be trapped by passing through it. The BET surface area of FeS was obtained from the respective nitrogen gas adsorption-desorption isotherms. Figure 10 attributed to the nitrogen adsorption-desorption isotherms and average pore diameter distributions from which the BET surface was estimated.



Figure 10 displays the nitrogen adsorption-desorption curve of all three composites, Fe_xS_y-SA#pH7.4, Fe_xS_y-SA#pH10 and Fe_xS_y-SA#pH13, respectively.

According to the IUPAC cataloguing, all FeS-SA composites exhibit Type IV isotherm, representing the mesoporous structure. The aggregate of particles with slit-like pores could explain the type IV isotherm curve with an unclosed hysteresis loop (H3). The composite FeS-SA#pH10 has the highest surface area, i.e., 19.772 m²/g, while FeS-SA#pH7.4 and FeS-SA#pH13 have 4.746 and 11.438 m²/g, respectively. Moreover, to know the pore diameter and pore volume of the composites, the Berrett-Joyner-Halenda (BJH) method was applied, from which using the desorption branch of the isotherm pore diameter distribution and pore volume distribution can be deliberated as exposed in Figure 11.



Figure 11 The pore diameter distribution curve of all FeS-SA composites formed at the gel-liquid interface by changing the pH of the Na₂S precursor solution from (a) 7.4, (b) 10, and (c) 13.

The BET analysis of the synthesised FeS-SA#pH10 composite discloses a specific surface area of 19.772 m²/g with a pore diameter and pore volume of 3.712 nm and 0.043 cm³/g, respectively. According to the findings above, FeS-SA#pH10 can supply enough photocatalytic active sites. FeS-SA#pH10 can be employed in various photocatalytic applications due to its high surface area, low band gap, and superior thermal stability. Table 3 shows the surface area, pore diameter, and pore volume of the synthesised FeS-SA composites.^{51, 52}

Photocatalyst	Surface Area (m²/g)	Pore Diameter (nm)	Pore Volume (cc/g)
FeS-SA#pH 7.4	4.746	3.128	0.019
FeS-SA#pH 10	19.772	3.712	0.043
FeS-SA#pH 13	1.438	3.701	0.036

Table 3. Representation of the surface area and pore diameter distribution of various FeS-SA composites obtained at the gel-liquid interface by changing the pH of the Na₂S precursor solution from (a) 7.4, (b) 10, and (c) 13.

CHAPTER 4

4.1 Results and discussion

4.1.1Photocatalytic dye degradation of Methylene Blue

Methylene blue is a toxic organic dye that is majorly produced in water effluents and is hazardous for humans and aquatic life.⁵³ The photocatalytic degradation of methylene blue dye molecules was accomplished with FeS-SA photocatalysts under the visible light illumination shown in Figure 12.



Figure 12 Photographs illustrating the decolourisation of aqueous methylene blue dye solution.

The degradation of MB was checked by a decrease of absorbance peak at 663nm to its minimal value. A UV-Vis spectrophotometer was used to study the photocatalytic reaction's kinetics. In the control experiment, the degradation of MB dye was also observed without a catalyst in the presence of Figure 13a visible light and 13b H₂O₂. After 140 min of visible light illumination, there is no such degradation. The aqueous solution of MB dye was taken with 2.5 mg of FeS-SA#pH10 photocatalyst and added 10µL of H₂O₂; then this reaction mixture was placed in a visible lamp for 140 min. Figure 13d displays the decrease in the time-dependent UV-Vis absorption spectrum, from which it can be said that MB was degraded by 96% approximately. The photodegradation was also accomplished by FeS-SA#pH7.4 and FeS-SA#pH13 photocatalyst, resulting in 95% and 87% degradation of MB dye molecules, respectively, detected by absorbance plot represented in Figure 13c and f. For the control experiment, the photodegradation of aqueous MB dye (10 ppm) solution was performed only with or without H_2O_2 in the presence of visible light; there is no such deprivation even after 140 min of race to visible light. Further, the same reaction mixture was taken in dark conditions with FeS-SA#pH10 photocatalyst, the peak at 663 nm remains almost unchanged, represented in Figure 13d.



Figure 13 (a) Only MB (b) MB+ H_2O_2 (c) MB+ H_2O_2 + FeS-SA#pH 7.4 (d) MB + H_2O_2 + FeS-SA#pH 10 (e) MB + H_2O_2 + FeS-SA#pH 10 in dark (f) MB + H_2O_2 + FeS-SA#pH 13 in the presence of light.

Thus, it can illustrate that in the dark condition, the role of the catalyst is negligible; it shows promising activity in the presence of light, working as a photocatalyst. All the above results are resolute from the UV-Vis photocatalyst. From the above detections, it can be assumed that H_2O_2 performs an active role in the photodegradation process, probably through the generation of hydroxyl radical ('OH) in the attendance of a photocatalyst under exposure to visible light. Figure 14 depicts the Ct/C₀ falling-off curve plotted against irradiation time under visible light illumination for the photodegradation of aqueous MB solution with the FeS-SA#pH10 photocatalyst assistance. Therefore, keeping all the parameters mentioned above in mind, it can be said that FeS-SA#pH10 is the best-synthesized photocatalyst that exhibits various photocatalytic applications not only the degradation of toxic dyes but also helps in advanced photocatalytic oxidation reactions.



Figure 14 Ct/C₀ curve of FeS-SA photocatalyst at various pH.

Further, to examine the recyclability of FeS-SA#pH10 photocatalyst for the consequent number of cycles, dye solution (10ppm) was taken with photocatalyst and H_2O_2 . After the degradation, the same catalyst was extracted with ethyl acetate to eliminate the residual dye particles and stuck byproducts and used for successive cycles. This process is done for up to five subsequent cycles, and it can be seen in Figure 15a that the degradation efficiency of FeS-SA#pH10 photocatalyst was slightly decreased by several times as it was used. As a result, FeS-SA samples can be reused in several subsequent cycles for the photocatalytic degradation of organic dyes without much affecting their catalytic performance. The decolourisation of MB dye was attained by decreasing the absorbance of dye at the maximum wavelength, i.e., 669nm, under visible light exposure. The degradation efficiency of the dye can be calculated by using Equation (1)

% Degradation =
$$\frac{C_0 - Ct}{C_0} \times 100$$
 (3)

Co = initial dye concentration and Ct = dye concentration after time t.

4.1.2. A Plausible photocatalytic mechanism

Moreover, the degradation of aqueous methylene blue was accomplished in the existence of scavengers to determine the role of primary active species that majorly participate in Photocatalytic reaction. For this experiment, several types of scavenging agents are used, such as benzoquinone (BQ) which is used for quenching the superoxide radicals (O2⁻), Ethylenediamine (EDTA) to quench photogenerated holes(h⁺), AgNO₃ used for quenching of photogenerated electrons and t-butyl hydroxide to quench hydroxyl radicals ('OH).55 With the assistance of the AgNO₃ scavenging agent, the rate of photocatalytic degradation of MB was significantly decreased to 25%, which describes the role of photogenerated electrons, which further generates 'OH radicals with the help of FeS-SA photocatalysts. The photocatalytic degradation rate of MB prominently reduces to 23% in the presence of EDTA, which may be caused by the effective scavenging of the photogenerated holes produced by the FeS-SA photocatalyst further converted into hydroxyl ions ('OH). The photocatalytic degradation rate MB remained almost uninfluenced by benzoquinone as there is no such role of superoxide radicals (O_2^{\bullet}) . In the presence of tertiary butanol t-BuOH, the photodegradation was approximately 3%, resulting in 'OH radicals having maximum participation in the

photocatalytic degradation of methylene blue. Figure 15b displays the scavenger study.



Figure 15 (a) Recyclability test for all FeS-SA composites at five consecutive cycles. (b) Controlled experiments using different types of scavengers shows the degradation %.

The photogeneration of the electron-hole pair was accomplished with the assistance of FeS-SA under the illumination of visible light having energy more significant than the bandgap (1.6 eV) of FeS-SA#pH10. As it is well known, holes are generated in the valence band when electrons get excited in the presence of light and go to the conduction band; similarly, the holes are produced in the valence band by the FeS-SA catalyst, which is encapsulated by OH⁻ions and gives 'OH radicals. The photoexcited electrons combine with H₂O₂, giving 'OH as the significant reactive oxidative species. We suggest a possible mechanism for this photocatalytic dye degradation by taking the above information. It has been marked that upon irradiation of visible light to the reaction mixture, $e^{-}h^{+}$ pairs are generated. Subsequently, the photoexcited FeS-SA transfers its electrons in the conduction band to adjacent H₂O₂ to produce 'OH.⁵⁶ Thus, the photogenerated 'OH radical produced in both conduction and valence bands directly oxidises the MB in the presence of FeS-SA catalyst. The photocatalysed degradation mechanism of methylene blue accompanied by FeS-SA represent in Figure 16



Figure 16 A Plausible mechanism for the degradation of methylene blue.

4.1.3 Conclusion

In the present work, we have successfully synthesised the ironcoordinated biopolymer catalyst, i.e., FeS-SA, at three pH ranges from 7.4 to 13, which can be used for visible-light-driven photocatalytic reactions. The photocatalytic degradation of methylene blue dye was best observed with the help of FeS-SA#pH10 photocatalyst. Thus, from the above results, it can be concluded that there is a role of visible light from which electrons and holes are generated, which further participate in photodegradation. Furthermore, we have demonstrated that the current photocatalyst can be recycled for several consecutive cycles with 50% recyclability effects. Our present work covers the way for nextgeneration photocatalysts toward a broad spectrum of photochemical reactions.

4.1.4 Future Scope

So many organic conversion reactions require harsh reaction conditions and a variety of catalysts, including biocatalysts, electrocatalysts, etc. Our synthesised catalyst is a photocatalyst that can perform a response without requiring such a specific condition and works in the presence of visible light. We plan to drive selective photocatalytic coupling reactions.

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