

PREPARATION AND CHARACTERIZATION OF IRON- METAL NANOCOMPOSITE OF CHITOSAN: TOWARDS HETEROGENEOUS BIOCATALYSTS FOR ORGANIC REACTIONS

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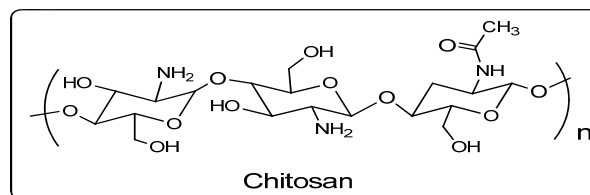
Abstract—Recently, heterogeneous biocatalysts and sustainable chemistry researchers are directed to develop new green methodologies that aim to reduce and prevent pollution at its source. Biocatalysts is a promising technique based on the use of natural renewable biological materials, such as enzymes and polymers that provide cleaner methodologies with high selectivity and energy-efficient operation under mild conditions in contrast to the traditional chemical catalysts. So we take Chitosan i. e. (2-acetamido-2-deoxy- β -D-glucose-(N-acetyl glucosamine) is a partially deacetylated polymer of chitin. It is an efficient eco-friendly basic biocatalyst. In this article we prepared Fe (II) and Fe (III) - chitosan heterogeneous biocatalyst. For the preparation of nanocomposite material low cost biopolymeric ligand Chitosan was used as a stabilizer to synthesize Iron (Fe)-chitosan biopolymer. The Fe (II)-Chit was prepared by adding Fe (NH₄)₂(SO₄)₂.6H₂O with chitosan powder under reaction condition. Further Both the Chitosan and Fe (II)-Chit synthesized were characterized using FT-IR spectroscopy, SEM, and UV-visible spectroscopy. The Fe (II)-Chit was further used as heterogeneous biocatalyst for organic reactions.

Keywords: Chitosan; Fe(II) immobilization; Heterogenized catalysts; FTIR; SEM; UV- Visible; organic reactions.

1. INTRODUCTION

Recently, biocatalyst and sustainable chemistry researchers are directed to develop new methodologies that aim to reduce and prevent pollution at its source [1-3]. Biocatalyst is a promising technique based on the use of natural renewable biological materials, such as enzymes and polymers, which provide cleaner methodologies with high selectivity and energy-efficient operation under mild conditions in contrast to the traditional chemical catalyst [4-5]. Chitosan (2-acetamido-2-deoxy-D-glucopyranose and 2-amino -2-deoxy-D-glucopyranose) is a partially deacetylated polymer of chitin and is usually prepared from chitin by reflux with a strong alkaline solution [6-8]. Chitosan is a naturally abundant and renewable materials it have broad application in the

pharmaceutical and biomedical industrial for enzyme immobilization. Chitosan is used in the chemical wastewater treatment, heterogeneous catalyst in the organic reactions and food industrial for food formulation as binding, gelling, thickening and stabilizing agent [9]. It is considered as most promising materials for future applications due to its excellent properties such as, multifunctional properties including high tensile strength, bioactivity, biocompatibility, non-toxicity, adsorption, biodegradability, antimicrobial activity, and its economic advantages [9],[10]



In organic reactions, the reactions are proceed by catalysts in several ways such as increase nucleophilicity, increase leaving ability as a nucleofuge and also increase the stability of transition state. The presence of catalyst can greatly increases the reaction rate. The reactions which are catalyzed by the heterogeneous catalysts have major area of research for many years. Heterogeneous catalysis occurs when the catalyst is in a different phase, which typically makes the separation process much easier. While homogeneous catalysis have extensive properties (low influence of diffusion mechanisms on reaction performance, for example), but the problem is that for the use of the homogeneous catalyst in any organic synthesis to include an additional separation process at the end of the reaction to recover the catalytic metal, especially

the case of precious and strategic metals. This separation process may represent a very difficult challenge in some cases. Due to this numbers of researches are focused on the

preparation and the immobilization of catalytic metals on inert materials, functionalized solids and the polymers. Chitosan shows increased attention for used it as the supporting catalyst material due to providing much interest in specific properties such as stereoselectivity and orientation of reaction and their ability to bind enantiomers. Chitosan, a bio-based polymer shows the cationic behaviour in acidic solutions and high affinity for the metal ions because it exhibits the considerable chelation activity^[11].

Immobilization of transition metal complexes on the surface of chitosan polymer supports allows to design new catalysts that combine the advantages of homogeneous and heterogeneous catalytic systems. Recently, organic polymers including chitosan is being considered as promising carrier for immobilization of complexes. This system is ecologically friendly material meeting the needs for catalysts of a new generation. The unique properties of natural polymers, such as non toxic, biodegradability, blood compatibility, etc. make them especially attractive for a number of potential applications^[12]. A low cost biopolymeric ligand Chitosan was used as a stabilizer to synthesize Iron (Fe)-chitosan biopolymer. The Fe (II)-Chit was prepared by adding Fe (NH₄)₂(SO₄)₂.6H₂O under reaction condition. The Fe (II)-Chit was further used as heterogeneous biocatalyst for several organic reactions. Both the Chitosan and Fe (II)-Chit synthesized were characterized using FT-IR spectroscopy, SEM, and UV-visible spectroscopy.

2. MATERIALS AND INSTRUMENTS

Materials- Medium molecular weight chitosan powder was obtained from india MART company, India. Fe (NH₄)₂(SO₄)₂.6H₂O, sodium chloride, sodium sulfide, nitric acid, acetic acid, ethanol was purchased from Merck-India. All aqueous solutions were prepared from reagent-grade chemicals using distilled water. All chemical reactions were carried under aerobic conditions.

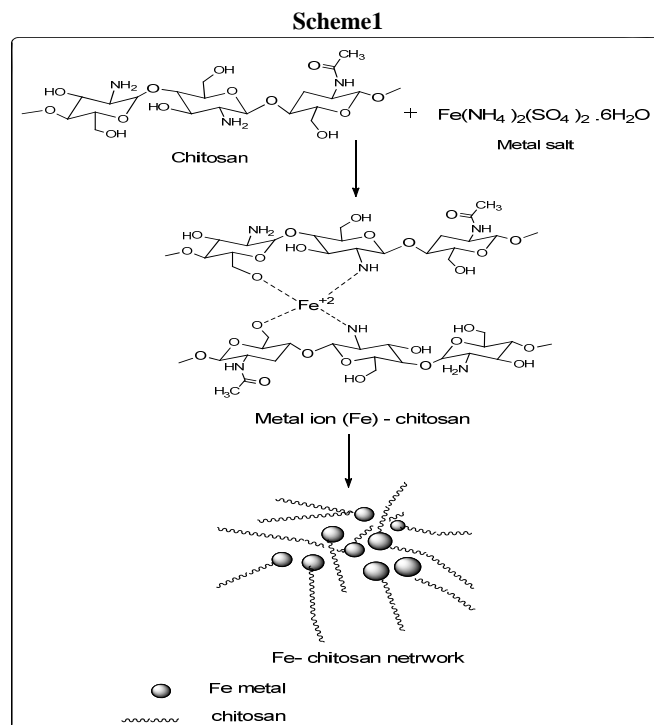
Instruments - FT- IR Spectra of polymer supported metal-complex at various stages of synthesis was recorded using Perkin Elmer spectrometer. The electronic spectra were measured in range of 200-800nm by using UV- visible spectrometer Instrument Cary 100, Instrument Version 12.00.

3. METHODS

3.1 Method of preparation-Preparation of chitosan – Fe metal nanocomposite:

Preparation of Fe(II)- chitosan complex by some previous reported (Adewuyi, S. et al^[13]).500 mg of chitosan powder dissolve in 2% acetic acid solution then chitosan converted into beads form and aqueous solution (10 ml) of Fe(NH₄)₂(SO₄)₂.6H₂O salt (4mmol) was added and shaken overnight at room temperature. After completion of reaction, the chitosan –Fe complex was filtered and washed with water

until no metal ions were detected against sodium sulfide or sodium chloride.



4. RESULTS AND DISCUSSION

4.1 FTIR Characterization Analysis Fe(II)-Chitosan Biopolymeric Complexes:

The Infra red spectra of Chitosan and Iron (II)/ (III)-Chit nanocomposite are shown in Figures 1 and 2 respectively. FT-IR absorption spectrum of chitosan showed band around 3471 cm⁻¹ which is associated with –OH and –NH stretching vibrations. The band at 2896cm⁻¹ attributed to –C-H stretching vibration, 1640 cm⁻¹ attributed to C=O of the N-acetyl unit of chitosan and bending vibration of C-H show between 1500-1300 cm⁻¹.

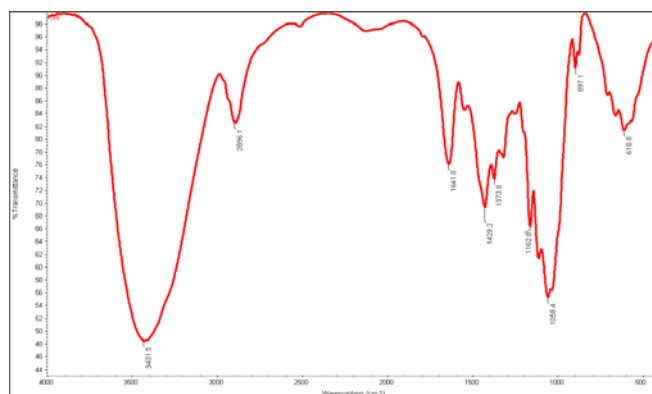


Figure 1- FT-IR Spectrum of Chitosan

A metal – chitosan interaction is generally revealed by shift in O-H and N-H stretching in the region of 3000–3600 cm^{-1} as well as bending vibrations of C-H between 1600 – 1000 cm^{-1} (Adewuyi et al., 2012). The FT-IR spectrum of Fe (II)/ (III) - chitosan coordination complex in this work showed some of these changes. The broad band at 3403 cm^{-1} attributed to the O-H stretch and overlapping N-H str groups of the chitosan shifted to 3225 cm^{-1} in Fe (II)-Chit. The band at 2900 cm^{-1} attributed to C-H stretching vibration, 1640 cm^{-1} attributed to C=O of the N-acetyl unit of chitosan. Bending vibration of C-H shows at 1432, 1396, 1318 cm^{-1} . The formation of M-N and M-O occurs at 667 cm^{-1} and 603 cm^{-1} shows sharp peak respectively.

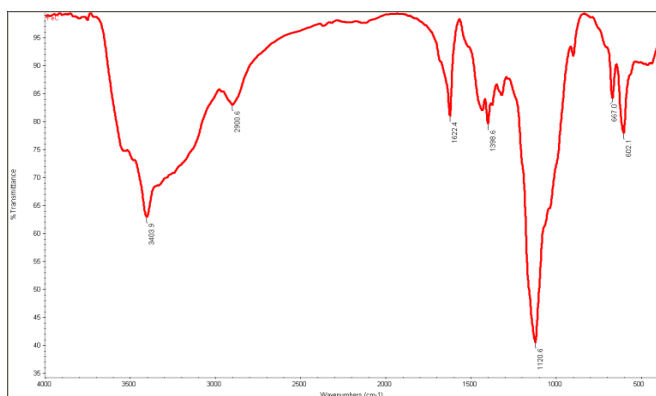


Figure 2- FT-IR Spectrum of Fe(II)-Chit Complex

4.2 UV-visible Characterization Analysis of Fe (II)-Chitosan Biopolymeric Complexes –

The UV-visible spectra of chitosan and Zn(II)Chit are shown in Figure 3 and 4. It is known from the literature that there is no peak observed in the UV-visible spectrum of chitosan at the range of 200 – 800 nm. However, the band around 280 nm can be attributed to the $n \rightarrow \pi^*$ intra ligand electronic transition due to the C=O of the N-acetyl group in chitosan (Fig. 3). Conversely, in the spectrum of Fe(II)/(III)-Chit, two absorption bands at 270 and 330 nm were observed (Fig. 4). The band at 270 nm is a red shifted $n \rightarrow \pi^*$ due to the C=O of the N-acetyl group in chitosan further suggesting interaction between chitosan and Fe metal. The absorption band at 330 nm is assigned to metal to ligand charge transfer.

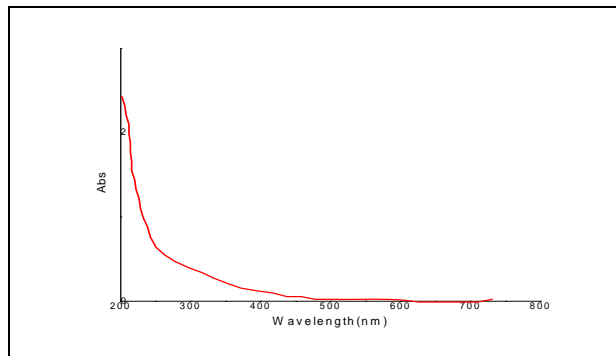


Figure 3: UV-visible spectra of Chitosan

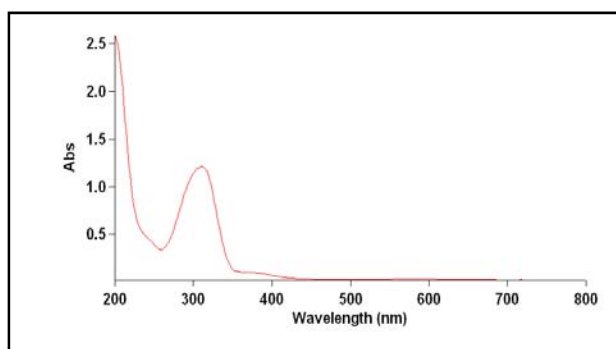


Figure 4: UV-visible spectra of Fe (II)-Chitosan nanocomposite.

4.3 SEM/EDX Characterization Analysis-

4.3.1 SEM analysis:

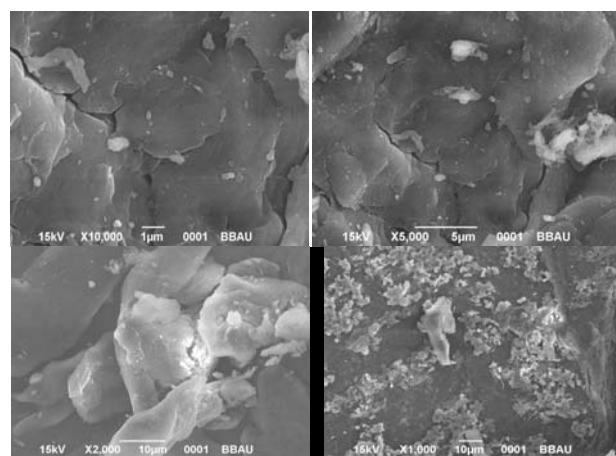


Figure 5: SEM of pure chitosan

SEM image of chitosan were analyzed in comparison with SEM image after chitosan –metal complex i.e. Fe- chitosan complex formation which shown in Figure-6. Before formation of Fe- chitosan complex chitosan has lamellar, porous and large grooves on the surface shown in Figure- 5.

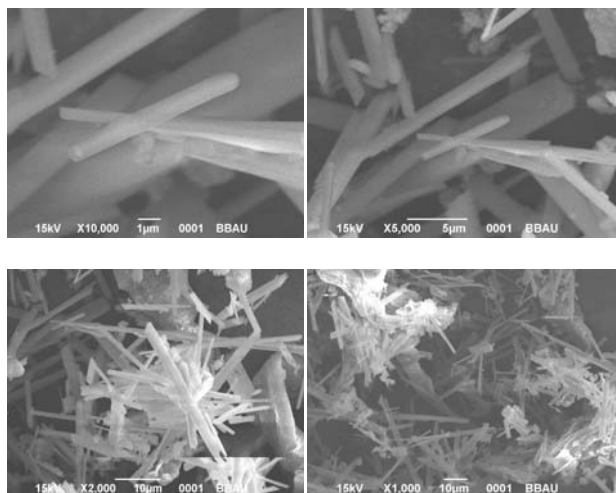


Figure 6: SEM of Fe-chitosan nanocomposite material

SEM exhibited great differences in the surface morphology upon complexation with Fe^{+2} , Fe^{+3} ions (Figure 6). From the SEM the fibrous nature of chitosan is lost upon complexing and regular rod like geometric shape appeared that were attributed to the coordination with Fe^{+2} , Fe^{+3} ions .

4.3.2 EDX Analysis-

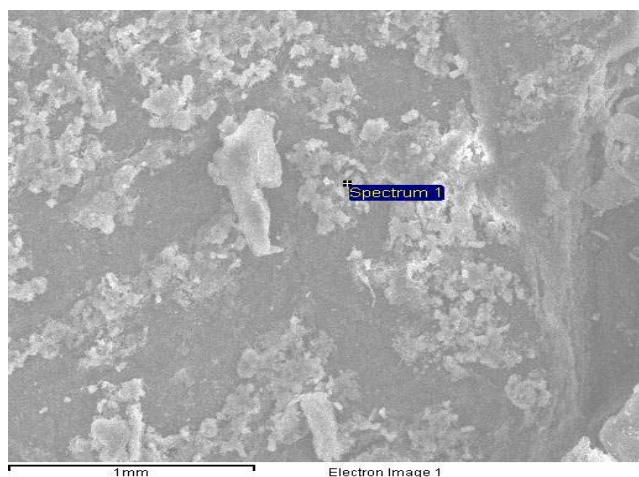
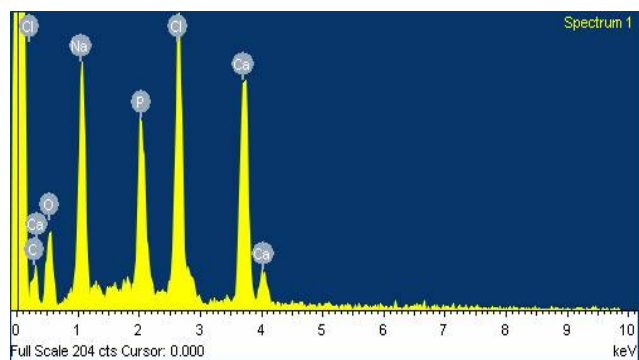


Figure 7: EDX of chitosan



Element	Weight%	Atomic%
C K	27.09	41.81
O K	26.26	30.42
Na K	13.12	10.58
P K	6.73	4.03
Cl K	12.72	6.65
Ca K	14.08	6.51
Totals	100.00	

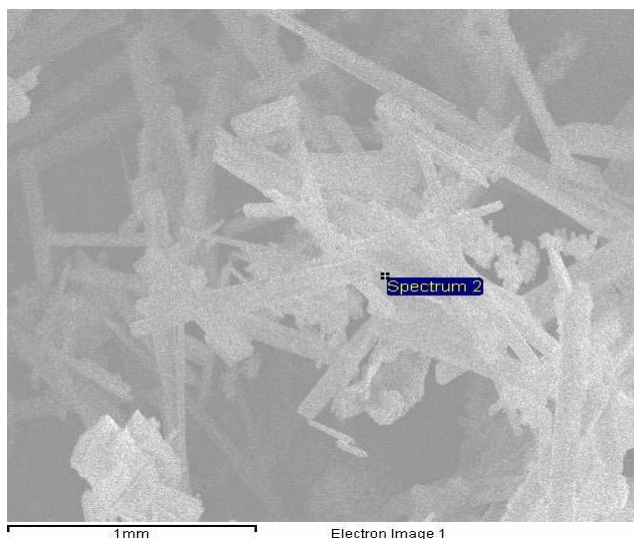


Figure 8: EDX of Fe – chitosan nanocomposite material

Element	Weight%	Atomic%
C K	15.45	22.77
O K	59.24	65.55
S K	10.87	6.00
Ca K	10.38	4.59
Fe K	2.44	0.77
Zr L	1.62	0.31
Totals	100.00	

The EDX graph of chitosan and Fe- chitosan nanocomposite which shown in Figure-7 and Figure-8 confirm the formation nanocomposite of Fe with chitosan.EDX graph of chitosan shows the Ca, Na, C, S, P and O peaks. While EDX graph of Fe-chitosan complex shows the Ca, S, C, O and three peaks of Fe.

5. CONCLUSION

Prepared Fe (II) – chitosan nanocomposite mainly used as heterogeneous catalyst for several organic r Reactions .This Fe- chitosan biocatalyst mainly used for polymerization reactions, coupling reactions, Michael addition and Oxidation reactions.

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