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Applications of Chitosan Based Schiff bases and its Complexes – A Review

Veena R Nair[1], Meera Jacob[2], Texin Joseph[2], Jaya T Varkey[3]

Assistant Professor, Department of Chemistry, The Cochin College, Cochin, India[1]

Assistant Professor, Department of Chemistry, St. Pauls College, Kalamassery, India[2]

Assistant Professor, Department of Chemistry, St. Teresa's College, Ernakulam, India[3]

Abstract: *Chitosan, a natural polysaccharides biopolymer is a versatile and promising biomaterial. Chitosan metal complexes stand out in their applicability in different research fields due to their biocompatibility and biodegradability properties. Presence of primary aliphatic amino group along the polymer chain allows for a variety of chemical modifications, of which the most significant is imine functionalization. The ability to easily perform complexation between chitosan Schiff bases and metal ions results in metal complexes, enhancing its application, resulting in further innovation in various fields. The most recent advances of chitosan Schiff base complexes in various fields, including biomedical, catalysis, environmental, and adsorption are summarised in this review.*

Keywords: Chitosan, Schiff Bases, Metal Complexes, Applications.

I. Introduction

In recent years researchers are more focussed on greener, cleaner and sustainable chemistry which has made lesser impact on the environment having lower levels of pollution and contamination. This is evident from the recent shift from petrochemical-based feed stocks towards biological materials [1]. Thus, biopolymers earned more attention than synthetic biodegradable polymers due to its biodegradability, renewability, and abundance [2]. Starch, cellulose, chitosan and cyclodextrin are some low cost, renewable and biodegradable polymers which has great economic and environmental importance [3].

Biopolymers a versatile class of materials have potential applications in various research field like agriculture, food, medicine, pharmaceutical and environmental. Because of its high nitrogen content (89.6%) chitosan, the second most abundant polysaccharide after cellulose [4], has commercial significance among the various naturally occurring polymers. [5-7]. It is the product of N-deacetylation of chitin which is found in the shells of crustacean's crab, shrimps lobsters and exoskeleton of insects and also in the cell walls of fungi. Chitosan is mainly composed of randomly distributed β-(1,4)-linked D-glucosamine and N-acetyl-D-glucosamine.

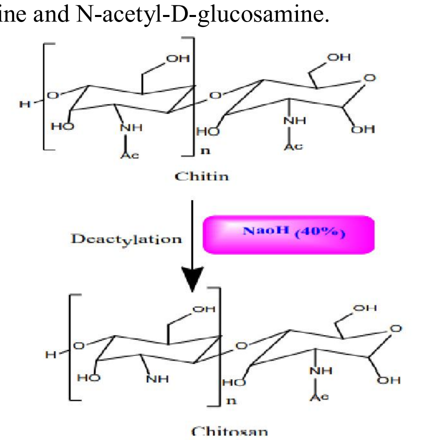

Fig. 1. Extraction of chitosan from chitin

The reactions of chitosan are versatile than other biopolymers like cellulose, starch etc due to the presence of chemically active primary $–NH_2$ groups and highly hydrophilic –OH groups. Various efforts have been made by researchers to find the chemical modification, [8] thus producing functional derivatives of chitosan with large spectrum of applications. Chitosan is functionalized to change its solubility, add metal ligands, and improve biological and catalytic activity. [9-11]

Among the functionalized biopolymers Schiff bases are unique which contain an imine group, formed by the condensation of primary amino group in the polymer structure with carbonyl compounds like aldehydes or ketones.[12] These bases enhance the adsorption and complexation properties of chitosan yielding a complexing material with extensive antimicrobial, catalytic and environmental applications.[13-15] Inherently chitosan exhibit antimicrobial property, but some reports show that Schiff bases of chitosan found to have stronger biological activity than chitosan. Also, among the different type of catalysis, polymer supported catalyst has potential applications for chemical synthesis, as it switched from homogenous catalyst to heterogenous ones. Major advantages of heterogenous catalyst are easy removal without loss of catalytic activity, and recycling. [16,17] Chemically modified chitosan received attention as versatile supporting material. [18,19].

II. Applications of Chitosan Schiff Base Complexes

In the recent years, chitosan anchored Schiff base complexes are being studied the most as they are gaining significance as biochemical, antimicrobial and catalytic reagents [20-22]. Various reports are available with chitosan anchored Schiff base complexes and its application. This review intended to give an overview of various applications of chitosan anchored Schiff base complexes.

2.1 Biological Activity

Using the biopolymer chitosan X. Jin et al. [23] synthesised Schiff base by the reaction of chitosan with citral working under high intensity ultrasound. The chemical structure was characterised and screened for their antibacterial activity against Escheria coli, Staphylococcus and Asper gillusniger. The results indicate that the activity of Schiff base was stronger than chitosan and its activity increases with an increase in the concentration. Rong-Min Wang et.al [24] in their work described the anticancer activity of LMW chitosan salicylaldehyde Schiff base and its Zn(II) complexes, which inhibit the growth of SMMC-7721 liver cancer cells and was by sulforhodamine B assay method in vitro method. Results revealed that the Zn complexes get bounded to DNA through electrostatic interaction and intercalation. Antibacterial activity of seven Schiff bases from O-carboxymethyl chitosan and p- substituted benzaldehyde was studied by Xueqiong Yin et al. [25] and also examined the impact of substituents i.e., nature and position on the biological activity. Studies indicate that the benzaldehyde with electron donating group like $-CH_3$ and $–OCH_3$ increases the activity and the electron withdrawing groups like halogens and $–NO_2$ group decreases the activity. Emad Soliman et al. [26] also synthesised a series of chitosan Schiff bases by the condensation of low molecular weight chitosan with benzaldehyde and its p-chloro, p-methoxy and p-$N(CH_3)_2$ derivatives. The antibacterial activity of chitosan Schiff bases were evaluated against gram positive (Staphylococcus aureus and Streptococcus pyogenes) and two type of gram-negative bacteria (Escherichia coli and Shigella dysentriae) and assessed by Optical Density method. Among the synthesised Schiff bases, anisaldehyde had the highest antibacterial activity. By the reaction of 5-chloro-3-methyl-1-phenyl-1H- pyrazole-4-carboxaldehyde with chitosan Amil. B. Dholakia et al. [27] developed a new chitosan Schiff base and its antifungal potential was investigated against Aspergillus niger and Penicillium by agar well diffusion method. In another work Singaram et al. [28] reported the antibacterial activity of Pd (II) Schiff base complexes prepared by the reaction of chitosan and aldehyde viz, 4-hydroxy-3-methoxy benzaldehyde and 2-hydroxy benzaldehyde. The Pd (II) complexes shows good activity against bacterial organism and activity increases with minimum concentration. High activity of the complex is due to the metal ion's permeation process.

Figure 2: Antibacterial effects of Palladium (II) complex of Chitosan salicylaldehyde schiff base (CSSB). Ref[28]

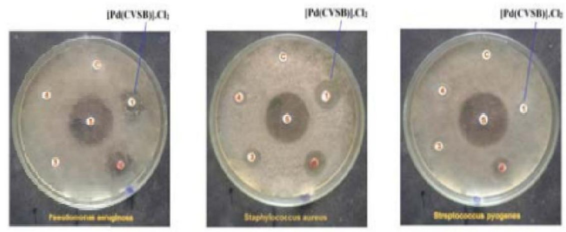

Figure 3: Antibacterial effects of Palladium (II) complex of Chitosan-vanillin schiff base (CVSB). Ref [28]

Metal complexes of Ni (II) and Co (II) are synthesised by Suresh et al.[29] with Schiff bases derived from water soluble carboxymethyl chitosan with 3,4-dimethoxy benzaldehyde and its biological activity were studied. Biological activity includes invitro cytotoxicity, antioxidant activity and ALP studies. The result indicates that the Schiff bases and the complexes are non-toxic and compatible. ALP activity of Ni complex is high compared to other samples and the antioxidant activity of Schiff base is found to be more pronounced than its metal complexes. Developing nontoxic pure nanomaterials allow a new path for its use in biological action, PavlineJelinkova et al. [30]synthesised complexes of Se nano-particles with chitosan and its schiff bases. Results revealed that chitosan with Se nanoparticles have inhibitory effect only on gram – negative bacteria – Escherichia coli, whereas the complexes of chitosan Schiff base with Se nanoparticles has the highest inhibitory effect against all the bacterial strains tested. Few studies have been performed by Araujo etal. [31] regarding Ni (II), Cu (II), and Zn (II) complexes with Schiff base derived from salicylaldehyde and its nitro and methoxy derivative anchored on chitosan. Characterisation shows that the complexes are square planar and also Cytotoxicity was examined by MTT assay performed using human HeLa cells. From the results Zn (II) complexes are found to be highly toxic and Cu (II) complex presented higher viability.

Six novel metal complexes of Pd (II) and Pt(II) were synthesised from biopolymer chitosan Schiff base by the reaction of chitosan and salicylaldehyde and its derivatives like 5-nitro and 5-methoxy salicylaldehyde by Helen et al.[32] The biological activity have been studied against two bacterial plant pathogen Pseudomonas syringaepv.tomato and antifungal activity against fungal plant pathogen Fusarium graminearum and their antitumour activity against a human breast cancer cell line (MCF-7). From antibacterial assay, chitosan Schiff bases and its complexes exhibit high anti-tumour activity against breast cancer cells. In this study Ahmed M. Khalil et al.[33] concerned with the synthesis, and characterization, of some chitosan Schiff- bases and carboxymethyl chitosan Schiff base by the interaction some pyrazole aldehyde derivatives loaded with AgNPs and evaluate the antimicrobial activities. The presence of AgNPs displayed the highest antibacterial activity against certain bacteria and fungi. Wei xiang Liu etal.[34] proposed chitosan derivative having amino pyridine group followed by co-ordination with Cu (II), Ni(II) and Zn(II) ions to form metal complexes. And its antifungal activity were evaluated against P.capsici, V.alboatrum, B.cinerea and R. solani. Among the series of complexes Cu complex (inhibit the growth of P. capsici 100) showed the best antifungal activity followed by Ni complex (inhibit by B.cincera 77).

Mohammed A Hassan et al. [35] developed two novel antibiotic phenolic chitosan Schiff bases by condensation of chitosan with indole -3 carboxaldehyde and 4-dimethyl amino benzaldehyde. Chemical structure of developed Schiff bases was verified by spectral analysis and its thermal stability were studied by TGA and DSC techniques. An innovative aminated methylacrylate chitosan Schiff base bearing p-nitro benzaldehyde has been reported by Samesh S

Ali et al. [36] Its biological studies were assessed in vitro, this new aminated chitosan derivative show remarkable antioxidant, antibacterial, and antibiofilm property than chitosan. Evaluation of cytotoxicity and hemolytic analysis revealed cell viability and proliferation without evident hemolysis. Vadivel etal.[37] reported the antifungal activity of Ru(III) complexes, synthesised by the complexation of metal with chitosan Schiff bases formed using the ligand salicylaldehyde, vanillin, and O-methoxy vanillin. The antifungal study was carried out by disc diffusion method against fungal pathogens such as Asperigillus flavus, Aspergillus niger, Pencillinchyrogenum, Fusarium oxysporum and Trigodermaveride. Result analysis concluded that Ru (II) complex show a significant antifungal activity than the parent Schiff base ligand due to their chelation effect on micro-organism.

N. Hidyati.etal.[38] prepared Cu(II) and Fe(II) complexes using the ligand N-(2-hydroxy benzylidene) chitosan. The complexes were screened for antibacterial activity against bacteria like Escherichia coli and Staphylococcus aureus, which was assessed by paper disc diffusion method. X-ray diffraction study indicate that the crystallinity of chitosan decreased by the formation of complex but the complex shows the best antibacterial activity due to the increased lipophilic nature of the complexes. Recently ManimohanMurugaiyan et al. [39] designed novel water soluble hydrazide-based O-carboxymethyl Chitosan Schiff base and its Zn (II) complex for potential application in various biomedical and pharmaceutical areas. In another paper in addition to Zn(II) complexes they described the synthesis of Co(II) and Cu(II) complexes and its antimicrobial studies. Among the three complexes Cu complex show enhanced anti-inflammatory, antioxidant and antidiabetic performances hence; it possesses the scope for pain killer, antitumor and diabetic treatment.

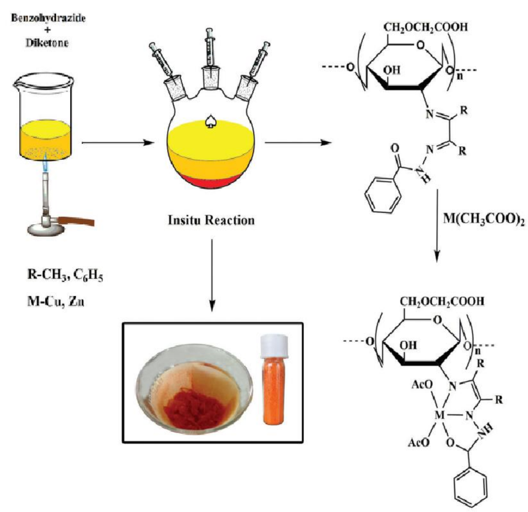

Figure 4: Design and synthesis of water-soluble hydrazide-based O-carboxymethyl chitosan Schiff bases and their Zn(II) complexes through an in situ reaction. ref [39]

Chitosan /Isatin Schiff base developed by A.M.Omer etal. [40] has been found to exhibit good antimicrobial activity in medical application especially in wound dressing. Antimicrobial activity was screened against gram positive pseudomonas aeruginosa, salmonella and Proteus vulgaris. Another similar work was carried out by Vasak.B.Gavalyan etal.[41] where chitosan Schiff base were prepared by the interaction of chitosan with 4-(2-bromoethyl) benzaldehyde, followed by dehydrohalogenation under basic conditions to get vinyl derivatives. Vinyl group in the polymeric chain can undergo polymerisation and co-polymerisation to create novel polymeric structure exhibiting catalytic biological and medicinal applications. Three novel chitosan Schiff bases were reported by Nadia.Q Haj etal.[42] by the reaction of chitosan with 2-chloroquinoline-3-carbaldehylde, oxazole-4-carbaldehyde and quinazoline-6-carbaldehyde. Antibacterial activity was studied against Gram negative and Gram-positive bacteria namely, Klabseilla pneumonia, Escherichia coli, Staphylococcus aureus Streptococcus mustans, and its antifungal activity was studied against fungi Candida albicans and Asperigillus fumigates. The chitosan Schiff bases showed significant activity against one or more bacterial and fungal strain and the absence of cytotoxicity was evaluated through MTT screening test. Due to the broad application of heterocyclic in medical field, M.K Yadav et al. [43] developed chitosan derivative of 2-imidazole carboxaldehyde and 2-thiophene carboxaldehyde and screened its antibacterial activity potency against gram positive and gram-negative bacteria. Only 2-thiophene carboxaldehyde was found to be active against Escherichia coli. Synthesis and biological application of novel N, N, O- tridentate isoniazed grafted chitosan Schiff bases and its Cu(II), Co(II), and Zn(II) complexes were described by Manimohan et al. [44] The metal complexes proved to be a good antibacterial, antifungal, anti-inflammatory, antidiabetic and antioxidant drug. Also, as a good DNA binder, they interact with CT-DNA by intercalation mechanism.

An innovative biomaterial, amino functionalised chitosan bearing nitro benzaldehyde was developed by EL Rafaie Kenway et al. [45] for biomedical application. This newly synthesised derivative revealed remarkable antioxidant, antibacterial, and anti-biofilm activity than chitosan, also its cytotoxicity and hemolytic analysis were also studied. From spectral and thermal analysis R.E.Malekshah et al. [46] confirmed the formation of chitosan Schiff base and its chelation with Cu(II), Ni(II) and Zn(II) metals and reported the cytotoxicity of complexes against MG-63(osteosarcoma cancer)cells and K562 chronic myelogenous leukemia. Functionalised chitosan and its complex exhibit better anticancer acivity against S against cancer MG63 cell line.

Another eco-friendly chitosan Schiff base, based on heterocyclic moieties was prepared by Amira A. Hamed et al. [47] from chitosan and heteroaryl pyrazole derivative namely 1-phenyl-3-(thiophene-2-yl)-1H-pyrazole-4-carbaldehyde, 1-phenyl-3-(furan-2-yl)-1H-pyrazole-4-carbaldehyde and 1-phenyl-3-(pyridine-3-yl)-1H-pyrazole-4-carbaldehyde, its biological activity against gram positive and gram-negative bacteria, certain fungi and its cytotoxicity was evaluated.

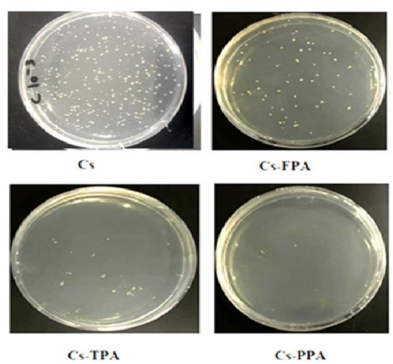

Figure 5: Representative images of viable S.aureus grown on different samples after 24 h of culture ref [47]

2.2 Catalytic Applications

Metal complexes build up from biopolymer chitosan play a significant role as heterogeneous catalyst in various reactions to increase its yield and selectivity of product. The catalytic activities of synthesised complexes depend on the nature of ligands, metal ions and coordination sites. A review on the catalytic activity of chitosan Schiff base complexes reported in various reactions such as oxidation, reduction, hydrogenation, coupling reactions etc are given below.

Biopolymer chitosan anchored Schiff base Cu complexes were prepared by Yue Chang et al. [48] using the ligands salicylaldehyde, o-nitro salicylaldehyde and m-nitro salicylaldehyde and studied their catalytic activity in the oxidation of cyclohexane with molecular oxygen was measured. Among the three different catalysts the chitosan m-nitro benzaldehyde derivative of Cu complex has high catalytic activity. J.Tong et al.[49] explored chitosan Schiff base complex of Co(II) and Pd(II) as heterogeneous catalyst for the aerobic oxidation of cyclohexane in the absence of solvents an reductants. Studies also proved that these complexes are efficient catalyst for the oxidation of bulky cyclic and linear alkanes. In another work highly stable, active chitosan supported immine palladacycle complex was developed by Xia Xue et al. [50] which tested as heterogeneous catalyst for Heck reaction. It was found to be a best choice in the C-C bond formation with high yield and regioselective for trans coupling**.** J.Liu et al.[51] developed (chitosan-Schiff base) cobalt(II) catalyst and reported as an efficient catalyst in the oxidative carbonylation of 2-aminoalkan-1-ols to form oxazolidin-2-ones which was an important intermediate for herbicides, pesticides and pharmaceuticals. Another innovative catalyst chitosan-Schiff base supported palladium and cobalt bimetallic complex was synthesized and characterised by W. Li-xia et al. [52] Its catalytic activity and stability was tested in the coupling reaction of acryl amide with the phenyl halide and reused up to ten times. A heterogenous catalyst chitosan 2,4-dihydroxy benzaldehyde Schiff base complexes were synthesised by Sahar.I. Mostafa [53] The catalytic activity of Schiff base complexes of Fe(II), Ni(II), Co(II), Pd(II), Rh(II), and Ru(II) in the oxidation of 1-hexene to epoxy hexene was investigated. Except for the Pd (II) complex, which has a selectivity of 55 percent, all catalysts have a high selectivity of 1,2- epoxy hexane formation (93-65%). B.C.E. Makhubela et al. [54] carried out the synthesis, characterization and catalytic evaluation of chitosan- and 6-deoxy-6-amino chitosan-supported Schiff base Pd(II) complexes in the Heck cross coupling and Suzuki–Miyaura reactions. Both the heterogeneous and homogeneous catalysts showed high activity for both reactions while the supported catalysts were recycled and reused up to five times.

Structural, surface, thermal and catalytic activity of three novel Cu complexes from the ligands chitosan and salicylaldehyde derivative namely salicyledene aniline (1), salicyledenethiourea(2) and o-vaniledene aniline(3) were studied by Antony et al. [55] All the Cu complexes successfully catalyse the oxidation of cyclohexane to cyclohexanol and cyclohexanone using eco-friendly H_2O_2 at ~70^{o}C and complex 1 shows high activity. In another work R. Antony et al. [56] synthesised three novel quadridentate Schiff base complexes [Cu(OIAC)Cl_2], [Co(OIAC)Cl_2] and [Ni(OIAC)Cl_2] and Schiff base by the condensation of chitosan and isatin i.e.([2-oxo-1H-indol-3ylidene]amino) chitosan. Chitosan's thermal stability and crystallinity were reduced when it was modified as a Schiff base and then complexed. All the complexes show catalytic activity in the oxidation of cyclohexane to cyclohexanol and cyclohexanone using the oxidant hydrogen peroxide. Among the three complexes synthesised Cu complex exhibit higher catalytic activity, and were recycled for four times without the major loss of its activity. Versatile magnetically recyclable catalyst, coreshell-Fe3O4@ chitosan Schiff base complexes of Cu(II), Co(II) and Mn(II) was developed by X.Cai et al. [57] using salicylaldehyde with different substituent's. Synthesised catalysts have been employed in aerobic oxidation of cyclohexane and show high catalytic efficiency with high turnover number and high selectivity for 2-cyclohexene-1-one.

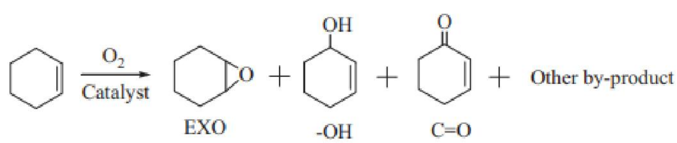

Figure 6: Oxidation of cyclohexene

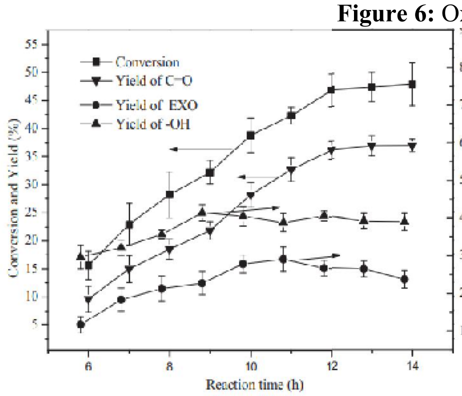

Fig.7. The effect of cyclohexene oxidation with different reaction time. Reaction conditions: cyclohexene 19.7 mmol, MG@NSal-Co 3.0 mg, reaction temperature 70 ◦C ref [57]

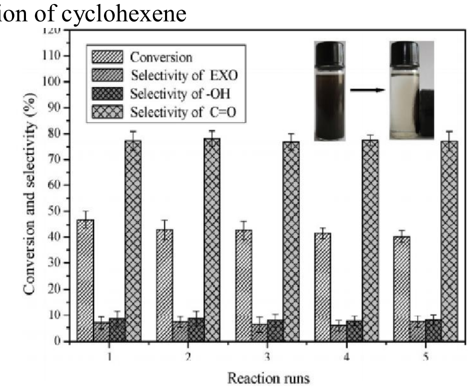

Fig.8. Reuse of the catalyst. a Reaction conditions: cyclohexene 19.7 mmol, MG@NSal-Co 3.0 mg, reaction temperature 70 ◦C, reaction time 12 h ref [57]

C.S Thatte et al. [58] synthesized chitosan-based Schiff base and complexed it with Mn (II), Co (II), and Cu (II) complexes which were used as excellent heterogenous catalyst in the air oxidation of β- isophorone to ketoisophorone. Mn complexes show significant catalytic activity and the catalyst was recycled for five times. ImtiyazRsoolParrey et al. [59] developed chitosan anchored Schiff base, ([2-oxo-1H-indol-3-ylidene] amino) chitosan and its Cu complex. This complex found to an efficient catalyst for the oxidation of alcohols namely, propanol, n-butanol, n-hexanol and benzyl alcohol using nontoxic ecofriendly molecular oxygen as an oxidant. Anuradha et al. [60] described the synthesis of an efficient recyclable heterogenous catalyst chitosan anchored Cu (II) complex for N-arylation of amines. Three different complexes were prepared by the reaction of Schiff bases of aniline, p-methoxy aniline and m-nitro aniline with Cu (OAc). H2O. Best results were obtained with complexes containing electron withdrawing NO_2 group which increases the Lewis acidity of complex and reused up to five times.

Synthesis of water soluble carboxymethyl chitosan Schiff bases supported by Ni^{2+} and Cu^{2+} catalyst was explained by R. Suresh et al. [61] These were tested as catalyst for oxidation reaction of cyclohexane. Catalytic activity was more pronounced in the carboxy methyl chitosan Schiff base complexes. Talat Baran and Ayfer Mentes [62] developed a versatile complex, O-carboxymethyl chitosan Schiff base Pd(II) and investigated their catalytic activity in suzuki coupling reaction for the synthesis of bi-aryls and its reusability were also tested. These new materials demonstrated high selectivity and higher efficiency even after six cycles.

Table I

Effect of complexes on Suzuki cross-coupling reaction.

Entry	X	Y	Yield (%) [OCMCS-2a-PdCl$_2$]	TON [OCMCS-2a-PdCl$_2$]	TOF [OCMCS-2a-PdCl$_2$]
1	Br	3-OCH_3	95	4750	396
2	Br	4-OCH_3	>99	5000	417
3	Br	3-CH_3	37	1850	154
4	Br	3-NH_2	99	4950	412
5	Br	4-NH_2	98	4900	408
6	Br	4 NO_2	92	4600	383
7	Br	4-CN	93	4650	387
8	I	4-CH_3	61	3050	254
9	Cl	3-OCH_3	8	400	33
10	Cl	4-CH_3	12	600	50

Reaction conditions: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, 0.02 mol % catalyst, 6 mL toluene, 100 °C, 12 h.
TON: (turnover number, yield of product/per mol of Pd).
TOF: (turn over frequency, TON/time of reaction).

Anuradha et al. [63] explored two novel chitosan -supported Copper (II)-Schiff base complexes by the condensation of chitosan with quinoline-2-carboxaldehyde and 8-hydroxy quinoline-2-carboxaldehyde and described its catalytic application in the synthesis of 5-substituted 1H-tetrazoles from oxime and sodium azide, as well as oxidative homo-coupling of terminal alkynes. The catalyst was recovered from the reaction medium by simple filtration and reused up to five times. High hydrophilic surface of chitosan allowed, Francoise Quignard et al. [(64] to develop an efficient chitosan supported aqueous phase–Pd catalysts and studied its application to the allylic substitution of (E)- cinnamyl ethyl carbonate by morpholine. Studies proved that the reaction rate can be increased by increasing the water content of solid catalyst and adding cationic surfactant in the reaction medium. An alternative for Pt based catalyst in oxygen reduction reaction, an electrocatalyst Fe_2O_3/NCS-Mn composite was developed by Tong etal. [65] from chitosan Schiff base. It proved to be a good electrocatalyst with high efficiency, stability and a promising catalyst for fuel cells.

2.3 Other Applications

A series of Cu (II) Schiff base complexes derived from the condensation of chitosan with different aromatic aldehydesiesalicylaldehyde, 4-hexadecyl oxy-2-hydroxy benzaldehyde and 2-hydroxy-1-napthaldehyde have been synthesised by Xu Hui Li et al.[66]. By the formation of chitosan Schiff base the thermal stability has slightly increased, but the stability of its copper complex has reduced. The difference in the crystallinity and thermal stability is mainly due to the formation of Schiff base and its complexation with copper ion. To exploit the potential application of chitosan and its derivative Xue Wen Wu and Yan Xiong[67] synthesised new chitosan Schiff base and its Zn complex. This work describes the modification of chitosan as Schiff base by the reaction between chitosan and 3, 5- di tetra butyl salicylaldehyde and its chelation with zinc. An innovative work using chitosan Schiff base complexes was carried out by W.Lie et al. [68] for ultraviolet-assisted oxidative desulfurization (UODS). For eliminating solubility problem of chitosan, Baran etal. [69] synthesised two novel O-carboxy methyl chitosan Schiff bases and its Cu(II) complexes. Characterisation by spectral analysis and its thermal studies indicate that the chitosan has higher crystallinity and thermal stability than that of the modified carboxymethyl chitosan Schiff base and its complex. For food packing application Laura Higueraset al. [70] designed an antimicrobial film from chitosan, where cinnamaldehyde was reversibly bounded to chitosan film through Schiff base formation. The antimicrobial properties of these films were tested in vivo and invitro against the food borne pathogens. In another work B.Yuan et al.(71) described the synthesis and characterization of covalently grafted chitosan Schiff base onto the surface of L-guluronic acid and also explained a method for the adsorption of congo red dye an anionic dye in a waste water treatment process.

R.Suresh and P.Moganavally et al. [72] reported Schiff bases of carboxymethyl chitosan/p-dimethyl amino benzaldehyde and its copper complexes. It has been tested for antioxidant activity by DPPH studies. The results summarize that the complexes are less toxic and have excellent antioxidant activity. In this research work, a new cinnamyl chitosan Schiff base was tested as antioxidant material by abdelrazik et al. [73] The antioxidant activity was tested by two methods ie hydroxyl and alkyl free radical scavenger was determined by rotational viscometry methods and its free radical scavenger activity by ABTS method. Results show that the hydrogen donation effect was depressed after coupling with cinnamaldehyde and electron donating behaviour was enhanced in cinnamyl chitosan Schiff base. F.S.Matty et al. [74] synthesised Co(II), Ni(II), and Cu(II) complex of schiff base by the reaction of chitosan with O-nitro benzaldehyde and this compound were characterized by spectral analysis and thermogravimetric analysis. Versatile applications of chitosan Schiff base as eco-friendly inhibitor for mild steel corrosion in 1M HCl was found out by R. Menaka and Subhashini [75]. The chitosan schiff base inhibitor get adsorbed and form a protective layer on the mild steel which reduces the metallic corrosion. For removing Co (II) ion from aqueous, AL. Shashrani H et al. [76] investigated chitosan vanillin (polymer I) and chitosan- ortho vanillin (polymer II) adsorbents under various conditions. Effect of various factors like temperature, pH, adsorbent mass, contact time and intial concentration of ion on the sorption process was verified. At pH 4 the maximum removal of 93.2$^{o}/_{o}$ of Co (II) was achieved. This study indicates that the new modified chitosan polymers are good adsorbents for the treatment of waste water.

P. Supriya Prasad and ThandapaniGomathi [77] carried out research work for the modification of chitosan as Schiff base using salicylaldehyde. To generate novel properties and applications this chitosan Schiff base (CSB) was further modified with polyethylglycol (PEG) to form CSB/PEG blend. Chemical structure and properties were confirmed by FTIR, XRD, SEM, porosity water uptake retention measurements etc. and the result analysis confirmed the amorphous nature of the synthesised CSB/PEG blend. Series of chitosan Schiff bases N-benzylidene chitosan, 4-dimethyl aminobenzylidene chitosan and 4-nitro benzylidene chitosan and their complexation with Cu^{2+},Zn^{2+} and Ni^{2+} were reported by Fernanda StuaniPereire et al. [78] X-ray diffraction pattern showed that the modification of chitosan Schiff base and its complexation decrease the crystallinity, due to the deformation of strong H-bonds by the formation of co-ordination of bond between metal ions and Schiff base, the new bond formation enhance its thermal stability.Novel eco-friendly antifouling biocides, polyelectrolyte grafted chitosan Schiff base was designed by R.F.M Elsharawfet al. [79] These developed ionic liquid chitosan N-salicylidenes were screened for their ability to inhibit Staphylococcus/ Escherichia biofilms and also incorporated into the paint matrix to formulate antifouling coating. These materials were proved to be a powerful eradicator against green, brown and red macro algae settlement. To eliminate the health issues caused by metal ions, an effective low cost and eco-friendly adsorbent, novel magnetic epichlorohydrin crosslinked chitosan Schiff base was developed by G.Yuvaraj et al. [80] for the removal of Cu(II) ions from waste water.

Another modification of chitosan as chitosan methylene bridge Schiff base was carried out by Ahmad Fatoni et al.[81] using the ligand 4,4-diamino diphenyl ether vanillin. It involves the reaction between chitosan and vanillin derivative to form the Schiff base, which was linked by methylene bridge by the reaction with HCHO through casting method. Ansari et al.[82] developed a new green corrosion inhibitor for the oil and gas industries using chitosan schiff base derived from the ligand salicylaldehyde. Computational studies, in addition to experimental studies, are published, and the DFT method was also used to achieve a theoretical estimate of the inhibition. Methyl orange an anionic dye even at low concentration can cause severe ecological issues, its removal from the aqueous environment was achieved by G.Yuvaraja et al.[83] using a novel, eco-friendly and highly potential sorbent aminated chitosan Schiff base (ACSSB@ZnO). The results revealed that highest sorption capacity was found to be 111.11 mg/g at 323 K and the kinetic data followed pseudo-second order and Langmiur model. Another attempt for the removal of anionic dyes like methyl orange using a new heterocyclic based chitosan Schiff base was made by A.S. Manchaiah and V. Badalamoole[84]. Influence of intial concentration of dye, p^H and contact time were carried out. Desorption studies indicate the kinetic and thermodynamic aspects as well as its reusability.

III. Conclusion

Chitosan, which can be easily functionalized by using the reactivity of the primary amino group as well as the primary and secondary hydroxyl groups, has a wide range of applications. The aim of this review is to improve understanding of the significance of chitosan modifications as chitosan schiff bases and its complexes. The pre-modifications on chitosan such as carboxymethylation and carboxyethylation have led to the synthesis of water-soluble chitosan schiff bases. According to the study, the crosslinking reaction of chitosan through schiff base formation is very important, which is very desirable for a variety of biomedical applications. The biological applications of chitosan schiff bases are numerous, as this analysis demonstrates, but the functional applications are yet to come. Because of their chelation effect, chitosan schiff bases have played an important role in the preparation of stable metal catalysts in heterogeneous catalysis. Improvements are still needed because chitosan schiff base-based catalysts are only reusable in a few cases. As the chelating ligands, chitosan schiffbasaes have been a good resource for the heavy metal adsorption and removal of dyes in the waste water treatment process. Chitosan Schiff base complexes have attracted a lot of attention in recent years, owing to their numerous applications in adsorbents, medicine and pharmaceuticals, catalyst systems, and environmental applications in general. However, there is still a need to investigate these complexes of different properties and applications, as well as to synthesise new complexes with additional applications.

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