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Chitosan-Based Green and Sustainable Corrosion Inhibitors for Carbon Steel

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Abstract

Development of non-toxic and environmental friendly corrosion inhibitors is highly desirable owing to the increasing demands of “green chemistry” throughout the world. In view of these several forms of green corrosion inhibitors such as drugs or medicines, plant extracts, ionic liquids and synthetic inhibitors derived from multicomponent reactions (MCRs) and mechanochemical mixing are being employed. Nowadays, MCRs in association with microwave and ultrasound irradiations represent one of the best green strategies. Natural polysaccharides particularly chitosan derivatives gained substantial advancement. Chitosan and its several derivatives have been employed effective as corrosion inhibitors for metals and alloys in various aggressive media. The present chapter features the collection of major works that have been published on the inhibition effect of chitosan and its derivatives. The utilization of the chitosan and its derivatives as effective corrosion inhibitors is based on the fact that they contain several polar functional groups such as amino ($-NH_2$), hydroxyl ($-OH$) and acetyl ($-COCH_3$) groups that effectively bind with metallic surface and behave as adsorption centers.

Keywords: chitosan, chitin, green corrosion inhibitors, aggressive solution, mixed-type inhibitors

1. Introduction

Alloys steel such as carbon steel and mild steel have been extensively utilized as construction materials for several purposes because of their high mechanical strength and cost-effective behaviors. However, they are highly reactive and undergo corrosion when exposed to the

environment particularly in acid treatment processes like acid cleaning, acid descaling, acid pickling and oil well acidification. Therefore, these cleaning processes require application of some external additive to avoid the corrosive dissolution of metallic materials. The external added chemical species are known as corrosion inhibitors. It is important to mention that the difference in the mild steel and carbon steel is the amount of carbon. Mild steel has relatively small amount of carbon ranging from 0.16 to 0.30%. Carbon steel contains larger amount of carbon, generally ranging from 0.30% to more than 2% [1, 2]. Among several available methods of corrosion protection, the utilization of organic compounds is one of the most appropriate and cost-effective methods. The extensive utilization of the organic compounds as corrosion inhibitors is also attributed due to their high effectiveness and ease of application. These compounds adsorb and form a corrosion protective barrier by transferring their non-bonding and π -electrons into the metallic d-orbitals. The electron transferring (Adsorption) ability of these compounds influences by several factors such as electronic structure of the compound, nature of metal and corrosive environment, surrounding temperature, presence of impurities, exposure duration etc. [3, 4]. The polar functional groups of heteroatoms (N, O, and S) such as $-\text{CN}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{OCH}_3$, $-\text{COOH}$, $-\text{CONH}_2$, $-\text{COOC}_2\text{H}_5$ etc. and double and triple bonds behave as adsorption centers [3, 4]. It is reported that these polar functional groups easily undergo protonation in strong acidic medium like 1 M HCl and exist in their cationic form. On the other hands, metallic surface becomes negatively charge due to the adsorption of counter ions of electrolyte (chloride ion in HCl). These two oppositely charged species attracted each other through electrostatic force of attraction (physisorption mechanism). In the later stage of the adsorption phenomenon neutral heteroatoms transfer their unshared electron pairs to the empty d-orbitals of the surface metallic atoms to form coordinate bonds that results in to the chemical adsorption. Recently, the growing natural awareness and severe environmental guidelines demand application of the compounds for different purposes that have been originated from natural and biological resources. The chemical synthesis of the organic compounds is not only expensive but also causes discharge of several toxic chemicals into the surrounding environment that can have several adverse effects on living beings. The increasing demands of “green and sustainable chemistry” throughout the world, forces to the scientists working in the field of corrosion chemistry to grow highly desirable “green and sustainable corrosion inhibitors” either by deriving them from natural resources or by synthesizing them using suitably modifying the available synthetic methods. In last two decades, use of multicomponent reactions (MCRs), chemical reactions catalyzed by energy efficient microwave and ultrasound irradiations, plant extracts, chemical medicines (drugs), ionic liquids etc. toward “green and sustainable corrosion inhibition” have gained significant milestone in this direction.

In recent decades, the use of carbohydrates and their derivatives as metallic corrosion inhibitors has been a growing effort to decrease the environmental pollution [3, 4]. Natural availability, biosynthesis using greenhouse (CO_2) gas, biodegradability, biocompatibility, and high solubility in aqueous media make the carbohydrates as “green” chemicals for variety of chemical transformations [5–7]. The carbohydrates act as inhibitor for protein glycosylation activities, medicines for bacterial infections (antibiotics), viral infections (antiviral), neuronal proliferation, cancer metastasis and apoptosis [8–10]. Additionally, carbohydrate derivatives

(including chitosan) are extensively used as detergent, food, and cosmetics, sweetening agents, cloths, paper, lumber and other variety of other purposes [10–12]. Chitosan is polymeric form of deacetylated chitin with a variety of properties such as immunological activities, low toxicity, wound healing and biodegradability [13, 14]. The chemical structure of chitosan is shown in **Figure 1**.

Similar to most of the carbohydrates, chitosan is rich in functional groups (hydroxyl and amino) it would be a potential inhibitor for metallic corrosion [15, 16]. The amount of amino group in chitosan is determines by degree of deacetylation. Chitosan and its derivatives are important materials having several industrial and biological applications. These materials are gaining attention in food, biomedical, agricultural, environmental and pharmaceutical industries because of their non-toxic, environmental-friendly, non-allergenic and biocompatible nature. Their diverse biological applications include anti-hypertensive, anti-oxidant, anti-diabetic, anti-coagulant, anti-inflammatory, anti-microbial, anti-obesity, anti-cancer and neuro-protective properties [17, 18]. The hydroxyl (-OH) group at 6-position and amino (-NH₂) group at 2-position are the most chemically reactive sites of chitosan for modification procedures. Chitin is natural source of chitosan which is mainly distributed in the shells of crabs and shrimp, in the cell of fungi and cuticles of insects [13, 14]. The chitosan can be derived by N-deacetylation of chitosan using several deacetylation agents. The chitosan and its derivatives are being utilized for variety of purposes because of their biocompatibility, non-toxic nature, high biodegradability, high 1 wound healing behavior and immunological activity, etc. [19–23].

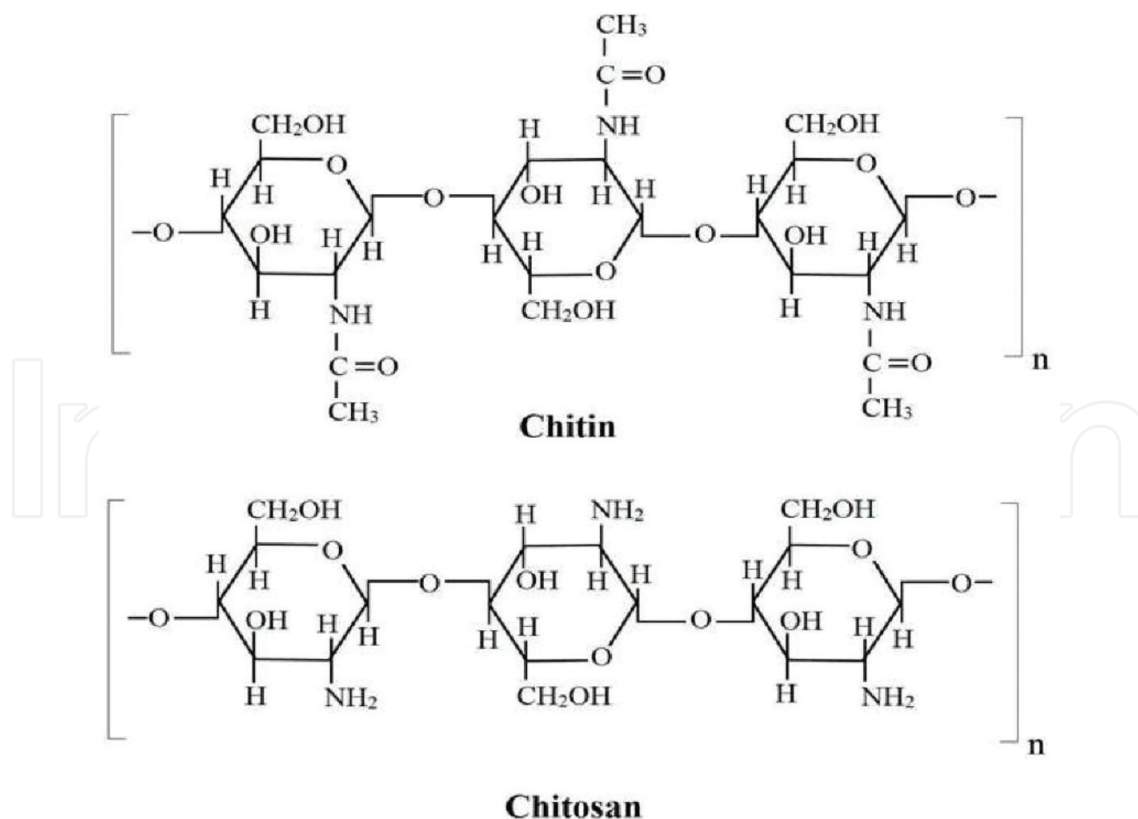


Figure 1. Chemical structure of chitin and chitosan.

2. Main body

Because of their green and environmental friendly nature chitosan and its derivatives are being utilized as effective corrosion inhibitors for metals and alloys for several electrolytic media including HCl, H₂SO₄ and NaCl etc. The corrosion inhibition property of chitosan and its derivatives in correlation with other commonly employed organic and inorganic corrosion inhibitors are presented in **Table 1**. Abd-El-Nabey et al. [24] demonstrated the inhibition properties of chitosan in 0.1 M HCl using potentiodynamic polarization (PDP) and electrochemical impedance spectroscopic (EIS) methods. Chitosan showed the optimum inhibition efficiency of 90% at 0.028 g/L concentration. EIS study revealed that chitosan adsorbs at metal/HCl interface and behaved as interface corrosion inhibitors. PDP study showed that chitosan behaved as mixed type corrosion inhibitor.

The inhibition property of the chitosan on mild steel corrosion in 0.1 M HCl has also been investigated using gravimetric, PDP, EIS, scanning electron microscopy SEM and UV-visible methods [34]. At 60°C temperature chitosan showed 96% inhibition efficiency which drops to 93% on increasing temperature 70°C [34]. Chitosan acted as mixed type corrosion inhibitors as observed by PDP study. Adsorption of the chitosan on mild steel surface obeyed the Langmuir adsorption isotherm. EIS study showed the chitosan acted as interface corrosion inhibitor that is retards the corrosion process by adsorbing on the metal/ electrolyte interface [35–37]. The inhibition property of chitosan for corrosion of copper in 0.5 M HCl has also been studied weight loss, PDP, EIS and electrochemical frequency modulation (EFM) measurements [38]. Chitosan acts as mixed type inhibitor and its adsorption obeyed the Langmuir adsorption isotherm. The high protection ability of the chitosan forced the people working in the field of corrosion to develop and use of chitosan derivatives as corrosion inhibitors. Cheng and his coworkers [13] demonstrated the inhibition property of carboxymethylchitosan (CM-chitosan) as ecofriendly corrosion inhibitors for mild steel in 1 M HCl using weight loss, EIS and PDP techniques. The structure of CM-chitosan is shown in **Figure 2**.

The CM-chitosan showed maximum protection ability of 93% at 200 mg/L concentration. Adsorption of the CM-chitosan on mild steel surface obeyed Langmuir adsorption isotherm. PDP study suggested that CM-chitosan acted as mixed type corrosion inhibitor. In other study [14], these authors studied the effect of cupric (Cu²⁺) ions on corrosion inhibition property of CM-chitosan toward acidic dissolution of mild steel in 1 M HCl. Results showed that CM-chitosan+Cu²⁺ showed better protection ability much more effectively than the inhibiting action of each additive separately. In continuation of this type of works, acetyl thiourea chitosan polymer (ATUCS) was synthesized and investigated as effective inhibitor for mild steel in aerated 0.5 M H₂SO₄ solution using EIS, PDP and SEM methods [19]. The chemical synthesis of ATUCS is shown in **Figure 3**.

Results showed that ATUCS acted as interface corrosion inhibitor and its adsorption on mild steel surface obeyed the Langmuir adsorption isotherm. The ATUCS acted as mixed type corrosion inhibitor. Two formaldehyde based chitosan derivatives based on thiosemicarbazide (TSFCS) and thiocarbohydrazide (TCFCS) (**Figure 4**) were synthesized and investigated as effective corrosion inhibitors for heavy metals [21]. TCFCS behaved as mixed type corrosion inhibitor and showed maximum efficiency of 92% at 60 mg/L concentration.

Type of inhibitors	Name of inhibitor	Nature of metal and electrolyte	Adsorption behavior	Highest efficiency and concentration	Ref.
Organic inhibitors	2, 2'-bis(benzimidazole)	Mild steel/ 1 M HCl	Mixed type/ Langmuir adsorption isotherm	97.8% at 10^{-4} M	[25]
	2, 5-bis (4-methoxyphenyl)-1,3,4-oxadiazole	Mild steel/ 1 M HCl	Mixed type/ Langmuir adsorption isotherm	96.19% at $\times 10^{-4}$ M	[26]
	Pyridine-2-thiol (P2T) and 2- Pyridyl disulfide (2PD)	Mild steel/in flow HCl	Mixed type/ Langmuir adsorption isotherm	More than 98% 200 mg/L	[27]
	4,4-dimethyloxazolidine-2-thione (DMT)	Mild steel/ 1 M HCl	Mixed type/ Langmuir adsorption isotherm	82% at 4×10^{-3} M	[28]
	2-mercapto benzimidazole (2MBI)	Mild steel/ 1 M HCl	Mixed type/ Langmuir adsorption isotherm	98% at 10^{-3} M	[29]
	1,3-dioctadecylimidazolium bromide and N-octadecylpyridinium bromide	Mild steel/ 1 M H ₂ SO ₄	Mixed type/ Langmuir adsorption isotherm	82% and & 88% at 100 ppm	[30]
	Tryptamine	Mild steel/ 0.5 M H ₂ SO ₄	Mixed type/ Langmuir adsorption isotherm	97% at 500 ppm	[31]
	N-Phenyl oxalic dihydrazide (POD-H) and oxalic N-phenylhydr-azide N'-phenylthiosemicarbazide (OPHPT)	Mild steel/ 1 M HCl	Mixed type/ Langmuir adsorption isotherm	92% for OPH-PT and 79% for PODH	[32]
Chitosan based inhibitors	Cysteine	Copper/1 M HCl	Cathodic type/ Langmuir adsorption isotherm	84.13% at 18 mM	[33]
	Chitosan	Al, Mild steel/ 0.1 M HCl	Mixed type	More than 90% at 0.028	[24, 34]

Table 1. Corrosion inhibition efficiencies of some common reported organic and chitosan based corrosion inhibitors in aggressive solution.

The new compounds were characterized and studied by Fourier transform infrared spectroscopy, elemental analysis, thermal gravity analysis and differential scanning calorimetry, and their surface morphologies were determined via scanning electron microscopy. The inhibition effect of two chitosan derivatives namely 2-N,N-diethylbenzene ammonium chloride N-oxoethyl chitosan (compound I), and 12-ammonium chloride N-oxododecan chitosan

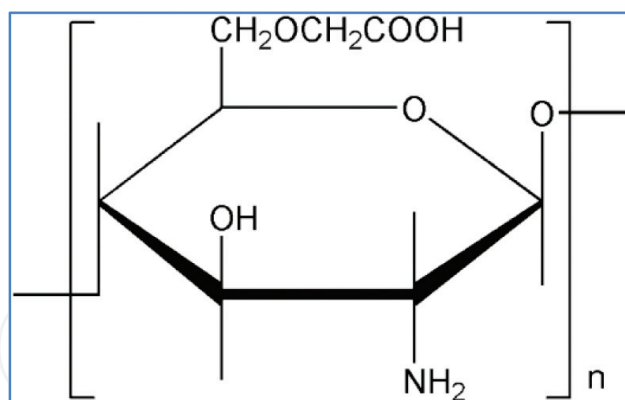


Figure 2. Chemical structure of carboxymethylchitosan (CM-chitosan).

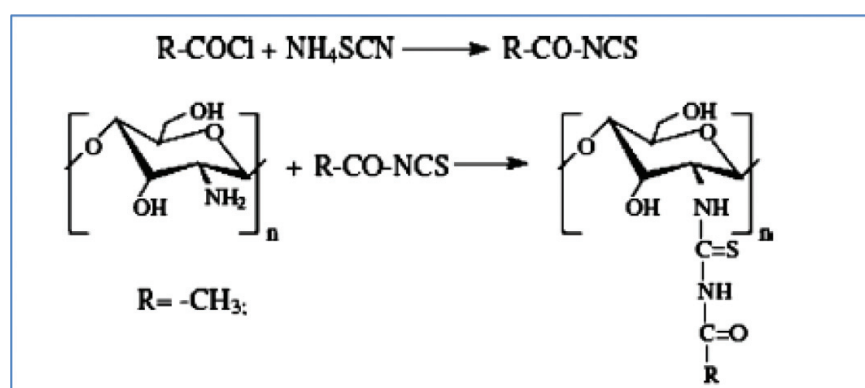


Figure 3. Synthetic scheme for ATUCS.

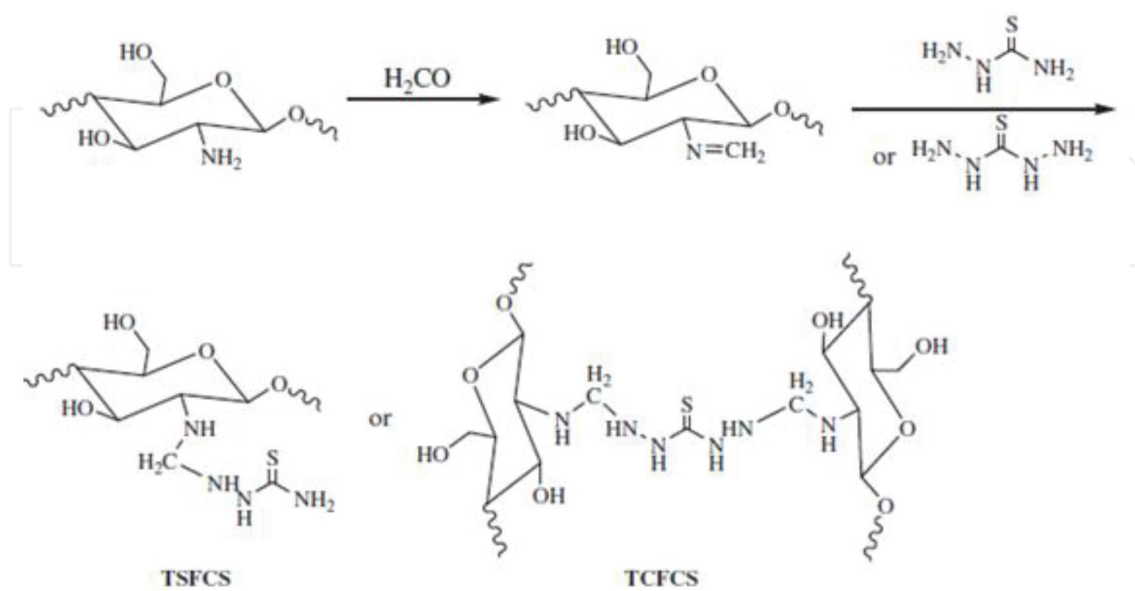


Figure 4. Synthetic scheme for TSFCS and TCFCS.

(compound II) on carbon steel corrosion in 1 M HCl using weigh loss method has been reported [15]. Along with the antibacterial property these compounds showed good corrosion inhibition efficiency toward carbon steel corrosion in acidic medium. The authors claimed that functionalization of the chitosan into compound I and II causes significant change in the physiochemical properties. The enhanced solubility in the polar testing solution (1 M HCl) due to presence of polar amino ($-\text{NH}_2$) and several hydroxyl ($-\text{OH}$) groups the functionalized chitosan molecules adsorb efficiently on the metallic surface and showed good corrosion inhibition efficiency. These compounds inhibit corrosion by adsorption mechanism and their adsorption of compound I and compound II obeyed the Langmuir adsorption isotherm. Compound I showed highest inhibition efficiency among the tested compounds. These authors also observed that the antibacterial activity of chitosan for *Enterococcus faecalis*, *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans* is higher than for its derivatives. Menaka and Subhashini [16] investigated the inhibition effect of chitosan thiophenecarboxaldehyde Schiff base, synthesized by a condensation reaction of the carbonyl group of thiophene 2-carboxaldehyde and free amino groups of chitosan on mild steel in 1 M HCl solution using weight loss, EIS, PDP, EDX, SEM and AFM methods. The synthesized Schiff's base was characterized by UV-visible spectroscopy method. After 12 hrs immersion time, investigated SB showed 92% inhibition efficiency. PDP study showed that SB behaved as mixed corrosion inhibitor and its adsorption on mild steel surface obeyed the Temkin adsorption isotherm. Wan and coworkers [39] synthesized carboxymethylhydroxypropyl chitosan (CHPCS) containing both carboxymethyl and hydroxypropyl groups was investigated as a corrosion inhibitor for mild steel in 1.0 M HCl solution using weight loss, open circuit potential (OCP), potentiodynamic polarization and EIS techniques. The CHPCS showed maximum inhibition efficiency of 95.3% at 1000 ppm concentration. CHPCS acts as mixed type corrosion inhibitor and its adsorption obeys the Langmuir adsorption isotherm. Further, inhibition effect of polyamine grafted chitosan copolymer for Q235 carbon steel in 5% HCl at 25°C [40] and β -Cyclodextrin modified natural chitosan for carbon steel in 0.5 M HCl [41] reported in other studies. Chauhan et al. [42] demonstrated the effect of two functionalized chitosan derivatives namely Chitosan-Thiosemicarbazide (CS-TS) and Chitosan-Thiocarbohydrazide (CS-TCH) as inhibitors for mild steel corrosion in 1 M HCl. The investigation was performed using gravimetric, electrochemical (PDP and EIS), AFM, DFT and MD simulation methods. The authors observed that CS-TCH is better corrosion inhibitors as compared to the CS-TS and showed maximum efficiency of 93.2% at 200 mgL^{-1} concentration. Adsorption of the CS-TS and CS-TCH on the metallic surface obeyed the Langmuir adsorption isotherm. Increase in the polarization resistance (R_p) values for inhibited case revealed that charge transfer from metallic surface to electrolytic solution become difficult owing to the formation of protective film by the CS-TS and CS-TCH molecules. The inhibition effect of two tested chitosan based corrosion inhibitors are shown in **Table 2**. In another study our research group [43], investigated the effect of chitosan as corrosion inhibitor for mild steel in 1 M sulfamic in combination with potassium iodide (KI) using weight loss, electrochemical and surface techniques. Results of the analysis show that presence of KI in the corrosive medium caused significant enhancement in the inhibitive performance of the chitosan. At 200 ppm concentration chitosan showed inhibition performance of 73.8% while in the presence of 5 ppm concentration of KI, inhibition efficiency of chitosan enhanced to 90%. Under both conditions, chitosan acts as mixed type

Inhibitors	Inhibitor Conc. (mg L ⁻¹)	C _R (mg cm ⁻² h ⁻¹)	Surface coverage (θ)	η%
Blank		12.27	—	—
CS-TS	40	5.36	0.5631	56.31
	60	4.99	0.5932	59.32
	80	4.66	0.6201	62.01
	100	4.04	0.6707	67.07
	120	4.03	0.7727	77.27
	140	2.42	0.8027	80.27
	160	1.67	0.8636	86.36
	180	1.47	0.8800	88.00
	200	1.39	0.8864	88.64
CS-TCH	40	5.24	0.5731	57.31
	60	4.75	0.6132	61.32
	80	4.48	0.6352	63.52
	100	3.93	0.6800	68.00
	120	3.53	0.7935	79.35
	140	2.07	0.8315	83.15
	160	1.42	0.8843	88.43
	180	1.23	0.9000	90.00
	200	1.17	0.9043	90.43

Table 2. Weight loss parameters obtained for mild steel in 1 M HCl in the absence and presence of different concentrations of CS-TS and CS-TCH.

corrosion inhibitor and its adsorption obeyed the Langmuir adsorption isotherm. Chitosan acts by adsorbing and blocking the active sites present on the metallic surface. The formation of inhibitive film by chitosan molecule is supported by SEM and AFM analyses.

Besides the use of chitosan and its derivatives as solution phase corrosion inhibitors, few organic and inorganic composites of chitosan have also been used as coating materials for protection of their dissolution in aggressive environments. Pang and Zhitomirsky [44] coated 316 L stainless steel hydroxyapatite-chitosan and characterized them using X-ray diffraction (XRD), thermogravimetric and differential thermal analysis, scanning and transmission electron microscopy, PDP and EIS methods. Electrochemical investigations showed that the obtained coatings provide the corrosion protection of the 316L stainless steel substrates. The heat treatment of the coating at

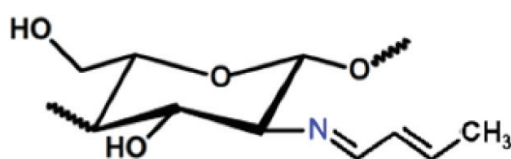


Figure 5. Chemical structure of Ch-Cr-SB.

140°C resulted in an improved corrosion protection. The crotonaldehyde based chitosan Schiff's base derivative designated as Ch-Cr-SB (**Figure 5**) was synthesized and coated on the surface of AZ91E alloy for its anticorrosive behavior [45].

The protection abilities of chitosan and chitosan derived SB was compared in the present study. The electrochemical corrosion behavior has been also studied for Ch-Cr-SB in aerated 3% NaCl solution containing different concentrations of Schiff's base, in the range from 0.03 to 0.075 mM, using different. Results showed that presence of these inhibitors in the corrosive 3% NaCl solution decreases the rate of corrosion. The chitosan electrochemically deposited over the metallic surface from the solution of chitosan in acetic acid. In order to further improve the effectiveness of coating, coated samples were further treated with formaldehyde solution. The coating of chitosan on mild steel surface was measured by FTIR, SEM, PDP and EIS methods [46]. The coating samples showed improvement in the protection ability up to 98.1% at 0.5 M H₂SO₄. A significant increase in the charge transfer resistance was observed for coated mild steel surfaces. The electro-deposition of Zn-chitosan composite coating on mild steel and its corrosion studies has been reported in 3.5% NaCl [47], Self-healing protective coatings with chitosan based pre-layer reservoir [48], chitosan/diclofenac coatings for medical grade stainless steel [49], copper modified chitosan inhibition of AA-2024 corrosion [50], 2-Mercaptobenzothiazole (MBT) based functionalized chitosan-based coatings for active corrosion protection of AA2024 alloy [51], chitosan/Silver nanoparticles composite on St37 steel corrosion in a 15% HCl solution [52], self-healing protective coatings chitosan doped with cerium nitrate for inhibition of aluminum alloy 2024 [53] and Poly(itaconic acid)-modified chitosan for inhibition of aluminum corrosion [54] and other composites materials have also been investigated as effective chitosan based coatings.

3. Conclusions

Chitosan and its derivatives are important class of natural/bio-polymers that have several biological and industrial applications. They are used as anti-oxidant, anti-hypertensive, anti-inflammatory, anti-diabetic, anti-coagulant, anti-obesity, anti-microbial, anti-cancer and neuro-protective agents. Their extensive use and demands based on the facts that these compounds are non-toxic, environmental-friendly, biocompatible, commercially availability and non-allergenic behavior. In view of the above it is concluded that chitosan and its derivatives are "green and sustainable materials" to be used for their various applications. Present chapter deals with the collections of reports available on the corrosion inhibition properties of chitosan and its various derivatives. The ongoing discussion showed that chitosan based compounds represent a green and sustainable class of corrosion inhibitors and can be successfully employed at the place of traditional toxic corrosion inhibitors. These inhibitors can be derived either from biological systems or can be synthesized in laboratories from the hydrolysis of chitin and further functionalization. Chitosan and its derivatives act as efficient solution phase inhibitors for mild steel, carbon steel, copper and aluminum. Generally, there adsorption on metallic surface obeyed the Langmuir adsorption isotherm. PDP study revealed that chitosan and its derivatives behaved as mixed type corrosion

inhibitors. Through electrochemical impedance spectroscopic measurement it can be derived that chitosan and its derivatives behaved as interface type of corrosion inhibitors that is they adsorb at the interface of metal and electrolytic solution. Chitosan and its derivatives have also been used in coating for protection of metallic and alloys dissolution in aggressive media like NaCl and HCl solution.

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