2

REVIEW OF LITERATURE

2.1 General Introduction- Natural polymers as corrosion inhibitor

Literature survey is a concise overview of the research work or investigation including substantive findings, as well as theoretical and methodological contributions to a particular work. The present research work is aimed at synthesizing the eco-friendly Chitosan Schiff bases for corrosion inhibition of mild steel in acid medium. The current extensive review focuses on the eco-friendly naturally occurring polymers as replacement for the toxic organic inhibitors. The review will provide a detailed insight to the use of natural polymers like cellulose, Chitosan, etc and their application towards corrosion inhibition. Consequently focused literature search on the use of natural polymers revealed that few researchers have worked in early1990's. But the urge and need of working in the field of natural polymers started only in recent years. The literature pertaining to the aforesaid themes was analyzed from 2002 to till date. The use of natural polymers and their derivatives in corrosion inhibition of different metals is the focus in the following review section.

The major natural polymers discussed will be Cellulose, starch, natural gums, pectin, Chitosan, etc. including their respective derivatives. Figure 4 represents the percentage of various reported natural polymers that are studied as corrosion inhibitors.

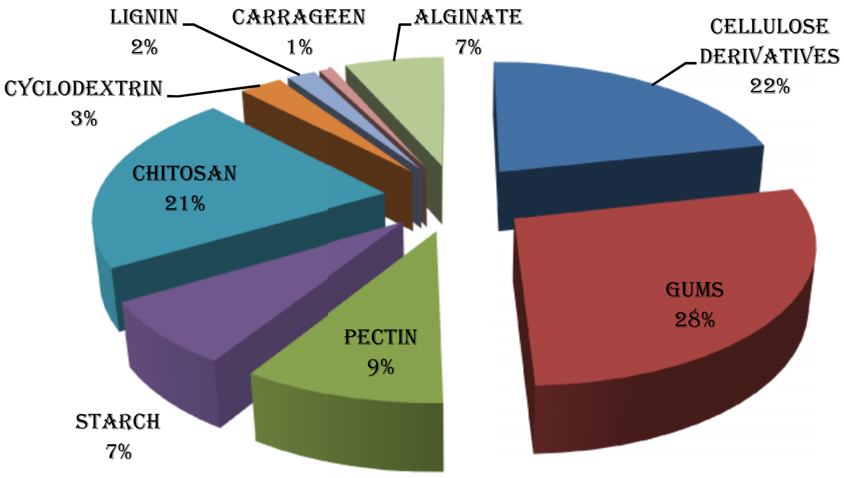

Figure 4 – Pictorial representation of natural polymers reported as corrosion inhibitors

2.2 Cellulose and its derivatives as corrosion inhibitor

Cellulose a biopolymer which is available abundantly in nature is utilized for the corrosion inhibition of mild steel in acid medium. Generally, derivatives of the cellulose are used for corrosion application. Methyl cellulose was tested as corrosion inhibitor for aluminum and aluminum silicon alloys in 0.1M NaOH solution (**Eid *et al.*, 2015**). The performance of this cellulose derivative has been evaluated using potentiostatic polarization, electrochemical impedance spectroscopy (EIS), cyclic voltammetry and potentiodynamic anodic polarization techniques. The adsorption of methyl cellulose on aluminum and Al-Si alloys surfaces in NaOH solution follows Freundlich isotherm. The inhibition action was explained by the formation of a barrier of mass and charge transfer leading to protection of metal surface.

Carboxy methyl cellulose and hydroxyl ethyl cellulose, the derivatives of cellulose have been extensively studied as corrosion inhibitors for metallic corrosion. Carboxy methyl cellulose and hydroxyl ethyl cellulose has the structural features as normal cellulose but with reactive carboxy methyl / hydroxyl ethyl groups attached to the hydroxyl groups of the cellulosic glycopyranyl moiety.

Carboxymethyl cellulose (CMC), a water soluble polymer, had widespread applications as a binder, thickener, stabilizer, suspension and water retaining agent in food industry, pharmaceutical, cosmetic, paper and other industrial areas.

Khairou and El-sayed, 2003 have studied the inhibitive effect of CMC for cadmium corrosion in hydrochloric acid. The major functional groups present in the CMC formed a bridge between the inhibitor molecule and the metal surface resulting in the chemical adsorption obeying Temkin isotherm. Mild steel corrosion inhibition was also investigated using different concentrations of Na-CMC by weight loss and electrochemical techniques (**Bayol *et al.*, 2008**). Inhibition efficiency values obtained from the electrochemical and analytical methods increased with the increase of Na-CMC concentration. The Na-CMC adsorbed on the mild steel surface followed Langmuir adsorption isotherm and the adsorbed metal surface was characterized using SEM

Solomon *et al.*, (2010) have reported Carboxymethyl cellulose (CMC) as a better inhibitor for the corrosion of mild steel in H_2SO_4 solution. The adsorption CMC on mild steel surface was achieved by Langmuir and Dubinin–Radushkevich isotherm models. The synergisitic and antagonisitic influence of halide ions with CMC on corrosion inhibition was studied by **Umoren *et al.*, (2010).** Addition of halide ions to CMC exhibited both antagonistic and synergistic behaviour. Antagonistic effect was observed with addition of Cl^- ions while synergistic effect was noted with I^- ions across all the temperatures studied. Adsorption of native CMC and on addition of halide ions followed Langmuir adsorption isotherm.

Sodium carboxymethyl cellulose (Na-CMC) have been evaluated for the inhibition behaviour of the copper corrosion in simulated cooling water by EIS and polarization measurement (**Li *et al.*, 2015**). Na-CMC offered a maximum IE of 83.34% for the concentration of 5mg/L at 20°C. The inhibitor obeyed Langmuir isotherm and the chemical nature of adsorption was confirmed by the thermodynamic parameters. AFM and FTIR spectral techniques have been used to examine the adsorbed layer.

2.2.1 Studies on CMC with Zn^{2+} binary system

Rajendran *et al.*, (2002) have studied the effect of CMC on the inhibition properties of 1-hydroxyethanole-1/1-diphosphonic acid (HEDP)-Zn^{2+}binarysystem for MS using weight loss techniques in neutral aqueous environment containing 60ppm Cl^-. IE of 40% have been obtained for the formulation of 10 ppm Zn^{2+} and 300ppm HEDP but the IE was reported to increase to 50% after the addition of 10 ppm CMC and to 80 % for 50 ppm of CMC. The inhibition was explained by the formation of Fe^{2+}- HEDP type and Fe^{2+}-CMC complexes/films on the metal surface. The formed protective film has been analyzed using XRD and FTIR. **Anthony *et al.*, (2010)** have investigated CMC-Zn^{2+}binary system for carbon steel in neutral aqueous environment containing 120ppm Cl^- using weight loss, EIS and potentiodynamic polarization techniques. The maximum IE of 97% was obtained for the inhibitor system comprising of 250ppm of CMC and 100ppm of Zn^{2+}. Similar to the results of **Rajendran *et al.*, (2002),** the inhibition action was attributed to the formation of Fe^{2+}-CMC complexes/films. This was confirmed by the EIS and AFM studies. Inhibition effect of CMC (250 ppm) along with Zn^{2+} (250ppm and 50ppm) for aluminium and carbon steel in ground water was studied by **Kalaivani *et al.*, (2013)** using chemical and electrochemical techniques. This inhibitor system also reported to protect the metal surface by the formation of Zn^{2+}-CMC type complex. The adsorbed metal surface was characterized by SEM and AFM. The electrochemical studies also confirmed the formation of complex formation.

2.2.2 Hydroxy ethyl cellulose (HEC) as corrosion inhibitor

HEC, water soluble polymer derived from cellulose is non-toxic and eco-friendly corrosion inhibitor. Like CMC, HEC also find its application as a binder, thickener, stabilizer, suspension and water retaining agent in food industry, pharmaceutical, cosmetic, paper and other industrial areas. The inhibitive performance of HEC for mild steel corrosion in 1.0M HCl and 1.5M HCl was investigated using weight loss techniques (**Arukalam, 2012).**

The maximum inhibition efficiency of 69.617% and 58.145% were reported at the concentration of 2.5×10^{-3}M for 1.0M HCl and 1.5M HCl respectively. The mode of inhibition was attributed to the formation of HEC elastic film on the metal surface. Arukalam along with co-workers studied HEC as corrosion inhibitor for mild steel and aluminium in 0.5 M H_2SO_4 (**Arukalam *et al.*, 2014a)**. The results of weight loss and electrochemical techniques revealed the inhibiting nature of HEC in the acidic environment. Adsorption of HEC followed Langmuir isotherm for aluminium and Freundlich isotherm for mild steel. Authors reported that comparatively, HEC was found to be more effective for mild steel inhibition than for aluminium. They also investigated the performance of HEC on the acidic corrosion of copper in aerated 1M HCl and 0.5M H_2SO_4 by weight loss experiments (**Arukalam *et al.*, 2014b)**. HEC was found to be concentration-dependent to inhibit the corrosion process by adsorbing onto the metal surface.IE increased with the concentration for H_2SO_4 medium whereas the reverse trend was observed for HCl medium. Synergistic addition of KI along with HEC improved the adsorption on the copper surface.

The corrosion inhibition effect of HEC on 1018 c-steel corrosion in 3.5% NaCl solution was investigated using potentiodynamic polarization, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) techniques **El-haddad (2014)**. Electrochemical techniques gave detailed information about the corrosion inhibition effect of HEC and the results from all the technique were in good agreement. The inhibitor adsorption followed Langmuir adsorption and the protective layer formation was confirmed by SEM and EDX analysis.

Arukalam *et al* in 2015 have investigated the inhibition performance of HEC along with hydroxypropyl methylcellulose (HPMC) on the acid corrosion of aluminium by gravimetric, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization Impedance results showed that HEC and HPMC adsorbed on the aluminium surface following Freundlich adsorption isotherm. Polarization measurements also supported the inhibition of the molecules (**Arukalam *et al*.**, **2015a)**. Same research group has reported the inhibitive effect of HEC on mild steel corrosion in 0.5M H_2SO_4 using gravimetric and electrochemical techniques. Mixed type of inhibition was shown by HEC in potentiodynamic measurements and the adsorption was confirmed by the EIS measurements. HEC molecule on the mild steel surface followed the Freundlich adsorption isotherm and the better efficacy was explained by the adsorption of bulky cyclic structure covering the larger surface area. Synergistic effect was also studied using KI and the results were greatly pronounced (**Arukalam *et al.*, 2015b**). **Deyab, 2015** investigated HEC as corrosion inhibitor for zinc-carbon battery using polarization and electrochemical impedance spectroscopy (EIS) measurements. Maximum IE of 92.07% was obtained with 300ppm in 26% NH_4Cl solution. The adsorption of HEC followed Langmuir isotherm and the mechanism of inhibition was attributed to both physisorption and chemisorption. The adsorbed layer on the metal surface was characterized using FTIR and SEM.

2.2.3 Other Cellulose derivatives:

Rajeswari *et al.* (2013) studied the effect of gellan gum and hydroxypropyl cellulose against the acid corrosion of cast iron. Glucose, monomeric unit of the foresaid polysaccharide compounds was also examined for corrosion inhibition for comparison. Techniques like weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) were used to evaluate the inhibition performance of those inhibitors. The inhibition efficiency followed the order **HPC** > **Gellan gum** > **Glucose** at room temperature with slight variations in their IE in all methods employed. The effect of KI addition to the corrosion-inhibition system was also studied to optimize the inhibitor potential of the system. The nature of adsorption i.e predominant physisorption than chemisorption was concluded based on the Langmuir adsorption isotherm and from the results of FTIR and WAXD.

Hydroxypropyl methylcellulose (HPMC) was individually evaluated for the mild steel corrosion inhibition in H_2SO_4 medium by **Arukalam *et al.* (2014c)**. Weight loss, impedance and polarization measurements were used as tools for the appraisal of HPMC as potential inhibitor in the studied environment. The adsorption of the inhibitor molecules was found to obey Langmuir isotherm. Hydroxypropyl methyl cellulose as corrosion inhibitor for aluminium in 0.5 M H_2SO_4 was investigated by the same group of researchers using weight loss and electrochemical techniques. The role of iodide ions to improve the inhibition efficiency was also assessed in this study. The inhibiting effect of the adsorbed HPMC was essentially restricted to cathodic sites on the Al surface because of a stable passive oxide layer covered the anodic sites which hindered HPMC adsorption. The effect of KI addition enhanced the adsorption of inhibitor on Al surface (**Arukalam *et al.*, 2014d**).

Arukalam (2014) also studied the durability tests and synergistic effect of KI of HPMC to showcase the performance of inhibitor. Time-dependent effect of inhibition efficiency showed that inhibition efficiency increased with time but waned after the fourth day. Generally, the KI synergistically improved the inhibition efficiency of HPMC but in this case it also improved the durability of the inhibitor. The inhibitor system followed Freundlich adsorption isotherm suggested the physisorption with tendency towards chemical adsorption. This was further confirmed by polarization and EIS techniques. Yet another work was reported by Arukalam along with co-workers about the assessment of capability of cellulosic derivative, ethyl hydroxyethyl cellulose (EHEC) for mild steel corrosion in 1M H2SO4 using weight loss and quantum chemical techniques. IE showed positive influence on the increasing concentration and showed further increase in trend with the addition of KI due to synergistic effect. Adsorption of EHEC followed modified Langmuir isotherm and the inhibitor protected the metal surface by the formation of chemisorbed layer on the metal surface (**Arukalam *et al*., 2014e**).

Aminated hydroxyethyl cellulose (AHEC) was synthesized, characterized by **Sangeetha *et al*. (2016a)** and evaluated its corrosion inhibition on mild steel in 1M HCl using chemical and electrochemical techniques. The inhibitor provided IE of 93% at 900 ppm concentration which is the highest IE obtained than the other cellulose derivatives discussed so far. The adsorption of AHEC was of physical type obeying Frumkin isotherm. The protective layer formed on the metal surface was confirmed by SEM and AFM studies.

The use of biopolymer derivatives in the development of eco-friendly inhibitors is evident in the study carried out by **Shi and Su (2016).** The derivatives of biopolymer hydroxypropyl methylcellulose (HPMC), hydroxypropyl methylcellulose phthalate (HPMCP), and hydroxypropyl methylcellulose acetate succinate (HPMCAS) film were investigated for the corrosion inhibition characteristics of the high speed metal based on electrochemical impedance spectroscopic measurements and potentiodynamic polarization. The results of the study proved the promising corrosion resistance performance of the HPMC derivative films. The film thickness played a major role and positively correlated to the corrosion resistance ability. On comparing the corrosion resistance performance of the HPMCP and HPMCAS, HPMCP found to be better because of the hydrophobic surface and low moisture content.

2.3 Starch and its derivatives as corrosion inhibitor

Starch is a natural and biodegradable polymer available in abundance at low cost. It is a polysaccharide consisting of large number of glucose units linked by glycosidic bonds. Normally, starch consists of two components namely amylase (linear and helical) and amylopectin (branched) and the composition of the components will vary with the sources from which the polymer is derived. Starch is widely used in different industries such as pharmaceutical, papermaking, textile, and in food preparation. The unique molecular structure with number of hydroxyl groups present in the starch suggested that the compound can be used in corrosion inhibition application also. The use of tapioca starch for the corrosion inhibition of AA6061 aluminium alloy in sea water environment was reported by **Rosliza and Nik (2010).** Gravimetric, potentiodynamic polarization, linear polarization resistance and electrochemical impedance measurements were employed to propose the capability of the inhibitor. Tapioca starch highly reduced the corrosion rate of aluminium alloy and showed better inhibition performance. Langmuir adsorption isotherm was followed and the nature of adsorption of starch on the metal surface was confirmed by SEM and EDS mapping.

Generally, physical or chemical modification of the compounds is quite interesting in terms of developing newer products, to improve the properties of the compounds and also to preserve the available resources. In this virtue, **Bello *et al.* (2010)** modified cassava starches as activated starch and carboxymethylated starch and tested these species for corrosion inhibition of XC 35 carbon steel in 200mgL^{-1} NaCl solutions using EIS studies. Activated starch was found to be better inhibitor than the carboxymethylated starch and the reason for better inhibition was attributed to the interaction of the active groups present in the molecule. The formation of protective film on the metal surface was confirmed by AFM studies.

Mobin *et al.* (2011) investigated the inhibition of mild steel corrosion in acid medium using starch and also studied the effect of corrosion behaviour with addition of surfactants (sodium dodecyl sulfate and cetyl trimethyl ammonium bromide). The results proved that the starch showed better inhibition performance in acid medium and improved results was observed in presence of surfactants. Physical adsorption of starch molecule was proposed and followed Langmuir isotherm. Similar to **Mobin *et al.* (2011),** synergistic effect between starch and 2,6-diphenyl-3-methylpiperidin-4-one (DPMP) was investigated by **Brindha *et al.* (2015a)**. Authors reported that the consistent results were obtained for the inhibitor system [0.4 mM (starch) and 0.2 mM (DPMP)] from all the techniques studied. The corrosion inhibition was attributed to the formation of protective layer which was confirmed by FTIR technique. Quantum calculations computed at B3LYP/6- 31 G (d) level was used as supportive evidence to confirm the inhibition action of starch. The influence of starch to control the corrosion of 6061 aluminum alloy in 0.25M Hydrochloric acid solution was studied by **Charitha and Rao (2015)** using potentiodynamic and electrochemical impedance spectroscopy techniques in the temperature range of 30-50^{o}C. The better inhibition performance was reported at 800ppm of starch at 50 ^{o}C. The nature of inhibition of starch was attributed to the chemical adsorption and obeyed Langmuir isotherm. The adsorption of starch on the metal surface was confirmed by SEM- EDX technique.

More recently, the work on inhibition action of millet starch extracted from the millet grains was reported by **Nwanonenyi *et al.* (2016)**. The author investigated the millet starch for the corrosion inhibition of mild steel in 0.5M H_2SO_4 using both experimental and theoretical methods. The maximum inhibition efficiency 87.14% was obtained for 1.4 g/L millet starch and the IE was increased to 94.03% with the addition of 0.4 g/L of KI. Mixed type of adsorption was confirmed by the polarization results. Theoretical calculations confirmed the ability of the starch molecule to adsorb on the metal surface.

The usage of starch and starch derivatives as inhibitors for protection of different metals is being presented inTable 1.

Table -1 Compilation of starch and starch derivatives used as corrosion inhibitors for different metals in different media

Polymer	Metal /Medium	Optimum conc / Max IE	Adsorption isotherm	Surface analytical techniques
Tapioca starch	AA6061 alloy / seawater	1000ppm / 96%	Langmuir isotherm	SEM and EDS techniques
Millet starch	MS / 0.5 M H_2SO_4	1.4 g/L – 87.14% 1.4 g/L + 0.4 g KI- 94.03%	Langmuir isotherm	-
Starch and Surfactants Additives	MS / 0.1 M H_2SO_4	200ppm – 66.21%	Physical adsorption	-
Modified cassava starches	Carbon steel / 200 mgL^{-1} NaCl solutions.	600 mgL^{-1}	-	AFM
Starch	6061 aluminum alloy / 0.25 M Hydrochloric acid	800 ppm / 58.93	Langmuir adsorption isotherm	SEM-EDX
Starch + 2,6-diphenyl-3-methylpiperidin-4-one (DPMP)	MS / 1N HCl	0.4 mM (starch) and 0.2 mM (DPMP) - 72%	-	FTIR

2.4 Natural gums as corrosion inhibitors for different metals in acidic media

Gums are naturally occurring polysaccharides obtained from the plants source in solid form. These naturally occurring polymers are either water soluble or absorb water and swells up to form a gel like texture in water. It is capable of increasing the solutions viscosity even in presence of low concentrations. Gums are formed by exudation, usually from the stem of a tree but in a few cases from the root. They naturally find application in food and pharmaceutical industries for thickening, suspending and as emulsifying agents. Many researchers have reported the natural gums as effective corrosion inhibitors. The use of gums as corrosion inhibitors for acid corrosion of different metals is summarized below:

Inhibition of Aluminium corrosion in HCl using exudate gum from *Dacroydes edulis* was reported by **Umoren *et al*. (2008a)**. Inhibition efficiency increased with increase in concentration of the *Dacroydes edulis* exudate gum but decreased with increase in temperature which confirmed the physical nature of adsorption. Phytochemical constituents in the exudate played a very vital role in the inhibiting action. The adsorption process for *Dacroydes edulis* exudate gum followed the Temkin adsorption isotherm. The authors also reported exudate gums from *Pachylobus edulis* (PE) and *Raphia hookeri* (RH) as corrosion inhibitors for aluminium in HCl using weight loss and thermometric measurements at 30 – 60°C (**Umoren *et al*., 2008b**). From the results obtained, RH exudate was concluded as an effective inhibitor than PE exudate. The adsorption process of the exudates followed Temkin isotherm (PE) and El-Awady kinetic model (RH).

The corrosion performance of the exudates gum from *Pachylobus edulis* was studied by **Umoren *et al*. (2008c)** for aluminium corrosion in acid medium with and without the addition of halide ions. The IE of 41% was reported for exudates gum and it enhanced to 63% in presence of halide ions. The inhibition effect was explained by the formation of intermediate bridges between the metal surface and the chemical constituents of the gum. Also the enhanced inhibition was attributed to the stabilization of adsorbed halide ions with the gums by electrostatic attraction leading to large surface coverage. **Umoren *et al*. (2009)** have reported the corrosion inhibition of MS in H_2SO_4 in the presence of exudates gum from Raphia hookeri (RH) along with addition of halide ions at 30–60 °C. Results from weight loss and thermometric techniques showed that the performance of RH improved with concentration and not with temperature. Also, the halide ions enhanced the performance of RH due to synergistic effect. The physical adsorption mechanism of RH was approximated with Temkin adsorption isotherm and Kinetic–Thermodynamic Model of El Awady et al. Aluminium corrosion inhibition in the presence of RH was attributed to the adsorption of its phyto-constituents.

Anogessus leocarpus gum (AL gum) was reported to be good adsorption inhibitor for the corrosion of mild steel in HCl solution. Langmuir adsorption isotherm supported the mechanism of charge transfer from the inhibitor to the metal. FTIR studies confirmed the formation Fe- AL complex (**Eddy *et al*., 2011**).

Ameh *et al*. (2012) studied the inhibitive effect of *Ficus glumosa* (FG) gum for mild steel corrosion in H_2SO_4 medium using weight loss, gasometric and thermometric techniques. The results obtained revealed that the gum as a potential adsorption inhibitor. Authors proposed the formation of multiple adsorption layers on the metal surface through the adsorption of active constituents of the *Ficus glumosa* (FG) gum. *Ficus platyphylla* gum was investigated by **Eddy *et al*. (2012a)** for the mild steel corrosion in HCl solution using gravimetric and gasometric methods. The inhibitor worked moderately in this medium which offered the maximum IE of 78% for the concentration of 0.5 g/L. Similar results were obtained in all the methods tested. Langmuir adsorption isotherm supported the physical adsorption and FTIR studies confirmed the adsorbed layer on the metal surface. **Eddy *et al*. (2012b)** investigated the corrosion inhibition potential of the *Daniella Oliverri* (DO) gum exudate for acidic mild steel corrosion using weight loss and FTIR methods. The author stated that the better inhibition efficiency shown by the gum was due to the presence of aromatic, suitable functional groups and heteroatoms in its chemical constituents that facilitated its adsorption. The results obtained obeyed the Langmuir adsorption isotherm model. **Eddy *et al*. (2012b)** investigated the inhibition potential of *Daniella olliverri* (DO) gum exudate using weight loss method for mild steel in acid medium. The results proved that the gum to be an efficient corrosion inhibitor. The exudate protected the metal surface via physical adsorption following Langmuir isotherm model.

The mild steel corrosion inhibition using *Gum Acacia* in different strengths (0.5 M, 1 M, 2 M) of HCl and H_2SO_4 was investigated by **Abu-Dalo *et al*. (2012).** Techniques like weight loss and hydrogen evolution were used to evaluate the inhibition efficiency of *Gum Acacia* and the effect of magnetic field on both the techniques was also studied. The corrosion rate decreased considerably due to adsorption of GA on the metal surface. The authors reported that the magnetic field could influence the inhibition effect of GA to greater extent. FTIR, SEM and XPS techniques were used to confirm the formation of adsorbed layer on the metal surface.

Acacia sieberiana (*AS*) gum was evaluated for the inhibition of zinc corrosion in H_2SO_4 by **Ameh and Eddy (2014)** using weight loss and thermometric methods. The effective efficiency was obtained at the concentration of 0.5 g/L and inhibitive action was attributed to the formation of protective layer on the metal surface. The adsorption data found to fit both Langmuir and Frumkin isotherm. The protective layer formation was confirmed by SEM analysis.

Another exudate gum, *Commiphora africana* was also reported for aluminium corrosion inhibition in acid medium by **Eddy *et al*. (2014)**. The weight loss of the aluminium in presence of inhibitor was reduced but at the higher temperature the increase in weight loss was observed. The adsorption behaviour of the inhibitor was confirmed by Langmuir isotherm and FTIR studies. Mild steel corrosion inhibition by *Anarcadium occidentale* gum (Cashew gum) was reported by **Arthur *et al*. (2014)**. The evaluation of the inhibitor was carried out using weight loss methods. Corrosion rate of the mild steel decreased with the increase in concentration of cashew gum and reached a maximum IE at the concentration of 1.0 g/L. The adsorption behaviour obeyed Langmuir isotherm which supported physisorption of the inhibitor molecule.

The inhibition effect of Gum Arabic (GA) on the corrosion of API 5L X42 pipeline steel in 1M HCl solution was investigated for the first time by **Bentrah *et al.* (2014)** using electrochemical impedance spectroscopy and potentiodynamic polarization curves. The results showed that GA as a good inhibitor in 1M HCl. The maximum inhibition efficiency obtained was 92% at 2 g L^{-1}. The adsorption of GA on pipeline API 5L X42 steel surface obeyed Langmuir adsorption isotherm, and involved physical adsorption. Polarization curves revealed that GA acted as a mixed-type inhibitor in hydrochloric acid.

A binary inhibitor system *of Azadirachta indica* gum and four different substituted piperidin-4-one derivatives was reported for the corrosion protection of mild steel in HCl medium (**Brindha and Mallika, 2015**). The inhibition studies of the system were evaluated by means of weight loss and electrochemical methods. The results revealed that the protection level of *Azadirachta indica* gum depended on the conformation of piperidin-4-one derivatives. FTIR studies were used to confirm the adsorbed layers on the metal surface. The authors also reported the inhibition performance of gum exudate of *Araucaria columnaris* (AC) for mild steel corrosion in 1M H_2SO_4 and further studied the synergistic effect with halides and metal cations. The maximum IE of the gum was at 400ppm and inhibition was attributed to the adsorption at the electrode/solution interface. The addition of halides and metal cations enhanced the IE and endorsed the complex formation between the gum and the metal (**Brindha *et al.*, 2015b**).

Mobin and Rizvi (2016) investigated Xanthum gum (XG) as corrosion inhibitor for mild steel in HCl medium. Using weight loss, electrochemical methods, quantum chemical calculations, scanning electron microscopy (SEM), and UV–visible spectrophotometry, the authors claimed that the XG gum inhibited the corrosion process by adsorbing onto metal surface. The authors also pointed out that the addition of surfactant (sodium dodecyl sulfate, cetyl pyridinium chloride and Triton X-100) synergistically improved the efficiency of XG. The adsorption of inhibitor on mild steel surface obeyed Langmuir adsorption isotherm and the existence of (XG+ surfactant) protective layer formed on the metal surface was confirmed by SEM and EDX results.

Ameh (2015) carried out the comparative study of the exudate gums of *Albizia ferruginea (AF) and Khaya senegalensis (KS)* for the corrosion inhibition of mild steel. Weight loss and gasometric methods were used to evaluate the effect of inhibition and the results proved them to be better inhibitors. On comparison, maximum inhibition efficiency was found in Khaya senegalensis with 82.56% inhibition efficiency at 0.5% g/L concentration of the gum. The better performance was attributed to the fact that more compounds with heteroatoms were identified in the GCMS spectrum of KS gum compared to the AF gum. These compounds may have enhanced their adsorption on the metal surface and inhibited the metal from corrosion.

The maximum IE obtained at the optimum concentration of the reported natural gums as acidic corrosion inhibitor for different metals are consolidated and presented in the Table 2.

Table 2 - Consolidated list of natural gums used as corrosion inhibitors for different metals in acidic medium

Polymer	Metal – Medium	Optimum conc - Max IE
Acacia Sieberiana (AS) Gum	Zinc- H_2SO_4	0.5 g/L – 57.93%
Daniella Oliverri Gum Exudate	MS - 0.1 M HCl	0.5 g/L – 72.36%
Exudate Gum from Pachylobus edulis + halide ions	Aluminium - 0.1 M HCl	63.00% (0.5g/L of exudate gum + 0.06M KI)
Exudate Gum from Acacia Trees	MS - (0.5 M, 1.0 M, 2.0 M HCl and H_2SO_4)	0.60 mg/L
Anogessus Leocarpus (Al) Gum	MS - 0.1 M HCl	0.5 g/L – 76%
Exudate Gum from Dacroydes edulis	Aluminium - 2 M HCl	0.5 g/L – 42%
Exudates gums from Pachylobus edulis (PE) and Raphia hookeri (RH)	Aluminium - 0.1 M HCl	0.5 g/L – PE- 41% RH -56%
Commiphora africana Gum	Aluminium - 0.1 M HCl	0.5 g/L – 84%
Azadirachta indica gum	MS -1 M HCl	0.08 g/ L
Exudates of Araucaria columnaris	MS -1 M H_2SO_4	400 ppm / 55.1
Anacardium occidentale Gum	MS - 0.1 M H_2SO_4	1.0 g/250cm3 - 88.74%
Ficus glumosa gum	MS – 2 M H_2SO_4	0.5 g/L – 71.11%
Ficus Platyphylla Gum	MS - 0.1 M HCl	0.5 g/L – 78.22%
xanthan gum +Surfactant	MS – 1 M HCl	
exudate gum from Raphia hookeri (RH) + halide additives	MS - 0.1 M H_2SO_4	0.5 g/L – 75.2%
Gum Exudates from Khaya senegalensis and Albizia ferruginea	MS - 0.1 M HCl	0.5 g/L KS– 82.56% AF- 66.80%
Iraqi Apricot Tree Gum	MS -1 M HCl	0.3 g/L – 73.60%
Xanthan gum and xanthan gum-graft-poly(acrylamide) (XG-g-PAM)	MS -15% HCl	0.5 g/L XG- 90.8% XG-g-PAM-93.18%
Gum Arabic	API 5L X42 pipeline steel – 1 M HCl	2 g/ L- 92%

Biswas *et al*. (2015) have recently reported the inhibition effect of Xanthan exudate gum and its graft polyacrylamide co-polymer on MS corrosion in a very high concentration of acid (15% HCl) using chemical, electrochemical and surface analytical techniques. In all the techniques used in this study, IE increased with inhibitor concentration and exhibited 92% of inhibition efficiency which was remarkably higher for the corrodent concentration (15% HCl). The gum inhibition system acted as a mixed type inhibitor with molecular adsorption at the metal surface initiating corrosion inhibition which was confirmed by SEM analysis. Improved inhibition was revealed in the presence of polyacrylamide. Inhibition mechanism was elucidated by means of thermodynamic and kinetic parameters and Xanthan gum adsorption and in combination with the copolymer on the metal surface followed Langmuir isotherm model. Authors also correlated the experimental results with theoretical evaluation of associated monomeric units using DFT in order to correlate inhibitor molecular structure with corrosion inhibition.

Recently, **Alwan and Mahdi (2016)** reported Iraqi apricot tree gum Arabic as corrosion inhibitor for mild steel substrate in 1 M HCl. Weight loss method was used to predict the efficiency of the inhibitor on corrosion of mild steel in a temperature range of 17–40 ^{o}C. The results showed that the IE increased with increase in concentration and temperature. The adsorption parameters were found to obey isotherms like Temkin, Langmuir and Freundlich.

2.5 Pectin derivatives as corrosion inhibitors

Pectin is a structural heteropolysaccharide present in the primary cell walls of terrestrial plants and contains large amount of poly(D-galacturonic acid) bonded via α-1,4-glycosidic linkage. It is mainly extracted from citrus fruits and other fruits including apples and berries. It is used in food industry as a gelling agent, particularly in jams and jellies. It is also used as a stabilizer in fruit juices and milk drinks, and as a source of dietary fiber (**Umoren *et al*., 2015**). The unique properties of pectin like polyfunctionality, biodegradable nature, flexible structural network, non toxicity, and low production costs nominated it as an eco-friendly corrosion inhibitor. **Fares *et al*. (2012a)** have studied the inhibition performance of Aluminium corrosion using pectin in different acid media (0.5-2 M HCl). The maximum IE of 91% was obtained for concentration of 8.0 g/L at 10 ^{o}C and the efficiency decreased at higher temperatures. The metallic defects caused by corrosion were highly diminished in presence of pectin and the defect free surface was confirmed by SEM analysis. Adsorption of pectin macromolecules on Aluminium surface followed Langmuir isotherm. Anionic polyelectrolyte pectate was tested for the corrosion inhibition of Aluminium in hydrochloric acid using gasometric and weight loss techniques by **Hassan and Zaafarany (2013)**. The corrosion rate of the aluminium was reduced in presence of pectate molecule and efficiency was assumed due to the adsorption of the functional group present in them on the metal surface. Pectate adsorption followed Langmuir adsorption isotherm. Pectin was used for the mild steel corrosion inhibition by **Fiori-Bimbi *et al.* (2015)** and the performance of the inhibitor was evaluated using weight loss and electrochemical methods. Weight loss results revealed that 2.0g/L was the best concentration exhibiting 90% efficiency. Electrochemical studies revealed that pectin as mixed type inhibitor. The geometric blocking effect of Fe-$^{2+}$ pectin complexes was confirmed using UV spectral analysis.

Pectin-g-polyacrylamide (Pec-g-PAAm) and pectin-g-polyacrylic acid (Pec-g-PAA) were synthesized by **Geethanjali *et al.*, (2014)** and their corrosion behaviour was electrochemically evaluated for mild steel in 3.5% NaCl. These polymers inhibited the mild steel surface with IE of about 85%.The adsorption model followed was Langmuir isotherm. Synergistic mixture of pectin along with propyl phosphonic acid (PPA) and Zn^{2+} ions was evaluated as corrosion inhibitor for carbon steel in aqueous solution (containing 60 ppm Cl^{-1}ions) using weight loss and electrochemical techniques. Addition of pectin as synergistic compound highly reduced the amount of Zn ions and PPA. Better inhibition efficiency of 94 % was obtained for the investigated mixture. The protective film responsible for the corrosion inhibition was examined using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) analysis (**Prabhakaran *et al.*, 2014**).

Pectin was reported as an inhibitor for X60 pipeline steel corrosion in acidic environment by **Umoren *et al.*, (2015)**. Electrochemical and chemical techniques were used to monitor the corrosion process. The surface analysis approach was employed to evaluate the potential of pectin as an effective inhibitor. The results showed that pectin acted as a good inhibitor for acid-induced corrosion of X60 steel. The corrosion inhibition effect was found to be inhibitor concentration and temperature dependent; inhibition efficiency increased with increasing pectin concentration and solution temperature. Potentiodynamic polarization studies revealed the mixed-type inhibition of pectin. Adsorption of pectin molecules onto the steel surface was approximated by the Langmuir adsorption isotherm model. SEM surface analysis and contact angle measurement results clearly pointed the significant influence of inhibitor concentration on the corrosion inhibition effect. Quantum chemical calculation results provided useful insights into the active sites and reactivity parameters governing the activity of pectin as a good corrosion inhibitor for X60 steel.

Different concentrations of pectin extracted from opuntia cladodes were used as inhibitor for mild steel corrosion in 1 M HCl. Weight loss and electrochemical methods were employed and the results revealed that the pectin extract performed as a better inhibitor showing 96% of IE at 1 g/L of concentration. Pectin molecules adsorbed on the metal surface obeyed Langmuir isotherm and the film formation reduced the metal corrosion (**Saidi *et al.*, 2015**).

Most recently, application of pectin as tin corrosion inhibitor was reported by **Grassino *et al.*, (2016).** Authors extracted pectin from tomato peel samples. The high quality of the pectin was confirmed by physico chemical tests and structural characterizations. Further they studied the corrosion inhibition performance using electrochemical measurements for tin in electrolyte solution (2% NaCl, 1%acetic acid and 0.5% citric acid). The inhibitor acted efficiently at very low concentration providing 73% of IE. The better inhibition action of pectin has been explained by the formation of tin complexes at the tin surface as physical barrier preventing the corrosion.

2.6 Alginates as corrosion inhibitors

Alginates are acid-type anionic polysaccharides which is the principal component in the colloidal gum found in the cell walls of algae and seaweeds. Alginate is a group of sugars also called alginic acid or algin; they are linear copolymers with covalently bound (1-4)-linked ß-D-mannuronate and C-5 epimer α-L-guluronate homopolymeric blocks . Alginates have numerous forms depending on their metal ions present (principally alkali or alkaline metals). Sodium (Na) alginate extracts from brown seaweeds are widely deployed as dental gelling agents, and their usage is common in pharmaceutical and food industries. K and Ca alginates are used as industrial alternatives to Na alginates while the organic forms of this compound have also been synthesized for various applications. These alginates have also been reported as corrosion inhibitors for different metals.

Zaafarany (2013) studied the influence of water-soluble anionic polyelectrolytes viz alginates (Alg) and pectates (Pect) on the aluminum corrosion in alkaline medium by gasometric and weight-loss techniques. The results showed that the addition of these polyelectrolytes highly reduced the dissolution rate of Al in NaOH. Factors like inhibitor concentration, corrosive medium, temperature and structure of the inhibitor affecting the corrosion process were also studied. The inhibition efficiency was greater for pectates compared to alginates. This was attributed to the geometrical configuration of pectates. **Hassan *et al.*, (2013)** reinvestigated the work for detailed information about the corrosion behaviour and mechanism. The inhibition action of the tested inhibitors obeyed both Langmuir and Freundlich isotherms models. The inhibition efficiency was increased with increase in inhibitor's concentration and decreased at higher temperature, suggested physical adsorption mechanism. Corrosion mechanism was proposed with the help of kinetic parameters.

The corrosion inhibition and adsorption behavior of sodium alginate on AZ31 magnesium alloy in 3.5wt% sodium chloride solution was investigated by **Dang *et al*., (2015)**. The results showed effective inhibition of sodium alginate for the corrosion of AZ31 magnesium alloy. Maximum IE of 90.00% was obtained with 500ppm of sodium alginate. The inhibition was attributed to the adsorption of sodium alginate on the bare magnesium alloy surface.

Tawfik (2016) synthesized Alginate surfactant derivatives and tested their influence on carbon steel in 1 M HCl using gravimetric and electrochemical techniques. Maximum IE of 96.27% was obtained for the concentration of $5*10^{-3}$ M. Potentiodynamic polarization results revealed that alginate derivatives as mixed-type corrosion inhibitors with predominant control of the cathodic reaction. The inhibitor showed positive influence on the temperature effect. Langmuir isotherm described the adsorption nature of the inhibitor. The adsorptive layer on the metal surface was analyzed by SEM and EDX analysis.

Hou *et al*., (2016) have reported the mixture of sodium alginate (SA) and sodium phosphate (SP) as corrosion inhibitor for magnesium (Mg) alloy AZ31 in 3.5 wt% NaCl medium. Their inhibiting effect was investigated by weight loss and electrochemical measurements. Results revealed the inhibiting effect of SA and SP with respect to Mg alloy AZ31 and anoptimal inhibition efficiency was yielded for the inhibitor concentration of 0.05 wt% SA and 0.15 wt% SP. Base on SEM-EDS examination, the authors have suggested promising combined inhibiting mechanism to the formation of a compact, homogeneous and protective composite film.

2.7 Other natural polymers as corrosion inhibitors

Other natural polymers like carrageenan, dextrin and cyclodextrin, lignin were also reported as corrosion inhibitors.

Carrageenan is a group of gel-like and mostly linear polysaccharides commonly found in seaweeds. They are used as food thickeners and stabilizers. **Fares *et al*. (2012b)** reported that i-Carrageenan a natural polymer along with pefloxacin mesylate mediator as corrosion inhibitor for aluminum in acidic medium. IE considerably improved in presence of the mediator and the maximum inhibition was obtained with 1600 ppm of polymer and 400 ppm of mediator. Activation energy of corrosion and other thermodynamic parameters of the adsorption process revealed better and well-ordered physical adsorption layers in presence of pefloxacin. Adsorption of carrageenan in presence of mediator was found to obey Langmuir isotherm. Scanning electron micrographs (SEM) had demonstrated smooth, glossy, and relatively coherent adsorption layers of the inhibitor on the metal surface in aqueous solution.

Lignin is one of the most abundant naturally occurring polymers and is a by-product of pulping processes which are normally discarded in large quantities. Due to the high content of diverse functional groups like carbonyls, carboxyls, phenolic and aliphatic-OH, along with phenyl propanoid structure, lignin can act as a neutralizer or inhibitor in the oxidation processes. The antioxidant properties exhibited by lignin can lead to broader applications as anti-microbial, anti-aging agent and corrosion inhibitor.

Hussin *et al*. (2015) modified lignin by incorporating aromatic scavengers (2-naphthol: AHN EOL and 1,8-dihydroxyanthraquinone: AHD EOL) during delignification process. The modified lignin with high phenolic –OH content has increased solubility and anti oxidant activity. The inhibitive property of these modified lignins was tested for corrosion inhibition of mild steel in 0.5 M HCl using electrochemical methods. Both AHN EOL and AHD EOL lignin exhibited better corrosion inhibition properties than the unmodified organosolv lignin (EOL). High percentage of inhibition efficiency (% IE) was obtained at the concentration of 500 ppm IE decreased with the increase in temperature. Results obtained also revealed that lignins are physically adsorbed onto the metal surface.

Cyclodextrin is a cyclic oligosaccharide consisting of glucose units linked by α-1,4 glucosidic bonds. The most abundant cyclodextrins are α-, β-, and γ-cyclodextrin, which are comprised of six, seven, and eight glucose units, respectively. Among the cyclodextrins, β-cyclodextrin (β-CD) has been widely used as the ‘‘supramolecular host’’ in the areas of biotechnology, pharmaceutical preparation, purification, and polymer science. They exhibited good corrosion inhibition property due to the presence of hetero atoms and polymeric structure. The inhibition effect of supramolecular polymer [poly (AA–AM–AMPS–MAH–β-CD)] for P110 carbon steel in 0.5 M hydrochloric acid was investigated by **He *et al*. (2014)** using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The obtained polarization curves revealed that the supramolecular polymer behaved as a mixed-type inhibitor.

β-cyclodextrin modified natural chitosan was investigated for inhibition of carbon steel corrosion in 0.5 M hydrochloric acid by weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results indicated that the inhibition efficiency increased with the inhibitor concentration at 298 K. The experimental results revealed that β-CD−chitosan (β- cyclodextrin modified chitosan) was a mixed inhibitor exhibiting inhibition efficiency of 96.02%. Adsorption of β-CD−chitosan followed Langmuir adsorption isotherm which involved both physisorption and chemisorption. The results of SEM and EDS studies further confirmed the inhibition action of the polymer (**Li *et al.*, 2016**).

The inhibition behavior of the divinyl sulfone cross-linked ß-cyclodextrin polymer (ß-CDS-P) in 3.5 M KOH on Zn anode was studied using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy measurements. Results showed that the increase in inhibition efficiency with the increase in the concentration of inhibitor and decreased with rise in temperature. The inhibition was proven to occur via adsorption of ß CDS-P on the Zn surface which was approximated by Langmuir adsorption isotherm model. The slight shift of corrosion potential (E_{corr}) to more negative values indicated the inhibitive action of the compound in tested medium. X-ray spectroscopy analysis (EDX) and scanning electron microscopy observations confirmed the presence of a good protective film on the Zn surface (**Abd El-Lateef and Elremaily, 2016**).

2.8 Chitosan and its derivatives as corrosion inhibitor for different metals in different media

Chitin is a natural polysaccharide found particularly in the shells of crustaceans such as crab and shrimp, the cuticles of insects and the cell walls of fungi. Chitosan is the N-deacetylated product of chitin and an attractive material because of its properties such as immunological activity, wound healing, biocompatibility, low toxicity, and biodegradability. Chitosan is a polysaccharide bearing-(1-4)-linked N-acetyl-d-glucosamine units as its monomeric moiety. Chitosan is also employed in the textile, paper and food industries for various applications. Chitosan's anticorrosion ability could be drawn from its molecular structure; it bears electron-rich hydroxyl and amino groups capable of bonding with metal surface and subsequent corrosion inhibition via coordinate bonding as these electrons are donated to the empty or partially occupied Fe orbitals. This section summarizes the Chitosan and Chitosan derivatives that were used as corrosion inhibitors for different metal substrates in different media.

El-Haddad (2013) reported chitosan as copper corrosion inhibitor in 0.5 M HCl using weight loss and electrochemical methods. The results revealed that the Chitosan behaved as better inhibitor owing to the adsorption of these molecules at copper/solution interface. Electrochemical techniques indicated the reduction of metal dissolution in presence of Chitosan and the adsorption phenomenon followed Langmuir isotherm. Adsorption of Chitosan on copper surface was confirmed by FTIR and SEM analysis. Quantum calculations revealed the active sites responsible for the inhibition and thus the author reported Chitosan as an efficient inhibitor for copper corrosion. Similarly, **Umoren *et al.*, (2013)** have investigated Chitosan for mild steel corrosion in 0.1 M HCl using gravimetric, potentiodynamic polarization, electrochemical impedance spectroscopy measurements, scanning electron microscopy, and UV–visible analysis. The polymer inhibited corrosion at a very low concentration of 4 μM. Inhibition efficiency increased with temperature with 96 % at 60^oC and then dropped to 93 % at 70^oC. Polarization curves indicated that chitosan functioned as a mixed inhibitor. Impedance results indicated that Chitosan was adsorbed on the metal/ solution interface. Adsorption of chitosan at the mild steel surface was found to be in agreement with Langmuir adsorption isotherm model. Chemical adsorption was proposed as mechanism for corrosion inhibition as there was increase in the trend of protection efficiency with temperature.

The inhibition performance of water soluble chitin (WSC) and its synergistic inhibition with potassium iodide (KI) in 1 M HCl was studied using gravimetric and electrochemical measurements (**Sangeetha *et al.*, 2016b**). From gravimetric measurement it was inferred that there was increase in inhibition efficiency with the increased addition of inhibitor and it further increased to a higher value in the presence of 0.1 % KI. Polarization studies revealed that there was mixed mode of inhibition by WSC. Impedance studies suggested the adsorption of the inhibitor at the interface between mild steel and acidic solution. The adsorption of inhibitor followed Frumkin isotherm. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) confirmed the co- adsorption of KI with WSC on the mild steel surface. FTIR, AFM and XRD indicated the formation of protective film by the inhibitor on the mild steel surface.

2.8.1 Modified Chitosans as corrosion inhibitor

Carboxymenthyl chitosan (CM-chitosan) was reported as corrosion inhibitor for mild steel in 1 M HCl solution evaluated by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. Polarization measurements showed CM-chitosan as a mixed-type inhibitor. The protection efficiency of the inhibitor increased with the inhibitor concentration reached 93% at 200 mg/L but decreased at higher temperature. The adsorption of CM-chitosan on the steel surface obeyed modified Langmuir's isotherm (**Cheng *et al.*, 2007**).

Acetyl thiourea chitosan polymer (ATUCS) was synthesized by **Fekry and Mohamed, (2010)** and evaluated as corrosion inhibitor. The electrochemical behavior of mild steel in naturally aerated 0.5M H_2SO_4 containing different concentrations of

ATUCS has been studied by potentiodynamic polarization and EIS measurements. The corrosion rate decreased with increase in polymer concentration as observed by the corrosion monitoring techniques. Electrochemical impedance spectroscopy measurements under open-circuit conditions confirmed well polarization results. ATUCS has shown very good inhibition efficiency of 94.5% in 0.5 M H_2SO_4 with 0.76mM concentration.

Water soluble Chitosan derivatives 2-N,N-diethylbenzene ammonium chloride N-oxoethyl chitosan (compound I), and 12-ammonium chloride N-oxododecan chitosan (compound II) were tested for the corrosion inhibition of carbon steel (**Hussein *et al.*, 2013**). The inhibition efficiency of compound (I) in 1 M HCl at varying temperature was higher than for chitosan and compound (II).

Aghzzaf *et al.* (2012) developed a novel inhibitor based on heptanoate anions encapsulated within chitosan-modified beidellite. This inhibitor ensured efficient protection of metals against wet corrosion via permanent controllable release of the heptanoate inhibitor. The interlayer Na^+ ions of beidellite from Agadir basin were exchanged with chitosan cations. Exceeding positively charged sites of the biopolymer were compensated by heptanoate anions. Electrochemical impedance spectroscopy (EIS) measurements were carried out on galvanized steel immersed in a 3% NaCl solution. The measurements revealed improvement of corrosion inhibition by chitosan-heptanoate modified beidellite in comparison with commercially available triphosphate aluminium (TPA) anti corrosion pigments. The improved corrosion inhibition was attributed to the continuous leaching of hepatanoate anions as inhibitors. However, the barrier properties of coatings containing chitosan-heptanoate modified beidellite were not as high as those of TPA-based coatings, probably due to insufficient dispersion of the modified beidellite particles within the polymeric matrix.

In continuation with the above investigation, the authors have also studied the corrosion inhibition performances of zinc immersed in 0.1M NaCl solution with and without $CaCl_2$, Na^+ and Ca^{2+} exchanged beidellite (BDT) clay by potentiodynamic measurements and electrochemical impedance spectroscopy. EIS results and surface analysis showed that Ca^{2+}-BDT as a smart inhibitor on zinc surface by modifying the physicochemical parameters of electrolyte near the surface. The exchange reaction in BDT involves the concentration decrease or the "suppression" of Na^+,CO_3^{2-} and Cl^- ions near the zinc surface (**Aghzzaf *et al.*, 2014**).

Li *et al.* (2014) synthesized two new chitosan (CS) derivatives modified with thiosemicarbazide (TSFCS) and thiocarbohydrazide (TCFCS) by a simple method using formaldehyde as linkage. The compounds were characterized and studied by Fourier transform infrared spectroscopy, elemental analysis, thermal gravimetry analysis and differential scanning calorimetry. Their surface morphologies were determined using scanning electron microscopy. The behavior of 304 steel in 2% acetic acid containing inhibitors in different concentrations had been studied by potentiodynamic polarization test. The results showed that the compound TCFCS acted as a mixed-type metal anticorrosion inhibitor by providing inhibition efficiency of 92% with 60 mg/L concentration.

Carboxymethyl chitosan was further modified by **Alsabagh *et al.* (2014)** by introducing a hydrophobic moiety to become surface-active polymers. Seven different hydrophobic substitutions were used to modify chitosan and carboxymethyl chitosan. The surface activity of the substituted compounds depended on the longer chains of the substituents present. Chitosan and its based surfactants were investigated as corrosion inhibitors for carbon steel in 1 M HCl using the potentiodynamic polarization method. The unique property of surface activity along with eco-friendly chitosan and its derivatives made them as better corrosion inhibitors. Among seven derivatives, the carboxymethyl chitosan thio-derivatives achieved maximum corrosion inhibition of 97% due to its more active sites and its high surface activity. Thus the authors have proved that the surface activity and the corrosion inhibition efficiency are related to each other.

N-(2-hydroxy-3-trimethyl ammonium)propyl chitosan chloride (HTACC) was synthesized by **Sangeetha *et al.* (2014)** and the influence of it on mild steel corrosion in 1M HCl was studied using gravimetric and electrochemical experiments. The inhibition efficiency increased with the concentration of the inhibitor and maximum of 98.9% with 500 ppm concentration was obtained. Polarization studies revealed that HTACC as mixed type of inhibitor with predominant cathodic inhibition. Electrochemical impedance studies confirmed that the inhibition was achieved through adsorption on the metal surface. Langmuir isotherm provided the best description on the adsorption nature of the inhibitor and SEM analysis indicated the presence of protective film of inhibitor on the metal surface. The authors have also reported O-fumaryl-chitosan (OFC) as corrosion inhibitor for mild steel in 1M HCl. Its performance was evaluated through corrosion monitoring techniques. Electrochemical measurements supported the inhibition of mild steel by the fumaryl derivative of chitosan. The formation of inhibitor film was assured by surface analytical techniques (**Sangeetha *et al.*, 2015**).

N-vanillyl-O-2'-hydroxypropyl trimethyl ammonium chloride chitosan (VHTC) was synthesized and evaluated for corrosion inhibition performance on Q235 steel in 1M HCl solution. Weight loss, polarization, electrochemical impedance spectroscopy (EIS) and stereo microscope analysis were used to evaluate the inhibition performance. The results showed VHTC as better inhibitor than chitosan. IE of 90% was obtained for the concentration of 200 mg L^{-1}. The polarization study demonstrated VHTC as a mixed-type inhibitor. EIS results revealed the protective film on the Q235 steel surface formed by adsorption of the inhibitor molecules (**Wang *et al.*, 2015**).

Polyamine grafted chitosan copolymers were synthesized for corrosion protection of carbon steel in acidic medium (**Li *et al.*, 2015**). First, methyl acrylate graft chitosan copolymer (CS-MAA) was prepared by Michael addition reaction. CS-MAA was reacted with ethylene diamine (EN) and triethylene tetramine (TN) to synthesize respective polyamine graft polymers CS-MAA-EN and CS-MAA-TN. These copolymers were investigated for corrosion inhibition of Q235 carbon steel using gravimetric measurements, metallographic microscope, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The compounds showed better efficiency in 5% HCl solution.

The synergistic effect of chitosan ascorbate ketimine (CAK) and Cu^{2+} in controlling corrosion of mild steel in 1 M HCl was investigated by **Vimal kumar and Appa Rao (2015)**. Weight-loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies were used to evaluate the corrosion inhibition of the binary system. The results have proved this combination as an effective inhibitor (89%) in controlling corrosion of mild steel in 1 M HCl. Potentiodynamic polarization studies showed that the inhibitor formulation acted as a mixed type inhibitor. The impedance data suggested the formation of protective layer. The surface morphology of the mild steel with protective layer was confirmed by field emission scanning electron microscopy (FE-SEM). Hence the authors concluded that the binary combination of chitosan ascorbate ketimine-Cu^{2+} was a potential inhibitor to control corrosion of mild steel in 1M HCl.

2.8.2 Ionic liquid/Nano Chitosan as corrosion inhibtior

Ionic liquid (IL) of Chitosan was synthesized by the amidation of chitosan p-toluene sulfonate salt with oleic acid. The corrosion inhibitive effect of the prepared polymeric ionic liquid on steel corrosion in acid chloride solution was studied using different electrochemical techniques. Potentiodynamic polarization data revealed that the prepared ionic liquid reduced both dissolution and hydrogen evolution corrosion reactions (**El-mahdy *et al.*, 2015**).

Recently an ionic liquid of Chitosan derivative has been reported as corrosion inhibitor. **Mighed *et al.* (2016)** synthesized a new Chitosan based ionic liquid and investigated for corrosion of X-65 steel in 1M HCl using electrochemical techniques. Results of electrochemical measurements revealed the reduction of metal dissolution in the presence of Chitosan based ionic liquid. Quantum calculation was also carried out to support the adsorption of inhibitor on the metal surface.

Amphiphilic chitosan (CS) nanogels were synthesized in water using surfactant free method by **Atta *et al.* (2015a)**. As per their report, first amidation of CS with unsaturated fatty acids such as oleic and linolenic acids was done to prepare hydrophobic CS. These CS fatty amides were grafted with polyoxyethylene aldehyde monomethyl ether to prepare CSLA-MPEG and CSOA-MPEG amphiphilic CS surfactants. These produced surfactants were converted to nanoparticles by emulsification and by crosslinking. Hydrophobicity, functional group and particle size analysis were carried out using appropriate analytical techniques. Corrosion inhibition studies were investigated using EIS and Tafel methods. Corrosion inhibition of this nanogel was attributed to the formation of protective film carrying chitosan molecules at the metal/solution interface; this was further confirmed by SEM analysis.

Chitosan (Ch) grafted poly(ethylene glycol) (Ch-g-mPEG) and its respective silver nano particles was synthesized and characterized by high-resolution transmission electron microscopy (HRTEM) and energy dispersive analysis of X-rays (EDAX). The synthesized compound and its nanoparticles were examined as corrosion inhibitors for carbon steel in 1 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques (**Hefni *et al.*, 2015**). The results revealed that the inhibition efficiency obtained by Ch-g-mPEG self-assembled on silver nanoparticles was higher than that of Ch-g-mPEG. Potentiodynamic polarization results revealed mixed type corrosion inhibition with predominant control of the cathodic reaction. The results of EIS indicated that the both charge transfer resistance and inhibition efficiency tend to increase with increasing the inhibitor concentration.

2.8.3 Chitosan coatings for corrosion inhibition

Novel corrosion protective self-healing coating was reported by **Zheludkevich *et al.* (2011)**. Coating composed of chitosan-based pre-layer deposited onto the metal surface and a barrier hybrid film. The chitosan film doped with cerium ions served as a reservoir for the corrosion inhibitor. The cerium ions form a complex with the functional groups of Chitosan macromolecules provided a prolonged release of the active agent on demand. The developed bi-layer protective coating was applied to aluminium alloy 2024 and the results obtained from electrochemical impedance spectroscopy clearly demonstrated a superior corrosion protection when the coating with the cerium-doped biopolymer pre-layer was used.

Electrophoretic deposition (EPD) of Chitosan (CS) on mild steel substrates was done with Chitosan– acetic acid solution. Coated samples were immersed in glutaraldehyde for 5 mins to increase the protective ability of Chitosan coating. The electrophoretic deposition (EPD) of Chitosan on mild steel substrates was investigated by FTIR, scanning electron microscopy, potentiodynamic polarization measurements, and electrochemical impedance spectroscopy (EIS). The results of EIS showed that the film stability increased with increasing immersion time in 0.5M H_2SO_4 solution. EIS measurements under open-circuit conditions confirmed well with the polarization results (**Ahmed *et al.*, 2012**).

Carneiro *et al.*, (2012) studied the corrosion behavior of aluminium alloy using Chitosan (CTS) and Chitosan derivatives doped with $Ce(NO_3)_3$ using EIS measurements. The impedance results demonstrated that undoped Chitosan/derivative coatings provided low barrier properties to the metallic substrate whereas the best performance was observed for CTS with 1% wt $Ce(NO_3)_3$ in smaller immersion times and CTS with 10% $Ce(NO_3)_3$ for longer immersion period. Same research group have also reported another active protective coating based on Chitosan (CTS) with 2-mercaptobenzothiazole (MBT). Structural and morphological analysis indicated that amount of MBT within the CTS matrix did not affect the properties of CTS. The performance of CTS-MBT was assessed using electrochemical impedance spectroscopy (EIS) and found to be promising for temporary coating for active corrosion protection (**Carneiro *et al.*, 2013).**

John *et al.* (2015) coated nanostructured Chitosan/ZnO films on mild steel by using sol–gel process and dip coating technique. Out of two techniques, authors reported sol–gel protective coatings as better coatings with excellent chemical stability, oxidation control and enhanced corrosion resistance for metal substrates. Moreover, they stated that the sol–gel method is an environmentally friendly technique of surface protection that can be used for increasing corrosion resistance of metals. Corrosion protection behavior of these coated mild steel substrates in 0.1 N HCl solutions was proved by potentiodynamic polarization studies, linear polarisation studies and electrochemical impedance spectroscopy studies. Also, the inhibition depends up on the number of layers of Chitosan /ZnO films.

Stable Chitosan coatings on mild carbon steel were generated through layer-by-layer (lbl) addition of Chitosan and hydrophobic polymer like poly (vinyl butyral) (PVB) and tested for anti- corrosion performance in 0.3 M salt solution. Corrosion inhibition of Chitosan in the lbl coatings was analyzed using electrochemical impedance spectroscopy (EIS) and Tafel measurements. Sandwiching of Chitosan between two hydrophobic PVB layers enhanced its bonding strength and chelation ability of Chitosan formed a stabilized iron oxide passive layer on the metal surface. The results clearly showed a superior corrosion protection of lbl coatings. SEM and Raman spectra confirmed the formation of passive oxide layer on the metal surface stabilized by Chitosan polymer backbone (**Elizabeth and Vikas, 2015**).

Abd El-Fattah *et al*. (2016) investigated the enhanced corrosion resistance, mechanical and chemical properties of epoxy coating with natural filler Chitosan. The authors had extracted Chitosan from locally collected shrimps and structurally characterized using elemental, FTIR and NMR analysis. Extracted Chitosan was mixed as filler with epoxy coating for the corrosion behaviour using salt spray test. The results showed that the Chitosan − epoxy coating composite showed uniform and lower corrosion rates than that of blank epoxy coating. The mechanical and chemical resistance was also improved and this improvement increased with increase in Chitosan loading up to 15%.

An anticorrosion coating film based on the formation of nanocomposite coating was reported by **Fayyad *et al*. (2016)**. The coating composite consisted of Chitosan (green matrix), oleic acid, and graphene oxide (nano filler). The nanocomposite coating was coated on the surface of carbon steel and the corrosion resistance of the steel was monitored using electrochemical impedance spectroscopy and potentiodynamic polarization. Compared to the pure Chitosan (CS) coating, the corrosion resistance of oleic acid-modified Chitosan/graphene oxide film (CS/GO-OA) increased by 100 folds. The higher resistance of steel was due to the fact that well-dispersed smart grafted nanolayer delayed the penetration rate of corrosive species and thus maintained long term anticorrosive stability.

Chitosan-polypyrrole-SiO_2 composites were synthesized, loaded in epoxy resin and coated on mild steel substrate using powder coating technique (**Ruhi *et al*., 2015**). Interaction and incorporation of the polymer and SiO_2 particles in the Chitosan matrix was confirmed by appropriate techniques. Tafel plots exhibited high corrosion protection efficiency (99.99%) for the epoxy coatings with 2.0 wt% loading of Chitosan-polymer composite. The weight loss measurements and salt spray test results clearly exhibited superior corrosion resistance offered by coatings with Chitosan- polymer composite. The synergistic interaction between the Chitosan and the polypyrrole in the composite improved the corrosion resistance properties of the coatings.

2.8.4 Schiff base derivatives of Chitosan

Chitosan-Crotonaldehyde Schiff's Base (Ch-Cr-SB) was chemically synthesized by **Mohammed and Fekry, (2011)** and coated on AZ91E alloy to study its corrosion resistance performance. The electrochemical corrosion behavior of Ch-Cr-SB in aerated 3% NaCl solution containing different concentrations of Schiff's base (0.03 to 0.075 mM) showed that corrosion rate decreased with increasing the polymer concentration.

New Schiff base derivatives of Chitosan namely chito-oligosaccharide Schiff base (CSB) and carboxymethyl chito- oligosaccharide Schiff base (CM-CSB) were investigated for corrosion inhibition of MS by means of weight loss and electrochemical methods in 3.5% NaCl solution at different concentrations. The results showed IE of CSB increased at first and reached the maximum at 200 mg/L and acted as a mixed type inhibitor whereas CM-CSB showed excellent inhibition performance and behaved as a cathode-based mixed corrosion inhibitor (**Ma *et al.*, 2012**).

2.9 Conclusion

Inhibition efficiency was found to be highly influenced by the concentration of inhibitor, polymer molecular weight, structure of inhibitor, and temperature. The corrosion inhibition mechanism of polymers is primarily attributed to the adsorption through multiple adsorption centres. The overview of the available literature also revealed that the high inhibition performance of the polymers and the film forming ability of the polymers paved the way to use them in corrosion inhibition studies. Moreover, the derivatives of the polymer also equally contributed to the inhibition of corrosion wherein the natural sources can be retained. So, the application of natural polymers and derivatives of natural polymers can be adopted for opening up new frontiers in the corrosion research.