2

REVIEW OF LITERATURE

2.1 Versatile polymers for corrosion inhibition

Corrosion inhibition using inhibitors is a vast research area in which plant materials, organic compounds, inorganic compounds, polymeric compounds etc. are investigated. Though organic compounds have appreciable corrosion mitigating ability, serious environmental issues limits their use. Similarly, the environmental scientists warn that if compounds acquired from a plant source such as plant gums are excessively used as corrosion inhibitors the plant kingdom will slowly diminish; metals will be protected at the cost of destruction of plant kingdom **(Arthur *et al*., 2013)**. These issues can be resolved by using environment-friendly polymers as corrosion inhibitors, as they come with interesting package of long chains of carbon linkages, hetero atoms, biodegradability, biocompatibility, water solubility and ability for effective surface coverage on metallic materials and cost effectiveness. As a consequence, study of polymers as corrosion inhibitors has generated profound interest both from the fundamental and applied stand points.

Several researches reviewed the use of polymers **(Ali fathima Sabirneeza *et al*., 2015; Umoren and Solomon, 2014**), organic compounds (**Kuznetsov, 2012; Loto *et al*., 2012),** natural products **(Raja and Sethuraman, 2008)** and so on as corrosion inhibitors. The section put forth will discuss selective polymers having versatile corrosion inhibition properties i.e. same polymer as corrosion inhibitor for different metals and mediums. The major water soluble polymeric systems discussed are polyacrylic acid, polyacrylamide, polyvinyl alcohol, polyethylene glycol, polyvinyl pyrrolidone, polyethylene imine, polyelectrolytes, polyphosphates and natural polymers. These water soluble polymers have diversified applications including rheology modification, surface coating, personal care and oilfield formulation, corrosion inhibitors, polymer flooding, precious metal-ion recovery and colloid stabilization. Some of the synthetic polymers like PEG, PVA etc., have extensively been used in medicinal field for drug delivery, implants, medical devices and injectable-polymer conjugates.

Figure 4 is a pictorial representation of exploration percentage of various water soluble polymers as derived from the literature.

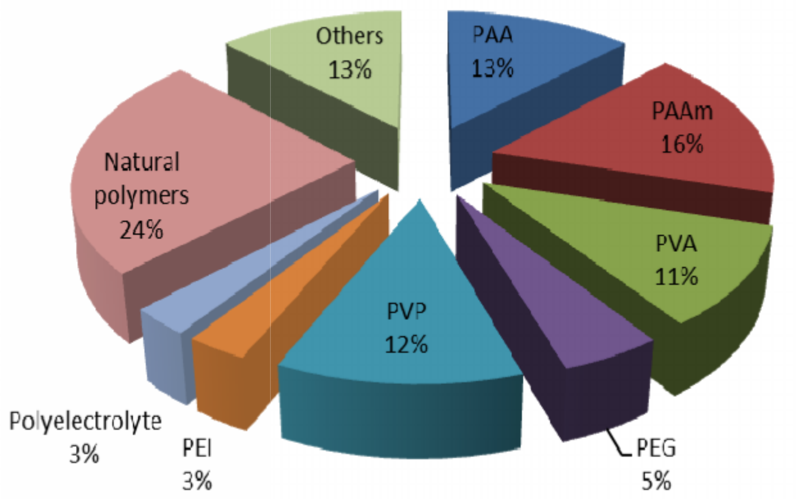


Figure - 4 Distribution ratios of various water soluble polymers studied as corrosion inhibitors

2.2 Polyacrylic acid (PAA)

Acrylic acid is an organic unsaturated acid and is a popular water soluble monomer with significant properties like multi-functionality and good biocompatibility. The monomer can be easily polymerized to produce linear and cross-linked polymers. The linear polymers are soluble in water and the cross-linked polymers can be used as hydrogels. This monomer and its polymer have to be neutralized using certain inorganic bases such as sodium hydroxide and potassium hydroxide to adjust the pH suitable for specific applications.

Grchev *et al.* (1991) conducted electrochemical investigation of adsorption of PAA on Fe, Au and Au/FeOOH-solution. The results show that PAA strongly adsorb on bare iron inhibiting the corrosion process in acidic solutions cathodically. PAA also strongly adsorb on the bare gold-solution interface and provide the same influence on the gold oxide-solution interface.

The inhibitory action of polyacrylic acid and sodium polyacrylate on cadmium in 0.5 M HCl was studied by **Khairou and El-Sayed (2003)**. Polyacrylic acid was found to be a mixed type inhibitor with predominant anodic action while sodium salt of polyacrylic acid exhibited cathodic action only at higher concentrations.

Sodium and potassium (20-100 ppm) salts of polyacrylic acid (PAA) was investigated for inhibition effect on mild steel (MS) and copper (Cu) metals in Jalgaon ground water for 4-24 h in reflux condition (100 °C) and for 5-30 days in ambient condition. The salt deposition was controlled after polymer addition and the effect was well pronounced in hot condition rather than in cold condition. With the potassium salt of PAA, the salt deposition increased with increase in the reflux time for upto 6 h and then decreased during the reflux period of 12-24 h. But in the case of sodium salt of PAA, the deposition increased with minimal concentration (40 ppm) up to 12 h and then the deposition decreased. The Na salt of PAA was concluded as more effective than K salt of PAA in water by **Mishra *et al.* (2005).**

The inhibitive performance of some synthesised water-soluble triblock copolymers (2-(diethylamino) ethyl methacrylate-block-2-(dimethylamino) ethyl methacrylate-block-2-(N morpholino)ethyl methacrylate [PDEA-PDMA-PMEMA] and 2-(diisopropylamino) ethyl methacrylate–block-2-(dimethylamino) ethyl methacrylate-block-2-(N-morpholino) ethyl methacrylate [PDPA-PDMA-PMEMA] of two different molecular weights on the corrosion behaviour of mild steel in 0.5 M HCl were investigated using potentiodynamic polarization, electrochemical impedance spectroscopy and linear polarization methods. The thermodynamic parameters of adsorption calculated revealed the physical nature of adsorption which follows Langmuir isotherm. The inhibition efficiencies of studied triblock copolymers were due to increased dipole moment of repeating units and charges on N atoms that act as active centres for adsorption. The correlation between the inhibition efficiencies and the molecular structure of the triblock polymers has been investigated using quantum chemical parameters obtained by PM3 semi-empirical SCF-MO methods **(Yurt *et al.*, 2007).**

The efficiency of three selected polyacrylic acids (PAAs) with different molecular weights (PAA1 = 1800, PAA2 = 11,000 and PAA3 = 14,000 g mol^{-1}) were tested for Al corrosion in weakly alkaline solutions (pH 8 and 10) at 30 ^{0}C. The determination of Tafel slopes is usually difficult in alkaline solutions because of the non-Tafel behaviour. Hence electrochemical frequency modulation (EFM), a non-destructive corrosion measurement technique was used for determination of corrosion current. The results revealed that the polymers inhibit the alkaline corrosion of Al by mixed mode of adsorption. The adsorption of the three polymers was found to be controlled by isoelectric point (IEP) of aluminium oxide (pH 9). All the polymers provide excellent inhibition efficiency at pH 8, and least efficiency at pH 10 **(Amin *et al.*, 2009).**

Polyacrylic acid (PAA) was tested for its synergistic inhibitive action with potassium iodide on pure iron in 0.5 M H_2SO_4 by **Umoren *et al.* (2010**a**)**. Inhibition efficiency increases with increase in PAA concentration and synergistically enhanced on addition of iodide ions. From the potentiodynamic polarization results the PAA is concluded as a modest cathodic inhibitor, and of PAA adsorption onto the iron surface followed Temkin adsorption isotherm.

FTIR analysis revealed that the synergistic effect was due to the co-adsorption of iodide ions and PAA.

Polyacrylic acid was synthesized, characterized and evaluated for its effectiveness in mitigating calcium carbonate and calcium sulphate scale formation by chemical screening and electrochemical impedance techniques. The gelation, iron dispersion ability and scale inhibition of the polymer were noted and found to have better effect at high temperature and pH when compared with a polyacrylamide based commercial product AQUASUPER B99. Hence the polymer was suggested for use in cooling water applications **(Kavitha *et al.*, 2011).**

The corrosion inhibiting performance of polyacrylic acid on bulk nanocrystalline ingot iron (BNII) fabricated from coarse polycrystalline ingot iron (CPII) by severe rolling technique was studied in 0.1 M H_2SO_4 using electrochemical techniques. BNII was more susceptible to the acid attack and PAA inhibited the acid induced corrosion with greater effect on BNII. The microstructure of the iron samples plays a significant role in corrosion inhibiting performance. The synergistic influence of iodide ions on the inhibition was well pronounced in case of CPII and marginally increased in the case of BNII **(Umoren *et al.*, 2011).**

A water-based acrylic terpolymer methyl methacrylate/butyl acrylate/acrylic acid was synthesised and its inhibiting action on the corrosion for SAE1018 steel in simulated sour petroleum corrosive solution (NACE 1D196) was investigated by AC/DC electrochemical tests. The terpolymer was tested at both static and dynamic conditions, and the maximum inhibitor efficiency was obtained at dynamic conditions **(Azghandi *et al.*, 2012)**.

A water-soluble polymer comprising of low molecular weight PAA and Polyaniline was prepared. The stable dispersion was utilised for retaining the dissolved minerals and preventing the calcium and magnesium scale formation. The polymer blends were studied under various experimental conditions viz. inhibitor concentration, temperature and cycles of concentration. Monthly water analyses were conducted by combining three methods: titration method, Hach method (Model DR/2010), and colorimetric method. The results revealed that the polymer blends effectively inhibited the formation of calcium scale up to 91% and magnesium scale of 82% at 100 ppm, and allowed significantly higher calcite saturation index (CSI) up to 128 when the cycles of concentration reach 4.5 **(Brinis and Samar, 2013).**

A mixture of benzotriazole, chitosan, polyacrylic acid and zinc salt has been investigated as a corrosion and scale inhibitor of A3 carbon steel in cooling water. Static anti-scaling test together with rotary coupon test was used for evaluation of corrosion mitigation.

This phosphate-free inhibitor was found to be superior to the traditional phosphate inhibitor as it does not cause eutrophication **(Zeng and Yan, 2013)**. The IE for controlling the scale and corrosion was determined as 96.14 % and 94.48 % respectively.

An environmentally friendly water-base acrylic terpolymer of methyl methacrylate / Butyl Acrylate / Acrylic acid was evaluated for its corrosion inhibitive performance on MS in 1M HCl. Electrochemical methods were employed for the analysis and a maximum of 97 % IE was obtained for 0.8 mmol/L of the polymer and the IE remained a constant till 45 ^{o}C. This behaviour was attributed to the chemical nature of the adsorption and the data was fitted to Langmuir adsorption isotherm **(Azghandi *et al.*, 2013).**

The mechanism of adsorption of synergistic pair comprising of polyacrylic acid-iodide ions on aluminium in H_2SO_4 was investigated by in-situ AFM microscopy. The morphological studies revealed the more orderly arrangement of the inhibitor molecules on the metal surface thus resulting in a more uniform coverage at potentials below and above potential of zero charge **(Umoren *et al.*, 2014).**

2.3 Polyacrylamide (PAAm)

Acrylamide is a neurotoxin but its polymerized form is safe to handle. Even some of the fried food stuffs develop polyacrylamide on heating. Acrylamide polymers can be synthesized as hydrogels and their sensitivity towards heat, light, pH have been exploited for different applications. In this context, their corrosion protection properties are highlighted below.

The effectiveness of PAAm as corrosion inhibitor for active and passive corrosion was analysed on Fe, Au and Au/FeOOH-solution interface. PAAm was reported to get strongly adsorbed on gold and gold oxide-solution interfaces in neutral solutions, and has negligible influence on the Au/FeOOH interface **(Grchev *et al.*, 1991).**

Rajendran *et al.* (1998) examined the synergistic and antagonistic effect existing between PAAm, phenyl phosphonate and Zn^{2+}. Zn^{2+} has positive synergistic influence with PAAm, PPA and PAAm-PPA systems on MS in neutral medium. But the PAAm-PPA system without Zinc ions showed an antagonistic effect. The author suggested that this may be due to less tendency of the PAAm-PAA to break and form complex with Fe^{2+} on the metal surface. This will lead to the breakage of PAAm-PAA film formed on the metal surface.

A solution of acrylamide and oligo oxyethylene methacrylate was polymerized by free radical polymerization. The corrosion and dissolution protection of steel by the polymer in aerated aqueous solutions was determined under varied medium composition, surface pretreatment conditions and temperature. Good protection efficiency was observed even to an already oxidized steel surface particularly in highly acidic solutions **(Elmorsi, 1999)**.

The effect of molecular weight of polyacrylamide (PAAm) samples (sample A = 3.4 x 10^4, B = 1.52 x 10^4 and C = 1 x 10^4 g mol^{-1}) and poly(propenoyl glycine) (sample D) having the same degree of polymerization as of sample C were analysed for the corrosion inhibition behaviour of tin in 1 M NaCl solution. The results demonstrated that these low molecular weight polymer C inhibit the corrosion excellently than the high molecular weight polymer A. The polymer D showed strongest inhibition efficiency. The adsorption data of polymers were found to fit Flory-Huggins isotherm **(Sayyah *et al.*, 2001)**.

A polymer-polymer complex [(PMAAN/PAAm)c], containing polymethacrylic acid and polyacrylamide were investigated as corrosion inhibitors for mild steel in cooling water systems. Corrosion tests and physicochemical methods were carried out for evaluation of inhibition abilities. The tests were conducted in two different solutions containing low concentration (LC) and high concentration (HC) of ionic species. The polymer complex was effective when added more than 50 ppm in LC solution and 20 ppm in HC solution. The adsorption of the polymers on steel surface was controlled based on the formation of polymer-polymer complexes in LC and scale dispersion based on the formation of polymer-polymer complexes respectively **(Morooka *et al.*, 2001)**.

The synergistic effect of adding iodide ions to polyacrylamide was studied at 30–60 °C on MS in H_2SO_4 using weight loss and hydrogen evolution methods. The adsorption of the inhibitor on the metal surface obeyed Freundlich, Temkin and Flory–Huggins adsorption isotherms at all temperatures studied. The synergism parameter was found to be greater than unity for PAAm and KI combinations. The driving force for the adsorption of the PAAM-KI combination was pertained to reduction in adsorption enthalpy rather than increase in adsorption entropy **(Umoren and Ebenso, 2007).**

Chamovska *et al.* (2007) studied the corrosion protection and/or adsorption of PAAm having a number average molecular weight in the range of 15,000-1,350,000 g mol^{-1} on mild steel and iron (99.99 % Fe) in 3 M HCl at room temperature. Different techniques viz. Spectrophotometry (the phenanthroline method), weight loss method and EIS (Electrochemical Impedance Spectroscopy) were employed for the investigation. The author came out with interesting results as follows:

- The thickness of adsorbed layer was 1.1 nm (for ε r = 15), derived from EIS data corresponds to the polymer segments attached on the metal surface.

- The thickness of adsorbed PAAm layer was 100-200 nm determined by the ellipsometry technique was attributed to the highly voluminous and relatively thick PAAm containing entangled polymer coils.

It was found that the corrosion protection efficiency of the PAAm strongly depends on both the molar concentration of PAAm in the solution and its molecular weight, reaching limiting values between 85 and 96 %.

The anticorrosive property of blended polyacrylamide with polyvinyl pyrrolidone (PVP) on aluminium in hydrochloric acid was determined from weight loss, hydrogen evolution and thermometric techniques. PVP has higher inhibition efficiency than PAAm which may be attributed to the differences in their molecular structures. The blending resulted in enhanced Inhibition efficiency when compared to the individual polymers. The optimum inhibition efficiency was obtained at 3:1 blending ratio for PVP: PA **(Umoren and Ebenso, 2008)**.

Grafting of acrylamide onto a naturally occurring substance or natural polymer is an interesting area followed by few researchers to produce an environmental-friendly polymer. In this context, a lignin terpolymer was prepared by graft-copolymerization of dimethyl diallyl ammonium chloride (DMDAAC) and AAm onto lignin. Highest corrosion inhibition of more than 95 % was reflected in 10 % HCl acid medium at 25 °C and 80 °C. The adsorption kinetics was retrieved from Temkin isotherm and adsorption capability was in reverse proportion to the temperature according to ΔG. The effects of corrosion inhibition are the comprehensive synergistic effect through the graft reaction among lignin, AAm and DMDAAC **(Ren *et al*.. 2008).**

Srivastava *et al*. (2010) grafted polyacrylamide with fenugreek mucilage to assess the anti-corrosive property MS in 0.5 M H_2SO_4 at 35 °C. The IE was observed to be 78 % for 1 ppm concentration of the inhibitor and drastically improved to 96 % at 100 ppm concentration. The polymer controlled the corrosion predominantly at the cathodic sites.

Palmitic acid-PAAm was synthesized using ethylenediamine and dimethyl benzene by condensation process. The investigated inhibitor revealed an IE of 78.1% on X-65 steel in salt water, at a suitable concentration of 0.1 g L^{-1} **(Han and Liu, 2010).**

An electrochemical approach for exhibiting the corrosion inhibition efficiency of PAAm for pure iron in 0.5 M H_2SO_4 was reported. The synergistic influence of iodide ions drastically enhanced the IE from 76 % to 97 %. The adsorption of the inhibitor was found to follow El-Awady kinetic–thermodynamic adsorption isotherm model via chemisorption mechanism **(Umoren *et al*., 2010b).**

A novel core-shell polymer magnetic nanogels was prepared using poly(2-acrylamido-2-methylpropane sulfonic acid) and its copolymers with acrylic acid (AA) and acrylamide. The nanogels having controllable particle size were produced through free radical aqueous polymerization. The corrosion controlling ability of the nanogel polymers was studied using electrochemical techniques. The surface coverage data was fitted to Langmuir isotherm and mechanism of adsorption was concluded as chemisorption **(Atta *et al.*, 2011).**

The effect of iodide ions on the corrosion inhibition of mild steel in 1 M sulfuric acid in the presence of PAAm with different macromolecular weight and polyacrylamide poly4-vinylpyridine (PAM/P4VP) (50%/50%) mixture were studied by weight loss measurements at 18 °C. The obtained results showed that the inhibition efficiency increased with increasing PAM concentration. The macromolecular weight of the PAAm polymer had no effect in the inhibition efficiency. It was also found that inhibition efficiency increased with addition the P4VP solution to PAAm solution. The addition of potassium iodide (KI) enhanced the inhibition efficiency. A synergistic effect was observed between PAAm, KI and (PAAm/P4VP) (50%/50%) mixture **(Mansri *et al.*, 2012).**

The corrosion-inhibiting performance of PAAm in controlling corrosion of carbon steel in ground water under the synergistic influence of Zn^{2+} was reported. The formulation consisting of 250 ppm PAAm and 50 ppm Zn^{2+} provided 98% IE. It is notable that the IE of 250 ppm of PAAm was 86 %. The synergistic platform was achieved by complex formation between Fe^{2+}–PAAm complex and $Zn(OH)_2$, which was confirmed by examining the film using FTIR spectra **(Manimaran *et al.*, 2012).**

A copolymer of polyacrylamide and poly-4-vinyl pyridine was subjected to corrosion inhibition studies for mild steel in 1M H_2SO_4 using weight loss and impedance techniques. The effect of iodide ions as a synergistic additive enhanced the inhibition efficiency of the copolymer (10 mgL-1) from 51 % to a maximal value of 88.60 % for a minimum concentration of the KI (0.008%) **Mansri *et al.* (2013)**.

Magnetite-containing polyaniline-polyacrylamide nanocomposite (PAni-PAAm/Fe_3O_4) was synthesized and reported to have an IE of 91% at 100 ppm concentration of the inhibitor. Potentiodynamic polarization studies clearly showed that the PAni-PAAm/Fe_3O_4 acted as mixed inhibitor **(Geethanjali and Subhashini, 2013).**

2.4 Polyvinyl alcohol (PVA)

Polyvinyl alcohol is a widely used non-toxic water soluble, bio-compatible and biodegradable synthetic polymer. It is suitable for fabricating bio materials due to its hydrophilic nature. The extensive use of PVA in food and pharma industries makes it an undoubted material of choice with environmental value for wide range of applications. Table 1 is a consolidated report of use of PVA as corrosion inhibitors in different combinations on various metals and media, which is discussed in detail in the following sections.

.Table - 1 List of PVA and its derivative polymers used as corrosion inhibitors for various applications

Polymer	Metal	Medium	Type of adsorption isotherms reported
PVA	MS	HCl	Langmuir and physical nature
PVA+ Halide	Al	NaOH	Freundlich and Frumkin
PVA+ Halide	MS	H_2SO_4	Langmuir, Flory-Huggins and Freundlich
PVA PEG	Al Cd	H_2SO_4 0.5M HCl	Temkin adsorption isotherm
PVA PEG	MS	H_2SO_4	Temkin, Freundlich and Langmuir
Halide+ PVA PEG	MS	H_2SO_4	-
Halide + PVA PEG	Al	H_2SO_4	Freundlich
PVA	SS	NaOH	-
PVA+ surfactants	MS	H_2SO_4	-
PVA+ amino acids	MS	HCl	Temkin, Langmuir
PVA+anthranilic PVA+sulfanilic	MS	HCl	Langmuir and Temkin isotherms
PVA+aniline	MS	HCl	Langmuir and Temkin isotherms
PVA+Zn^{2+}	CS	NaCl	-

A formulation consisting of 100 ppm of PVA and 75 ppm of Zn^{2+} provided 81 % IE to Carbon steel immersed in a solution containing 60 ppm of Cl^-. The synergistic influence Zn^{2+} on PVA was also observed. The protective film was UV-fluorescent and contained Fe^{2+}-PVA complex and $Zn(OH)_2$. A maximum IE was obtained when 200 ppm of SDS was added to the PVA-Zn^{2+} system, which is the critical micelle concentration. The oxygen-scavenging effect increased with Na_2SO_3 concentration, because at lower concentrations the transport of the inhibitors played a significant role rather than the removal of dissolved oxygen. With increase in pH and time, the IE of the PVA-Zn^{2+} system decreased **(Rajendran *et al.*, 2005).**

The synergistic influence of halide ions on the anticorrosive property of PVA on MS in H_2SO_4 was investigated at 30-60 °C and the mechanism of action was studied. Gravimetric and gasometric methods were used for the study. A maximum IE of 63 % was obtained for PVA with synergistic additive of 0.05 M potassium iodide **(Umoren *et al.*, 2006[a]).**

PVA and PEG were tested for its corrosion protection efficacy on aluminium in H_2SO_4 at 30–60 ^oC using gravimetric, gasometric, and thermometric techniques. The adsorption of the inhibitors was found to be physical in nature. Thermodynamic parameters calculated for both PEG and PVA proved the spontaneity of the adsorption process. PEG was found to be a better inhibitor than PVA **(Umoren *et al.*, 2007a)**. Similarly the inhibition efficiency and adsorption characteristics of PVA and PEG were evaluated for MS in H_2SO_4 **(Umoren *et al.*, 2006b)**

PVA was investigated for corrosion protection efficiency on aluminium in NaOH at 30 and 40 ^oC. The synergistic influence of halides ions was also reported. The adsorption was physical in nature and was found to obey Freundlich and Frumkin adsorption isotherms. The synergistic co-operative effect that enhances the inhibition efficiency caused by the addition of halide ions to PVA follows the order $Cl^- < Br^- < I^-$ as the radii and electronegativity plays an important role **(Umoren *et al.*, 2007b)**.

The synergistic influence of halides on the corrosion inhibition of aluminium in H_2SO_4 in the presence of PVA and PEG was investigated. The IE decrease with increase in temperature from 30 to 40 °C in the absence and presence of inhibitor and halides. The synergism parameters were evaluated to be greater than unity for both PVA and PEG, indicating the enhanced inhibition efficiency by the addition of halides **(Ebenso *et al.*, 2007)**. Similarly, the effects of PVA and PEG on the corrosion of cadmium in 0.5 M hydrochloric acid were studied by electrochemical impedance spectroscopy and Tafel plot techniques. PVA was found to be an effective inhibitor than PEG **(Khairou and El-Sayed, 2003).**

PVA was analysed for corrosion mitigating effect on the stainless steel in 0.9 % NaOH solution using electrochemical measurements. The uniformly adsorbed layer was confirmed from SEM images and composition of the layer formed on stainless steel surface was estimated using X-ray Photoelectron Spectroscopy (XPS) technique. XPS analysis indicated that the surface layer consists of PVA containing a small amount of other elements, such as Na and Cl **(Samide *et al.*, 2010).**

Poly (vinyl alcohol – aniline) composite was chemically synthesized by free radical polymerization and analysed for its corrosion protection efficiency for MS against corrosion in 1M HCl. A maximum efficiency of 92% was furnished at a concentration of 2000 ppm. The inhibitor was found to be a mixed type from electrochemical studies **(Karthikaiselvi *et al.*, 2010^{a})**.

Sulphanilic acid and anthranilic acid and was polymerized with polyvinyl alcohol as composites and their corrosion inhibition efficiency on mild steel in 1 M HCl medium was studied. Maximum inhibition efficiency was 91 % and 84 % at 6000 ppm concentration at 3 h and 24 h respectively. Langmuir and Temkin isotherms were used to fit the experimental data. Phenomenon of spontaneous physical adsorption was proposed from kinetic and thermodynamic parameters. The inhibitor was reported as a mixed type inhibitor **(Srimathi *et al.*, 2010; Srimathi *et al.*, 2011).**

Amino acid based composites viz. Polyvinyl alcohol-leucine; histidine, threonine and cysteine were synthesized and explored for their corrosion inhibition performances. The results showed that the inhibition efficiency of PVA has been increased on compositing with amino acids. The composite provided more than 95% IE at an optimum concentration of 0.6% by weight. The Temkin and Langmuir adsorption isotherms were proposed. The high performance of the composite compared to PVA was attributed to the presence of polyamino acids, which aids the inhibition synergistically. The adsorbed films were stable up to 60 °C. The mechanism of adsorption is elaborated as follows: The nitrogen/oxygen atom present in the inhibitor molecules can be easily protonated in acidic solution and gets converted into quaternary/oxonium ions. The protonated species can get adsorbed on the cathodic sites of the MS and decrease the hydrogen evolution and/or to anodic sites by forming bridge with chloride ion, thereby decreasing the metal dissolution. The adsorption on anodic sites may also occur through the lone pair electrons of the non-protonated nitrogen/oxygen atoms which will decrease the anodic dissolution of the MS. Hence the high performance of the inhibitor was ascribed to the presence of hetero atoms like nitrogen atom, oxygen atoms, larger molecular size, and linearity in the polymeric chain **(Ali Fathima Sabirneeza *et al.*, 2013; Ali Fathima Sabirneeza, and Subhashini, 2013; Subhashini and Ali Fathima Sabirneeza, 2011; Ali Fathima Sabirneeza and Subhashini, 2014).**

Mobin and Khan (2013) reported the synergistic influence of some surfactants with PVA. When surfactants like sodium dodecyl sulfate (SDS) and cetyl pyridinium chloride were added as synergistic additive to PVA, the inhibition efficiency of 81.41% at 100 mg/L increased to 85%. The cationic cetyl pyridinium ions bind with electronegative oxygen atoms of PVA molecules via a lone pair of electrons, and aid in effective adsorption at the MS surface. The direct PVA-SDS seems to be unfavourable due to repulsion between the anionic nature of SDS and the electronegative oxygen atom of PVA. However, in acidic solution, the protonated OH may strongly interact with SDS ions and favour greater adsorption over the steel surface.

PVA of different molecular weights 14,000, 72,000 and 125,000 g mol^{-1} respectively were investigated for their anticorrosion ability using EIS, linear polarization resistance (LPR) and potentiodynamic polarization (PDP) techniques at 25°C. The IE increases with concentration and molecular weight of the polymer **(Umoren and Gasem, 2013).**

2.5 Polyethylene Glycol (PEG)

Polyethylene glycol is an amphiphilic polymer. Due to the biocompatible nature of PEG, it has been approved by the Food and Drug Administration (FDA) for use in different pharmaceutical applications, food and cosmetics. PEG's of molecular weight less than 1000 are rapidly removed from the body and hence their use in the medicinal application is considerable. Due to the presence of several OH groups and its environment-friendly nature, PEG is well appreciated for corrosion inhibition applications as described below.

Ashassi-Sorkhabi evaluated the inhibition efficiency of Polyethylene glycol having different molecular weights (400, 1000, 4000, and 10,000 g mol^{-1}) for Carbon steel in 3N Sulphuric acid and MS in 0.5 N HCl **(Ashassi-Sorkhabi and Ghalebsaz-Jeddi, 2005; Ashassi-Sorkhabi *et al.*, 2006)**.The inhibition efficiency proportionally increased with concentration in the case of lower molecular weight PEG, and remains constant with increasing concentration in the case of higher molecular weight PEG. This behaviour was attributed to the number of OH groups present in the PEG. The mechanism of physical adsorption was described as follows: PEG was oriented on surface such that the $-CH_2-CH_2-O$ group was faced to the surface with its carbon atoms which constitute the positive pole of the dipole, while oxygen atoms are oriented towards the solution. The author also investigated the influence of 24 kHz ultrasound wave upon the corrosion of carbon steel in 3 N sulphuric acid at 25 ^{o}C in the presence of PEG of different molecular weights (400-10,000 g mol^{-1}). The SEM images confirmed that these inhibitors prevent propagation of pits on the eroded specimen. The inhibition effect of PEG can be attributed to cushioning effect of adsorbed polymers on cavitation phenomenon produced by bubble collapse.

Polyethylene glycol methyl ether (PEGME) was evaluated for the corrosion inhibition of mild steel in 1 N sulphuric acid in relation to the concentration of the inhibitor as well as the temperature using electrochemical polarization (galvanostatic and potentiostatic) techniques. The adsorption characteristics of the polymer were found to follow Langmuir's adsorption isotherm. PEGME was found to be a good passivator from the electrochemical experiments. (around 90% IE) **(Dubey and Singh, 2007).**

An effort was taken to study the efficacy of natural polymer (Gum Arabic (GA)) as a synergistic additive with polyethylene glycol (PEG) using weight loss, hydrogen evolution and thermometric methods at 30–60 ^{o}C. PEG was found to be a better inhibitor for MS corrosion in 0.1 M H_2SO_4 than GA. The effect of halides (KCl, KBr and KI) as a synergistic additive was also studied. The efficiency increased with increase in GA and PEG concentration, and addition of halides increased the IE with increase in temperature. The IE rendered by the halide ions was in the order: $Cl^- < Br^- < I^-$ indicating the significant role of the radii and electronegativity of the halide ions. Phenomenon of chemical adsorption was proposed by fitting the data to Temkin adsorption isotherm **(Umoren *et al.*, 2008).**

Banumathi *et al.* 2010^{a,b}, evaluated the corrosion inhibition properties of polyethylene glycol aniline and anthranilic acid composites. The inhibition efficiencies of PEG composites were low compared to that of PVA composites. The inhibition efficiency of 90 % reached only at very high concentrations above 10000 ppm by weight loss studies.

PEG was modified as carboxylate-ended poly(ethylene glycol) macromonomers, viz. allylpolyethoxy carboxylate (APEC). The modification was carried out by means of a carboxy methylation technique with the obvious advantage of energy conservation. Then, copolymerization of APEC and acrylic acid (AA) lead to AA=APEC copolymers. The AA=APEC acted as a much better inhibitor both for calcium phosphate and calcium sulfate compared to the commercial inhibitors, and it was also an effective inhibitor, even at elevated temperature, pH, Ca^{2+} and Fe^{2+} concentration or in the presence of biocides **(Fu *et al.*, 2012).**

2.6 Polyvinyl pyrrolidone (PVP)

PVP is one of the most interesting derivatives of acetylene chemistry. PVP was initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production. But still its monomer form is toxic to the aquatic life. The description of use of PVP as corrosion inhibitors is given as follows.

Polarization and weight loss studies were conducted for analysing the inhibition efficiency of polyvinylpyrrolidone and polyethylenimine for low carbon steel over a wide concentration range of aqueous phosphoric acid (H_3PO_4) solutions. The polymers controlled both the anodic and cathodic corrosion reactions with emphasis on the former **(Jianguo *et al*., 1995).**

Similarly the corrosion inhibition behaviour of PVP and Polyethylene imine (PEI) were tested on copper in aerated 2M H_2SO_4 was studied by weight loss, potentiodynamic and in situ-surface enhanced Raman scattering techniques. The mechanism for adsorption was proposed as follows: When PVP is added to the acid protonation of the carbonyl group occurs and thus the electronegative oxygen atom could interact with positively charged species of the copper. In the case of PEI, protonation takes place at the nitrogen atom resulting in the net positive charge thereby interacting with the metal. Though the inhibitors retard both anodic and cathodic dissolution of copper, their efficiencies were not much high with values around 62-67% at $1*10^{-3}$ M concentration **(Schweinsberg *et al*., 1996)**.

Yadav and Singh (2004) has evaluated the corrosion inhibition properties of mild steel in H_2SO_4 for a temperature range of 35 to 65 ^oC using some organic polymers like polyvinylpyrrolidone, polyvinyl alcohol and polysorbate– 40.

Polyvinyl pyrrolidone and polyacrylamide were tested as corrosion inhibitors for mild steel in 1 M H_2SO_4 using gravimetric and gasometric techniques. Temkin adsorption isotherm and Kinetic-Thermodynamic Model of El-Awady were used to fit the data. PVP was found to be better inhibitor than PAAm and the nature of adsorption was physical **(Umoren and Obot, 2008).**

The synergistic influence of Polyvinyl pyrrolidone on 2-Phosphonobutane-1,2,4 tricarboxylic acid (PBTCA) for carbon steel corrosion in cooling water systems was investigated. The inhibiting properties were analysed using weight loss method, open circuit potential measurements and potentiodynamic techniques. Considerable protection efficiency was achieved with increase in the concentration of PBTCA and PVP. The mixture PBTCA and PVP synergistically improved the inhibition efficiency to 96.7% **(Abulkibash *et al*., 2008).**

An electroactive copolymer was synthesized using maleic anhydride and N-vinyl-2-pyrrolidone and its inhibitive action was evaluated for mild steel in sulphuric acid medium. The polymer acted as an efficient inhibitor and provided an IE of 88 % at 303 K with 1.6 % concentration **(Ganesha Achary *et al*., 2008).**

.The inhibition of mild steel corrosion in 1M H_2SO_4 by PVP and synergistic effect of iodide ions were investigated using weight loss and hydrogen evolution methods in the temperature range of 30– 60 ^{o}C. A physical adsorption mechanism was proposed as the inhibition efficiency decreased with rise in temperature. Freundlich and Temkin adsorption isotherms were used to fit the experimental data **(Umoren *et al*., 2009)**

A chemical oxidative synthesis of Polyaniline (PANI) in stable aqueous solution/dispersion form, using polyvinylpyrrolidone as an efficient steric stabilizer was reported by **Karthikaiselvi *et al.* (2010^{b})**. This Poly (VinylPyrrolidone - aniline) (PVPA) water soluble composite was evaluated as corrosion inhibitor for mild steel in 1M HCl at different concentrations. Maximum inhibition efficiency was noticed for 0.2 % percentage of PVPA. The adsorption of the compounds on mild steel surface was found to obey Langmuir's and Temkin's adsorption isotherm. The values of activation energy, free energy of adsorption, heat of adsorption, enthalpy of activation, entropy of activation were also calculated to elaborate the mechanism of corrosion inhibition.

The inhibitive effects of polyvinyl pyrrolidone PVP10 (Mol.Wt. 10,000) and PVP45 (Mol.Wt 45,000) on the corrosion properties of 316L stainless steel were investigated in reverse osmosis water containing 1 ppm $FeCl_3$ and a drop of H_2SO_4 **(Khaled, 2010a)**. The inhibition effect of the polyvinyl pyrrolidone was found to increase with the molecular weight.

Umoren (2011) has studied the corrosion inhibition of mild steel in sulphuric acid solution in the presence of polyethylene glycol, polyvinyl pyrrolidone, and their blends at temperature range of 30–60 ^{o}C using weight loss and hydrogen evolution methods at 30 and 60°C. Inhibition efficiency was found to be synergistically enhanced on blending polyethylene glycol and polyvinyl pyrrolidone in the ratio of 1:3.

The effect of a green corrosion inhibitor polyvinyl pyrrolidone on carbon steel was investigated in an aerated medium containing 0.1 M NaCl. The synergistic effect of iodide ions and antagonistic effect of untreated clay on the inhibition efficiency of PVP was also reported **(Juhaiman *et al*., 2012).**

An attempt was taken to study the interaction of PEG and PVP with mild steel in aerated acid mixture of 0.5 N H_2SO_4 and 0.5 N HCl solution using electrochemical studies and surface morphological studies. The presence of PEG and PVP decreased the double-layer capacitance and increased the charge-transfer resistance. The adsorption of the inhibitor molecules followed Langmuir adsorption isotherm. Surface analysis by scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed better performance of PVP (97.5 %IE) than PEG (96.62 %IE) **(John *et al*., 2013).**

2.7 Polyethylene imine (PEI)

Polyethyleneimine is a branched chain polymer with a ratio of 1:2:1 for primary : secondary : tertiary amines. The polymer has 3-3.5 N atoms at every branching site. The branching and exceptionally high colloidal charge, filtrate turbidity, and drainage characteristics of the anionic furnish make it an excellent choice for variety of applications like metal chelating, adsorption, corrosion inhibition etc.

Some cationic polymers like polyethyleneimine (PEI) and its derivative (PEID), polyarylamine and polydicyanodiamide derivative, and anionic polymers like polymaleic acid derivative (PMAD), polyacrylic acid derivative (PAAD) and polyacrylic acid (PAA) were analysed for the corrosion mitigation effect. The tests were carried out in two pseudoconcentrated solutions with low (LC) and high (HC) concentrations of ionic species like Ca^{2+} and Cl^{-}. The cationic polymers were found to be poor inhibitors when compared to the anionic polymers. The anionic polymers were capable of adsorbing on the metal surface in LC solution, and function as both corrosion and scale inhibitors of calcium carbonate. Moreover in LC solution, the inhibition efficiency value of anionic polymers was dependent on number-average molecular weight and concentration of COOH. In HC solution, the inhibition efficiency of anionic polymers depends on concentration and Ca^{+} ions **(Sekine *et al*., 1992).**

Quaternized polyethyleneimine (QPEI) prepared via two procedures of macromolecular reactions, tertiary amination reaction and quaternization, was investigated for its corrosion inhibition property on low carbon steel (A_3 steel) in H_2SO_4 solution. The polymeric quaternary ammonium salt, QPEI afforded an IE% of 92 % at 5 mg L^{-1} concentration, after 72 h of immersion time. The increase in inhibition efficiency was characterized in terms of increase in QPEI concentration and cationic degree (quaternized degree of QPEI). QPEI is an anodic inhibitor and extends its adsorption through double filming, adsorption filming and polymer filming, thus producing a compact barrier film on A_3 steel surface **(Gao *et al*., 2008).**

The inhibiting effect of PEI as a corrosion inhibitor for AISI 430 stainless steel in 3% aqueous NaCl solution was investigated by linear polarization and cyclic polarization measurements. The cyclic polarization measurement revealed the pitting corrosion-inhibiting property of PEI. The immersion tests proved the remarkable corrosion protection against uniform corrosion. Film persistency immersion testing was carried out to show the extensive stability of the protective layer. X-ray photoelectron spectroscopy measurements were carried out to understand that PEI binding was mediated by electrostatic interactions between PEI and the substrate. The diffusion of ionic species from the film and/or attack by chlorine from the salt water is effectively prevented by a dense layer of PEI **(Finsgar *et al.*, 2009a).**

2.8 Polyelectrolytes

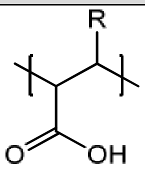
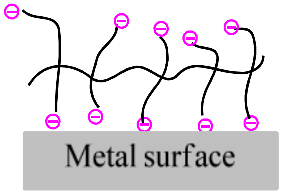
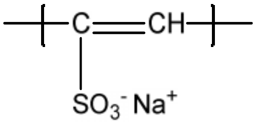
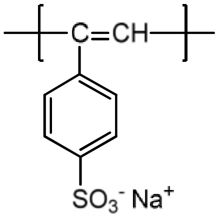
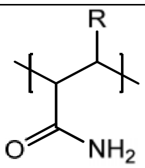
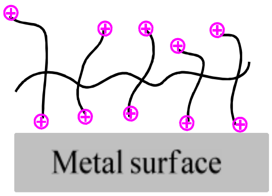
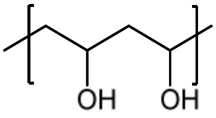
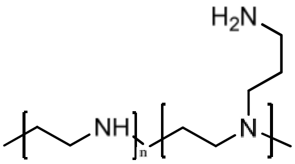
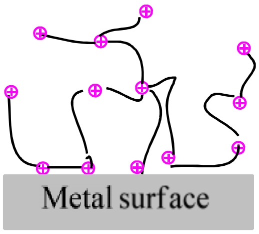
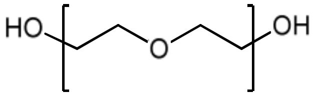
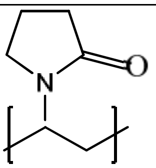
Ali and Saeed (2001) synthesized a variety of N,N-diallyl compounds, capable of undergoing cyclopolymerization, from 1,6-hexanediamine and 12-dodecanediamine. The synthesized monomers were subjected to homo and copolymerization with sulphur dioxide to produce polyelectrolytes. The polymers thus obtained when used as corrosion inhibitor were reported with a corrosion protection efficiency of more than 95% for MS in different molar concentrations of HCl, H_2SO_4 and NaCl media.

Poly(styrenesulphonic acid)-doped polyaniline was evaluated for corrosion inhibitory action on mild steel in 1M HCl using gravimetric and electrochemical techniques. The polymer was found to be an anodic inhibitor and its effective inhibition performance was revealed by hydrogen permeation studies and AC. impedance measurements. The adsorption of the compound on the mild steel surface obeyed Temkin's adsorption isotherm **(Manickavasagam *et al.*, 2002).**

The influence of 2,6-ionen and 2,10-ionen type polyvinyl-benzyl-trimethyl-ammonium chloride, and latex, on corrosion of low carbon steel in hydrochloric acid solution was investigated by potentiodynamic polarization measurements and impedance measurement techniques over the temperature range of 20-60°C at different inhibitor concentrations **(Bereket *et al.*, 2003).**

The water soluble polymers as far as discussed above can have different modes of adsorption mechanism based on the charges present on them. The polymers can be anionic, cationic or neutral. Table 2 is a list of some water soluble polymers and pictorial representation of their mode of inhibitory action.

Table - 2 General structure of some water soluble polymers and pictorial representation of their mode of inhibitory action

Chemical name	General chemical structure	Schematic representation of inhibition
Polyacrylic acid		
Polyvinyl sulfonic acid		
Polystyrene sulfonic acid		
Polyacrylamide		
Polyvinyl alcohol		
Polyethylene imine		
PEG		Neutral copolymer **(Deyab *et al.* 2009)**
PVP		

2.9 Natural polymers

The use of natural polymers as corrosion inhibitors is appreciated due to their unique properties like biodegradability, non-toxicity, easy availability and cost effectiveness. This review mainly focuses on some commercially available natural polymers which are used in corrosion inhibition.

Sedahmed *et al.* (1982) investigated the use of a formulation containing polyethylene oxide, polyacrylamide, and carboxymethyl cellulose as corrosion inhibitors for iron in acidic and neutral media using electrochemical methods and found that this formulation was an excellent inhibitor

Pectin and carboxy methyl cellulose were evaluated for their corrosion mitigating effect on cadmium in 0.5 M HCl. The polymers were found to be cathodic inhibitors at higher concentrations **Khairou and El-Sayed (2003).**

The corrosion inhibition behaviour of carbon steel in 1 M H_2SO_4 solution in the presence of guar gum was investigated. The pitting corrosion was analysed by potentiodynamic polarization method in the presence of chloride ions. The pitting corrosion potential was shifted to more positive values indicating an increased resistance to the pitting attack **(Abdallah, 2004).**

The influence of some sulfated water soluble natural polymer (carrageenan) compounds viz. kappa, iota and lamda, on the corrosion of iron in 1M HCl was investigated. All the polymers provided IE around 75% and the decreasing order of the polymers in terms of their corrosion inhibition potential is lamda>iota>kappa **(Zaafarany, 2006).**

Gum Arabic was tested for its efficiency on aluminium in 0.1-2.5 M NaOH at 30 and 40 ^{o}C. Adsorption under these circumstances was of chemical in nature which was also corroborated by kinetic and thermodynamic parameters **(Umoren *et al.*, 2006c).**

The inhibitory action of Carboxymenthylchitosan (CM-chitosan) on the corrosion of mild steel in 1 M HCl solution was revealed by **Cheng *et al.* (2007)**. The mixed type inhibitor provided a protection efficiency of 93% at 200 mg/L but decreased slightly with the rise of temperature. The adsorption of the inhibitor on the steel surface followed Langmuir's isotherm. The efficient inhibition was accompanied by greater activation energies of corrosion reaction in the presence of CM-chitosan at various concentrations.

Gum Arabic, a natural polymer was investigated for its corrosion protection efficiency on mild steel and aluminium exposed to H_2SO_4 solution at temperatures ranging from

30–60 °C using weight loss and thermometric techniques. Gum Arabic controls the corrosion effectively on aluminium than MS **(Umoren, *et al.*, 2008).**

The corrosion inhibition performance of sodium carboxymethyl cellulose (Na-CMC) on mild steel in 1.0 mol·L^{-1} HCl solution was investigated. Corrosion inhibitive effect was increased with increasing concentration of Na-CMC and the phenomenon of physical adsorption was proposed from decrease in inhibition efficiency with increase in temperature. The inhibition mechanism was further corroborated by the values of thermodynamic and kinetic parameters obtained **(Bayol *et al.*, 2008).**

Solomon *et al.* (2010) studied the inhibitive and adsorptive behaviour of carboxymethyl cellulose for mild steel in H_2SO_4 solution at 30–60 ^{o}C which provided good inhibition at high concentration, and the efficiency decreased with increase in temperature. The adsorption of the CMC onto the mild steel surface was found to follow Langmuir and Dubinin–Radushkevich adsorption isotherm models.

Tapioca starch was tested for improvement of corrosion resistance of AA6061 alloy in seawater by standard gravimetric and electrochemical measurements. The IE % was around 93 % for 1000 ppm concentration of the inhibitor studied **(Rosliza and Wan Nik, 2010).**

Cassava starch was modified and used for mitigation of corrosion of carbon steel in 200 mg/L NaCl as simulated tap water. The derivatives tested were an activated starch (AS) and a carboxymethylated starch (CMS) with two different degrees of substitution. AS was found to be better inhibitor than CMS, and its inhibition ability increases with the degree of substitution. Electrostatic potential mapping of monomeric units confirmed strong ionic interaction between AS and ferrous cations **(Bello *et al.*, 2010).**

The corrosion of carbon steel in 120 ppm chloride solution was evaluated in the presence of carboxymethyl cellulose (CMC)–Zn^{2+} by mass-loss method, potentiodynamic polarization study, and AC impedance spectra. A formulation consisting of 250 ppm of CMC and 100 ppm of Zn^{2+} was found to be best lending inhibition efficiency of 97% at pH 7 **(Anthony and Sherine, 2010).**

A chitosan derivative viz. acetyl thiourea chitosan polymer (ATUCS) was evaluated for corrosion mitigating property on mild steel in naturally aerated 0.5 M H_2SO_4 by standard gravimetric and electrochemical methods. The surface morphology was examined via scanning electron microscope technique. ATUCS were found to be effective in 0.5 M sulphuric acid providing an IE of 94.5% for 0.76 mM concentration **(Fekry and Mohamed, 2010).**

Umoren *et al*. (2010c) studied the corrosion inhibition effect of carboxymethyl cellulose (CMC) on mild steel in sulphuric acid medium by weight loss and hydrogen evolution techniques at 30–60 °C. The inhibitory action was enhanced by the addition of halide ions (Cl^-, Br^- and I^-). Chloride ions were found to be an antagonistic additive while the iodide ions exerted synergistic effect on the corrosion inhibition with CMC. The physical nature of adsorption of the inhibitor was supported with Langmuir isotherm model.

Mobin *et al*. (2011) studied the corrosion inhibition potential of starch on mild steel in 0.1 *M* H_2SO_4 at 30-60 °C by standard techniques. The maximum inhibition efficiency obtained was 66.21% at 30°C for 200 ppm starch concentration. In order to enhance the inhibition efficiency of starch, surfactants like sodium dodecyl sulfate and cetyl trimethyl ammonium bromide were added.

Hydroxy ethyl cellulose was employed as corrosion inhibitor for Aluminium AA1060 in 1 M HCl and 1.5 M HCl. The inhibitor provided 27.74 %IE for the lowest inhibitor concentration and 57.31 %IE for the highest concentration. Similarly, in 1.5 M HCl the inhibitor shoed in 35.89 %IE for lower concentration which was increased to a maximum of 58.157 % IE at higher concentration **(Arukalam and Obidiegwu, 2011)**.

Pectin was tested for its corrosion prevention efficacy on aluminium metal in 2 M HCl by weight loss technique. A maximum of 91 %IE was obtained for a concentration of 2 g/L pectin **(Fares *et al*., 2012a).**

Some hydrolyzed pectin-based graft copolymers were synthesized and their effect on the crystal formation of calcium sulfate was investigated. The ability of prevention of precipitation of calcium sulfate from homogeneous condition was almost independent of temperature and pH. When the morphology and crystal structure of the precipitates were observed using imaging and X-ray diffractometer (XRD), the change in the morphology and shape of the crystal structure of $CaSO_4$ precipitates was found to be changed from tubular to spherical **(Kalpana Chauhan *et al*., 2012).**

I-Carrageenan was used as corrosion inhibitor of aluminium in presence of pefloxacin mesylate, acting as zwitterionic mediator, in 2M hydrochloric acid by weight loss technique. The mediator enhanced the inhibition efficiency and the thermodynamic parameters calculated revealed well-ordered physical adsorption layers of the inhibitor. The relatively coherent adsorption layers were well demonstrated in aqueous medium whereas a smaller but regular shaped fractured layer was observed on the metal surface after exposing to the 2 M HCl for 2 hours **(Fares *et al.*, 2012b).**

Alginates and pectates are water-soluble polysaccharides of linear block copolymer structures consisting of D-mannuronic and L- gulurunic acid units linked through β(1→4) positions. The influence of these anionic polyelectrolytes containing secondary alcoholic groups on the rate of dissolution of aluminum metal in alkaline medium has been investigated by gasometric and weight-loss techniques. The results showed that the magnitude of inhibition efficiency was found to be larger in case of pectates **(Zaafarany, 2012).**

Umoren *et al.* (2013) investigated the efficiency of naturally occurring polymer chitosan as a corrosion inhibitor for mild steel in 0.1 M HCl by gravimetric and electrochemical measurements. The polymer was found to inhibit corrosion even at a very low concentration. The Inhibition efficiency increases with an increase in temperature up to 96 % at 60 °C and then drops to 93 % at 70 °C, while concentration of the chitosan has marginal effect on IE. Adsorption of chitosan at the mild steel surface was found to be in agreement with Langmuir adsorption isotherm model. The trend in the protection efficiency manifests the chemical nature of adsorption mechanism and the calculated kinetic and thermodynamic parameters corroborated the proposed mechanism.

Anionic polyeletrolyte pectates (PEC) as a water-soluble natural polymer polysaccharide was assessed for corrosion inhibition of aluminum (Al) in hydrochloric acid by gravimetric and gasometric techiques. When compared with the results obtained for pectates in alkaline medium by **Zaafarany (2012)**, the pectates were found to be less effective with IE% of 48.89%. This is because that sodium pectate carrying secondary alcoholic functional groups has a high tendency for protonation in acidic solutions to produce positive alkoxnium ions. The alkoxonium ions in turn hinder the formation of positive sites on Al surface, thus making the adsorption of the inhibitors on the metal surface less favourable **(Hassan and Zaafarany, 2013).**

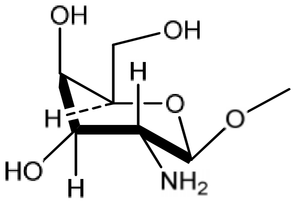
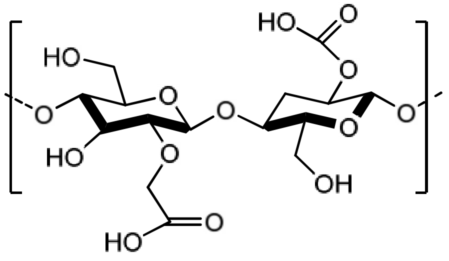
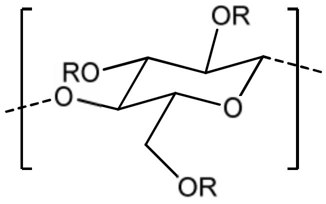
Hydroxyethylcellulose was analysed for corrosion protection efficiency on 1018 C-steel corrosion in 3.5% NaCl solution by potentiodynamic polarization, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) techniques. Corrosion control under the conditions was found to be mixed type and fits into Langmuir adsorption isotherm. Results obtained from EFM technique were corroborative with electrochemical results. Surface morphology was investigated using SEM-EDX analysis, and DMol3 quantum chemical calculations were carried out to prove the adsorption mechanism with the structure of HEC molecule **(EL-Haddad, 2014).** Similarly the corrosion inhibition performance of HEC on aluminium and mild steel in 0.5 M H_2SO_4 **(Arukalam *et al*., 2014a)** and on copper in aerated 1 M HCl and 0.5 M H_2SO_4 **(Arukalam *et al*., 2014b)** was also reported.

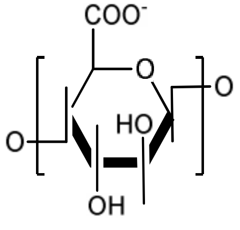
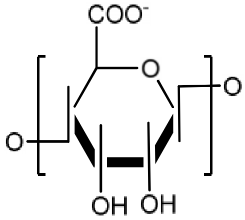
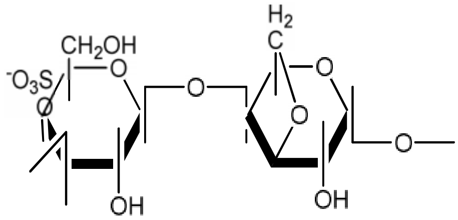
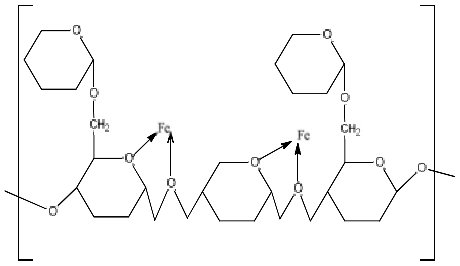
Acrylamide was grafted onto the pectin and evaluated for anticorrosive property on mild steel in neutral media. This water-soluble polymer was found to be efficient in inhibiting chloride corrosion pertaining to a IE value of around 85%**.** A water soluble polymer was synthesized by grafting acrylic acid onto the pectin. The polymer showed an efficient control of chloride corrosion with an IE of 85 % **(Geethanjali *et al*., 2014).**

Gum Arabic was used as an inhibitor for the corrosion of API 5L X42 pipeline steel in 1M HCl solution. The best efficiency was recorded to be 92% at 2 g L^{-1} **(Bentrah *et al*., 2014).**

The following Table (No. 3) is a list of some selected natural polymers, their structure and metals on which the corrosion inhibition properties were studied.

Table - 3 List of general chemical structure of some natural polymers and its application as corrosion inhibitors on various metals

Natural polymer	Chemical structure/Name	Metals reported
Gum Arabic	Complex and variable mixture of arabinogalactan oligosaccharides, polysaccharides and glycoproteins.	Mild steel and aluminium in H_2SO_4 solution
Chitosan		Mild steel in 0.1 M HCl
Acetyl thiourea chitosan polymer		Mild steel in naturally aerated 0.5 M H_2SO_4 acid
Carboxy methyl cellulose PEO+PAAm+CMC		Mild steel in H_2SO_4 solution Iron in acidic and neutral media
Hydroxy ethyl cellulose		Aluminium AA1060 in 1 M HCl and 1.5 M HCl. 1018C-steel in 3.5% NaCl solution

Natural polymer	Chemical structure/Name	Metals reported
Pectin pectin-based graft copolymers Pectin-g- Acrylamide and Pectin-g-acrylic acid		Aluminum metal in 2 M HCl Calcium sulphate scale removal Mild steel in 3.5% NaCl media cadmium in 0.5 M HCl
Alginates and pectates		Aluminum in Aqueous Alkaline Solutions
I-Carragenan		Iron in 1 M HCl Aluminium in 2 M HCl
Starch	Amylose and amylopectin	Mild steel in 0.1 *M* H_2SO_4 AA6061 alloy in seawater Carbon steel in 200 mgL−1 NaCl
Guar Gum		Carbon steel in 1 M **H_2SO_4**

2.10 Polyphosphates

The corrosion inhibition of iron by polyphosphates in NaCl medium in the presence of oxygen, calcium and chloride ions was discussed by **Uhlig *et al.* (1955)**. Corrosion was accelerated when the critical oxygen concentration is low as 1 ml/L and Ca^{2+} ion concentration is 60 ppm. The corrosion was effectively inhibited in the solutions having less than 0.01 % NaCl. The results indicated that corrosion control by sodium polyphosphates was achieved by passivation of iron by dissolved oxygen. The FeO film present in the iron surface reacts with sodium polyphosphate and thereby permitting higher surface concentrations of oxygen for a given concentration in solution. Addition of calcium salt formed a diffusion barrier layer on cathode areas which appreciably controlled the corrosion.

Sodium polyphosphate was evaluated for its corrosion inhibition performance on mild steel in synthetic sea water by **Lahodny-sarc and Kastelan (1976)**. The results revealed that mild steel corrosion can be effectively reduced by the addition of small amounts of polyphosphates in the presence of divalent cations such as Ca, Mg, Zn and dissolved oxygen. The inhibition was achieved by the formation of glass-like film by polyphosphates-cations mixture on cathodic areas which increases the cathodic polarization. The mechanism of inhibition was accelerated in the presence of oxygen, by favouring passivation**.** The corrosion inhibition performance of zinc and polyphosphates on the zinc metal in near neutral solution was analyzed by **Rangel *et al.* (1992).** The effect of calcium on the corrosion inhibition performance of polyphosphate was also studied and the best composition was determined. Corrosion control in the presence of calcium exhibited mixed kinetics which changed to diffusion control in the absence of calcium ions.

McNeill and Edwards (2000) conducted a four-year study to examine the effect of phosphate inhibitors on the corrosion of iron pipes under extended stagnant water conditions. The parameters fixed for the study includes pH and alkalinity, age of the pipe, water stagnation time, and inhibitor type. Due to undesirable anti-corrosion properties of zinc orthophosphate, polyphosphate-based anti-corrosion pigments were developed. **Naderi and Attar (2008)** evaluated the corrosion performance of steel samples after immersing in 3.5% NaCl containing zinc aluminum polyphosphate (ZAPP) pigment extract and the results were compared with conventional zinc orthophosphate pigment solution and blank solution. The results revealed that ZAPP is most effective inhibitor and the presence of a precipitated layer on the steel surface was confirmed by SEM-EDX.

2.11 Other polymer systems

The inhibitor performance of chemically synthesized water soluble poly (aminoquinone) (PAQ) on iron corrosion in 0.5 M sulphuric acid was reported by **Jeyaprabha *et al.* (2005)**. The author reported that the inhibition of the polymer at 100 ppm is 90% but for the monomer at 1000 ppm is 80%. FTIR and UV-reflectance studies were conducted to prove the adsorption of inhibitors on the metal surface.

In view of the major limitation of insolubility of polyaniline, water-soluble and functionalized self-doped conducting polymer of polyanthranilic acid was reported for the first time for the corrosion inhibition of mild steel in 0.5 M HCl by **Shukla *et al.* (2008).** Corrosion resisting efficiency of polyphosphate derivative of guanidine and urea copolymer (PGUC) was tested on Armco iron in molar hydrochloric acid (1 M HCl) at 30 °C using electrochemical impedance spectroscopy method (EI) **(Lebrini *et al.*, 2008).**

A chemically synthesized copolymer of conducting poly(aniline-co-orthotoluidine) was synthesized by a chemical route and characterized by UV, FTIR, TGA and XRD techniques. The synthesized inhibitor was proven to have an inhibition efficiency of 70% at 100 ppm concentration for carbon steel in 3% NaCl **(Benchikh *et al.*, 2009).**

The inhibition efficiency of electro-prepared P(o-phenylenediamine) on the corrosion rate of MS in HCl solution was investigated by **Abd El Rehim *et al.* (2010)**. **Xu *et al.* (2012)** have synthesized a polyaspartic acid grafted melamine copolymer using polysuccinimide and melamine and its anti-scale behaviour in artificial cooling water system was reported (optimum efficiency: 97%) by conducting static scale inhibition test. The polymer was tested for retarding the formation of $CaCO_3$ and $Ca_3(PO4)_2$ scales. The synergistic influence of KI on the inhibition effect of polyaspartic acid for mild steel corrosion in 0.5 M H_2SO_4 solution was reported by **Qian *et al.* (2013).** The inhibition efficiency had a positive influence with the concentration of PASP and addition of 1 mM KI. The zero charge potential measurement revealed that iodide ion promotes the film formation of polyaspartic acid effectively. An adsorption model was proposed to elucidate the synergistic mechanism. A new biodegradable scale and corrosion inhibitor Polyaspartic acid/5-aminoorotic acid graft copolymer (PASP/5-AOA) was synthesized by the reaction of maleic anhydride, urea and 5-aminoorotic acid (5-AOA). The grafted polymer was reported to have an excellent inhibition efficiency close to 100% against $CaCO_3$ when the dosage is 1 mg/L and close to 100% for $Ca_3(PO_4)_2$ when the dosage is 12 mg/L **(Xu *et al.*, 2013).**

2.12 Conclusion

The preceding comprehensive review focussed on green alternatives to chromate corrosion inhibitors oriented towards water soluble polymers. New avenues of corrosion inhibition using different polymers, copolymers, terpolymers, polymer blends, composites, doped polymers and polymers extracted from natural products have also been discussed. 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 dependant on adsorption through multiple adsorption centres. The overview of the available literatures also revealed the high inhibition performance of the polymers compared to its monomer against corrosion of various types of metals in acid and neutral media. So, polymeric compounds can be appreciated for opening up new frontiers in the corrosion research.