Electrochemical studies of reinforced bars in simulated pore solution using natural polymers

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Abstract
An attempt was made to study the application of natural polymers for mitigating the corrosion of reinforcement bars in simulated pore solution. Natural polymers like iota-Carrageenan(i-Carr), Pectin(Pec) and Dextrin(Dex) was used as inhibitors to mitigate the rebar corrosion. Corrosion monitoring was done by implementing electrochemical techniques like impedance spectroscopy and polarization studies. Rct values increased with increase in concentration of the inhibitors. Polarization curves implemented the anodic nature of inhibitors. Adsorption of inhibitors was found to fit well with Langmuir adsorption isotherm model. Influence of Cl$^-$ ions and a detailed mechanism of their intrusion was also discussed

1. Introduction

Reinforcement steel bar also called rebar are commonly reinforced with concrete for construction of buildings, bridges, roads etc. due to its improved strength and durability. But these construction works face serious corrosion problems over a period of time and get deteriorated. Degradation of these structures are considered to be severe threat to the society leading to the huge economic loss. Though various factors are blamed for early distress in reinforced concrete structures it is experiential that in majority of cases, it is because of the corrosion of steel. Therefore, it is found practically significant to study the corrosion behaviour of the reinforcing steel[1,2]. Many researchers[3,7] showed that this deterioration is due to the presence of chloride ion in the solution which accelerates the electrochemical process at the metal/solution interface especially in salt water. The protective passive layer formed on the surface of the steel at high pH thus gets damaged due to penetration of chloride ions prefiguring the corrosion process leading to cracks and spalling of concrete. Thus in the presence of chloride ions, depending on the Cl^- : OH^- ratio the protective film may be destroyed even at pH values significantly above 11.5. Thus to increase the durability of concrete structures corrosion inhibitors are used as chemical admixtures with concrete.

Various types of inhibitors especially anodic, cathodic and penetrating type corrosion inhibitors have been studied by researchers. Still now the use of calcium nitrite is considered to exhibit its effectiveness in preventing chloride corrosion on rebar structures[8-10]. Further long-term tests proved the ability of lactate ions to retard corrosion damage on rebars**.** Also **Verbruggen et a1[11].,** evaluated different inhibitors like $Na_2MoO_4.2H_2O$, $Ce(NO_3)_3.6H_2O$ and thiadiazoles for both types of corrosion that can occur in reinforced concrete. Furthermore **Bhuvaneshwari et al [12].,** synthesised azomethine- based polyester and employed as inhibitor against the corrosion of rebar in artificially simulated concrete pore solution with chloride contamination. Additionally **Krishna Kumar et al [13].,** reported in their article on coating the rebars with cement polymer composite to retard the corrosion. However very little evidence are available in the literature

about effectiveness of these CPCC and their inhibitive action on steel rebar[14]. But still corrosion of reinforced concrete structures and detection techniques of reinforced concrete steel rebars were analysed by many researchers by utilizing electrochemical techniques[15-19]. Thus all the literature survey clearly indicates that no significant research work has been reported on the application of any natural polymers as corrosion inhibitors on the steel rebar corrosion. In view of this an effort was made to study the corrosion inhibitive effect of natural polymers(I-Carrageenan, Pectin and Dextrin) on rebar corrosion by using concrete pore solution simulated with Cl^- ions. So the present work deals with the corrosion inhibition characteristics of selected natural polymers in concrete pore solutions simulated with chloride ions under alkaline conditions by using two resourceful electrochemical techniques *viz,* potentiodynamic polarisation and impedance spectroscopy.

2. Experimental methods
2.1 Inhibitors used
Natural Polymers
Selected Natural polymers Iota-Carrageen, Pectin and Dextrin purchased from Sigma-Aldrich has been used for evaluating their efficiency for rebar corrosion in alkaline medium. The structures of the polymers are:
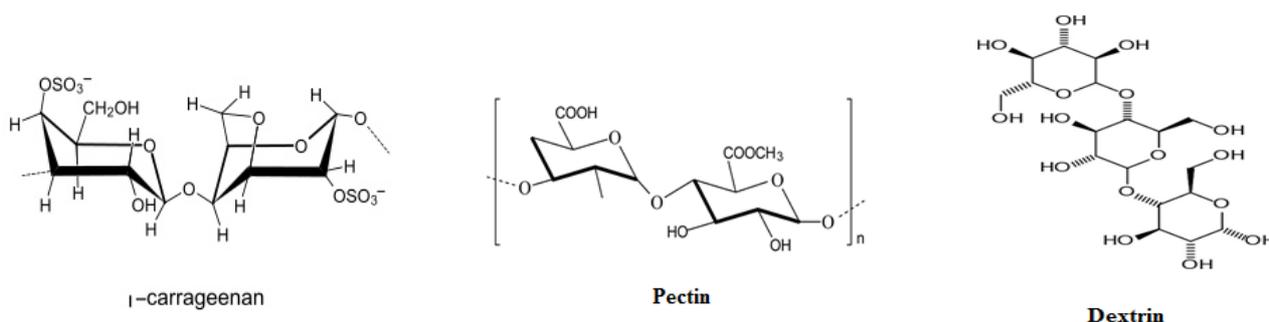
2.2 Simulation of pore solution
Pore solution without sodium chloride (0.5 M $Ca(OH)_2$+ 0.5M KOH + 0.1M NaOH) is used as reference. The pH of the blank pore solution is maintained at 12.8. The simulated pore solutions contaminated with chloride ions have the composition 0.5M KOH + 0.1M NaOH +0.5M NaCl. The pH of this electrolyte is 11.7. In the present study, the pore solutions have been simulated by using halide ion (Cl^-) in such a way that they simulate an environment similar to that of coastal zone to study the inhibitor efficiency towards corrosion.

2.3 Electrode used
Three electrode system comprising platinum electrode as the counter electrode and saturated calomel electrode (SCE) as the reference electrode, mild steel rebar as the test specimen was used. As per ASTM standards mild steel rebar test specimens cut from steel rebar grade 60 (ASTM A615) was used as the working electrode. The size of the electrode is 32mm with a cross sectional area of 804.6 Sq mm and mass 6.31(kg/m). The chemical composition was 0.42% C; 1.040% Mn; 0.180% Si; 0.033% P; 0.065% S; 0.450% Cu; 0.150% Ni; 0.240% Cr; 0.029% Mo; 0.025% Sn; 0.005% V, 0.003% Ti; 0.002% B; 96.773% Fe. The specimen surfaces were polished using a series of silicon carbide papers of grades #120 to #1500. Finally, the specimens were washed thoroughly with deionized water, degreased with acetone and dried[24,25].

2.4 Corrosion monitoring techniques by electrochemical methods
(i) Electrochemical impedance measurements
The impedance measurements were made at corrosion potentials over a frequency range of 10 kHz to 0.01 Hz with signal amplitude of 10 mV. The real part (Z') and the imaginary part (Z") were measured at various frequencies. A plot of Z' vs Z" were made. From the plot, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated from the data using the corresponding IVIUM software. Impedance measurements were carried out for steel sample in pore solution/simulated pore solution with and without inhibitors. The inhibition efficiency was calculated using the formula

$$\text{Inhibition Efficiency}(\%) = \frac{R_{ct}^* - R_{ct}}{R_{ct}^*} X100$$

where R_{ct} and R_{ct}^* are the charge transfer resistance obtained in the absence and presence of the inhibitors.

(ii) Potentiodynamic polarization studies

Polarization measurements were performed to evaluate the corrosion kinetic parameters such as I_{corr}, E_{corr} and Tafel slopes b_a and b_c. The polarization measurements were carried out from a potential range of -200 mV to +200 mV with respect to open circuit potential at a scan rate of 1 mVsec^{-1}. The experiments were carried out in pore solution, simulated pore solution without and with various concentrations of the inhibitor. The log of current and the corresponding potentials were fed into the plotter and potential E vs. log I plot was obtained. The inhibition efficiency was calculated from I_{corr} using the formula

$$\text{Inhibition Efficiency (\%)} = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

where I_{corr} and $I_{corr(inh)}$ signifies the corrosion current density in the absence and presence of inhibitors.

3. Results and Discussion

3.1 Electrochemical studies for corrosion and corrosion inhibition

(i) Impedance studies

The plots obtained from EIS measurements are presented in Figs. 1-4 and the impedance data presented in Tables 1 & 2 . The impedance plot of blank solution without Cl$^-$ ions are also presented for comparison purpose. From the figure it was found that in the absence of inhibitors only spike and no semicircle was obtained (for blank). This could be attributed partially to the OH$^-$ ions generated by the hydration of cement which is thought to be most conductive in nature as a result no semicircles were obtained. Whereas in the presence of inhibitors, the inhibitor molecules would tend to decline the OH$^-$ evolution leading to decrease in conductance and semicircles were attained. Further the figures reveal that diameter of capacitive circles increases with increase in concentration of the inhibitors.
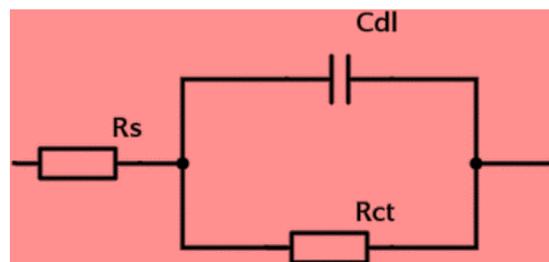

Fig.i Randle's equivalent circuit

Table 1: AC-impedance parameters of pore solution with and without chlorine

Inhibitor Concentration (mM)	R_{ct} (ohm cm^2)	C_{dl} (μF/cm^2)
Pore solution without Cl$^-$	10.6	21.2
Simulated pore solution with Cl$^-$	6.9	25.6

The values of impedance measurements best fitted with Randle's equivalent circuit as mentioned below (Fig.i). Incomplete capacitive reactance arcs are obtained suggesting that corrosion was wholly inhibited at the steel/electrolyte interface and passive film formed was stable. The part resistance obtained is completely due to charge transfer between electrode/solution interface. Furthermore the capacitive loops are obtained at low frequency range which is related to time constant of charge transfer resistance and electrical double layer capacitance rebar/concrete solution interface. The values of R_{ct} are found to increase with increase in concentrations of the inhibitor in simulated pore solution whereas C_{dl} values have reduced considerably. This can be attributed to the strong adsorption of the inhibitor on the reinforcing steel surface[35-38]. The order of inhibition efficiency was i-carr>Pec>Dex. The higher inhibition efficiency of i-carr could be attributed to the presence of electrostatically negative sulphate atoms in the polymer moiety. Moreover higher molecular weight of i-carr and Pec compared to Dex have correspondingly led to increase in inhibition efficacy of the polymers[26-30].

Table. 2: AC-impedance parameters for rebar corrosion for selected concentrations of the Natural polymers

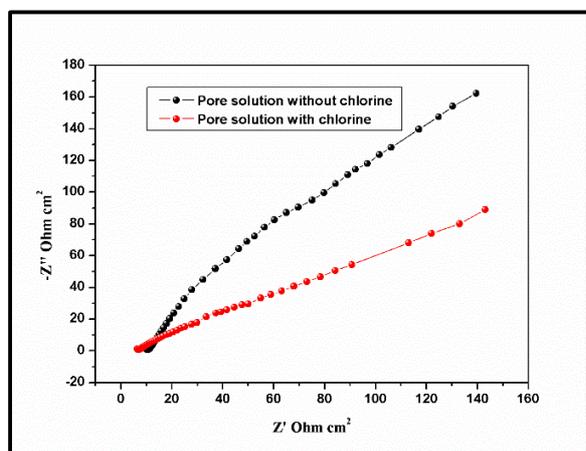| Name of the inhibitor	Con (ppm)	R_{ct} (Ohm cm^2)	C_{dl} (μF/cm^2)	Inhibition efficiency (%)
Simulated pore solution with Cl$^-$	-	6.9	25.6	-
i-carr	1	24.2	20.1	71.4
	10	48.6	18.7	85.80
	100	64.3	15.6	89.26
	1000	110.1	9.6	93.73
Pec	1	14.5	22.4	52.41
	10	33.3	16.7	79.27
	100	49.3	12.8	86.00
	1000	80.2	8.9	91.39
Dex	1	22.5	19.6	69.33
	10	47.8	14.4	85.56
	100	53.4	10.3	87.07
	1000	63.2	8.8	89.08

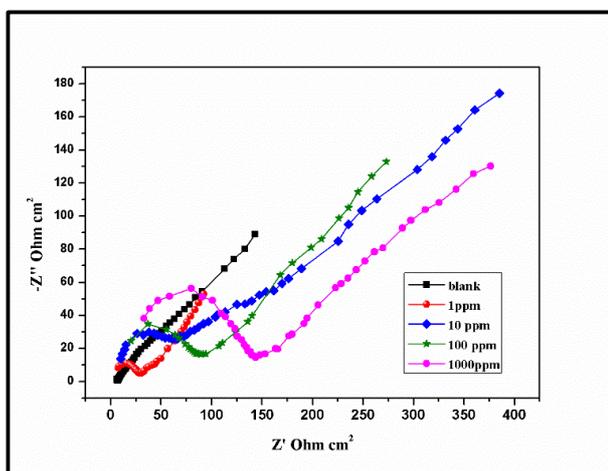**Fig. 1:** Nyquist plots of pore solution with and without chlorine

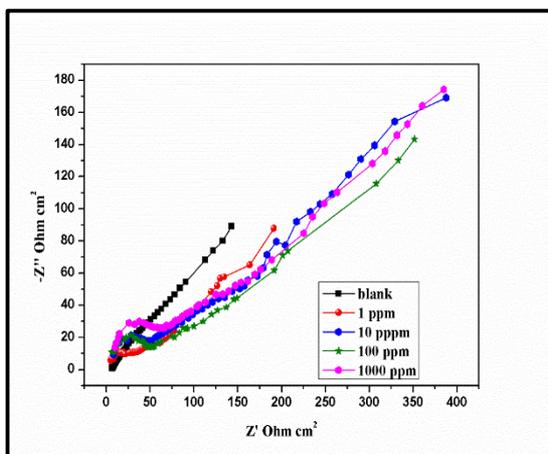**Fig. 2** Nyquist plot of i-Carr for corrosion of rebar

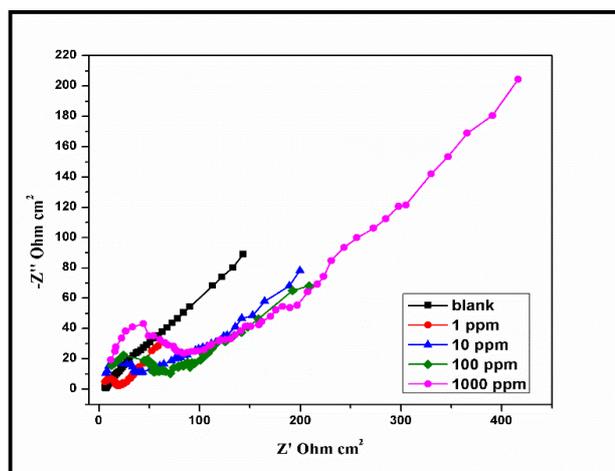**Fig. 3** Nyquist plot of Pec for corrosion of rebar

Fig. 4 Nyquist plot of Dex for corrosion of rebar

(ii) Polarization studies

The electrochemical parameters comprising corrosion current (I_{corr}), Tafel slopes (b_c and b_a) and corrosion potential (E_{corr}) are computed from the potentiodynamic polarisation data for the system containing polymer inhibitors used in the present study. The polarization graphs obtained from this study are shown in Figs 5- 8. and the data are presented in Tables 3&4.. As it can be seen from the Tables, the I_{corr} value of the pore solution with Cl⁻ ions is higher when compared to pore solution without chloride. This is evident for the corrosion of rebar in the presence of chloride ions (blank), as it is known will undergo severe corrosion in presence of chloride ions. Whereas the polarization graph obtained for electrolyte system with inhibitors and the corresponding data presented in Table indicates that inhibition efficiency gradually increases with increase in concentration. This indicates the formation of highly protective film which prevents the ingress of Cl⁻ ions towards rebar. It was also observed that corrosion potential was shifted to noble side to some extent with i-Carr and that with Dex and Pec the shift was fairly on the noble side compared to blank. This emphasises the mixed type nature of inhibitor behaviour for natural polymers but more predominantly anodic type[31-33].

Table. 3 Polarization parameters of pore solution with and without chlorine

Inhibitor Concentration (mM)	b_a (mV/dec)	b_c (mV/dec)	$-E_{corr}$ (mV/SCE)	I_{corr} (μAmp/cm^2)
Pore solution without Cl⁻	64	104	496.6	310.71
Simulated pore solution with Cl⁻	263	40	648.8	390.2

Table. 4 Polarization parameters for rebar corrosion for selected concentrations of Natural polymers

| Name of the inhibitor	Con (ppm)	Tafel slopes (mV/dec)		$-E_{corr}$ (mV/SCE)	I_{corr} (μA/cm^2)	Inhibition Efficiency (%)	Surface coverage C/θ
		b_a	b_c				
Simulated pore solution with Cl⁻	-	263	40	648.8	390.2	-	
i-carr	1	203	54	514.9	230.9	40.8	2.78
	10	322	42	561.6	200.2	48.69	23.13
	100	205	75	545.7	113.8	70.83	148.47
	1000	110	132	580.2	91.7	76.49	1390.62
Pec	1	344	49	612.1	245.1	37.18	3.07
	10	187	55	546.2	229.4	41.20	18.94
	100	210	52	446.0	142.6	63.45	172.83
	1000	132	78	443.8	97.2	75.08	1362.58
Dex	1	184	43	406.3	255.5	34.52	2.96
	10	232	48	366.1	202.6	48.07	20.34
	100	214	52	500.9	156.7	59.84	170.32
	1000	156	89	438.7	108.4	72.21	1341.02
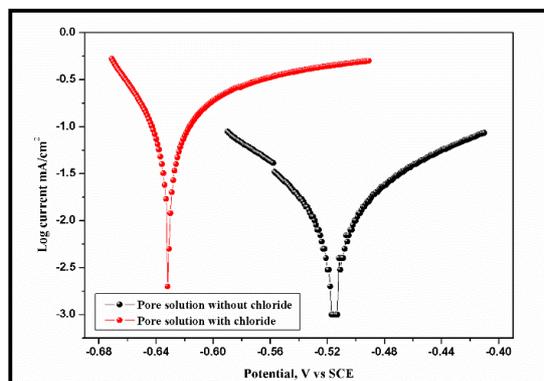
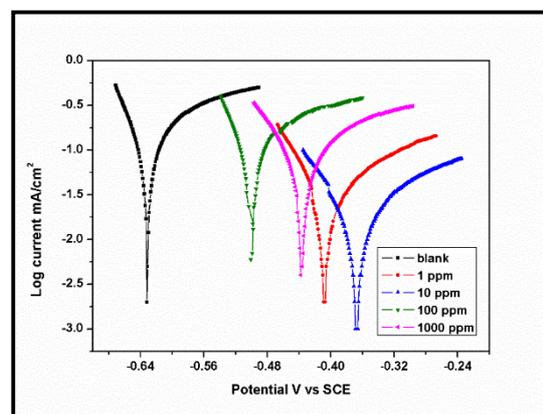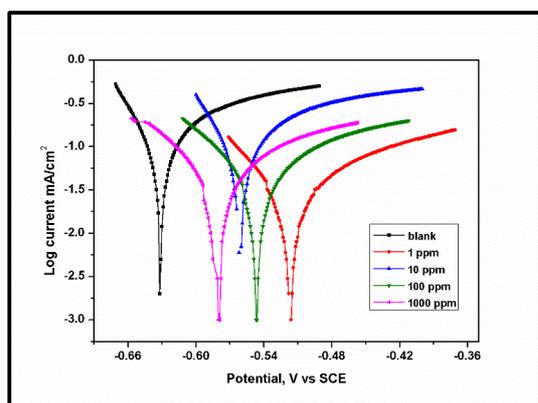**Fig. 5** Polarization plots of pore solution with and without chlorine

Fig. 6 Polarization plots of i-Carr for corrosion of rebar

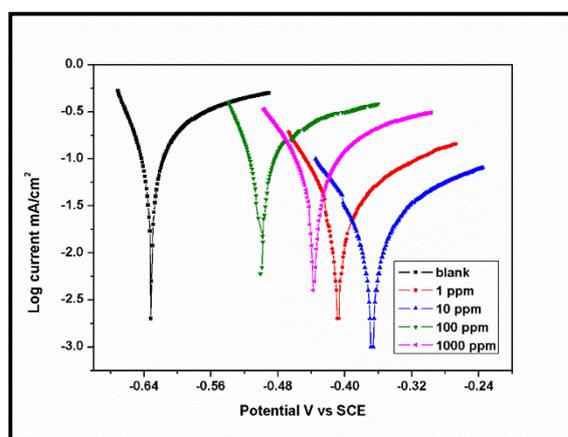**Fig. 7.** Polarization plots of Pec for corrosion of rebar

Fig. 8 Polarization plots of Dex for corrosion of rebar
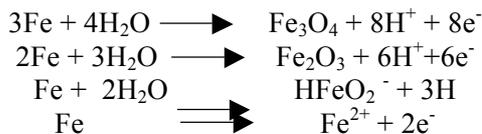
3.3 Influence of Cl- ions

The Cl ions present in the concrete influences the corrosion of rebars and that chloride levels between 0.4 and 1% (by weight of cement) produces a medium risk of corrosion and above 1%, it causes a high risk. The oxidation state of iron passive layer generally varies across the layer and it is assumed that the outer layer which is mainly composed of Fe^{3+} rich oxides and hydroxides is nonprotective, and the inner oxide layer adjacent to the steel which is rich in Fe^{2+} is protective. Further Fe^{3+}/Fe^{2+} ratio increases in the presence of chloride ions. It was presumed that when chloride ions diffuse through the non-protective outer layer and come into contact with the inner layer, they convert some Fe^{2+} oxides/hydroxides to Fe^{3+} oxides/hydroxides that reduce the protective nature of the inner layer. Chloride ions that come mostly from deicing salts or seawater, and carbon dioxide from the atmosphere, are two major factors that can break the passive film on the surface of steel and initiate corrosion. Insufficient oxygen to preserve the passive film, galvanic cell formation from the contact of different metals, and stray currents are the other factors that may cause active corrosion in reinforced-steel structures. Literature states that many organic inhibitors decreases the corrosion rate by diminishing the chloride ion ingress into the concrete. In consideration with the above point, it is expected that inhibitors selected being organic polymer will produce greater effect towards the ingress of chloride ions. Thus the R_{ct} value increases in the presence of blank and corrosion current value (I_{corr}) reduces and protects the metal surface by displacing Cl^- ions and protects the metal surface.

3.4 Mechanism of inhibition

For a steel reinforcing bar (rebar) in concrete, the surface of the corroding steel can act as a mixed electrode containing both anode and cathode regions connected by the bulk steel. Macro cell corrosion can also form on a single bar exposed to different environments within the concrete or where part of the bar extends outside the concrete. In both cases, concrete pore solution functions as an electrolyte. Chloride ions or carbon dioxide penetrates the concrete cover depth to reach the surface of the reinforcing steel by a number of mechanisms. The surface of the concrete may be dry, allowing the dissolved chlorides or carbon dioxide to be absorbed by capillary action together with moisture through the interconnected pores in the cement paste. At deeper levels,

concrete rarely dries out in the atmosphere so the continued penetration by aggressive ions is by diffusion through the pores, which is a much slower process than absorption

For steel entrenched in concrete, depending on the pH of the concrete/electrolyte and presence of aggressive ions, the possible anodic reactions are

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ + 8e^-$$
$$2Fe + 3H_2O \longrightarrow Fe_2O_3 + 6H^+ + 6e^-$$
$$Fe + 2H_2O \longrightarrow HFeO_2^- + 3H$$
$$Fe \rightleftharpoons Fe^{2+} + 2e^-$$

The cathodic reactions probably depends on the accessibility of O_2 and pH of the pore solution adjacent to the steel surface. The most expected reactions are as follows

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$
$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$
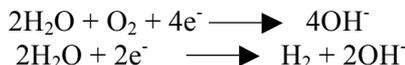
Generally a typical organic compound containing amino alcohols or fatty acids block both the cathodic and anodic reactions on the metal surface. In case of organic polymers which contain n number of chains or repeating units it is expected that efficacy will be more for corrosion protection. However, most inhibitors play the dual role as adsorptive as well as in layer formation. The following are the important mechanisms proposed:

1. Binding of Cl ions with the molecules of inhibitor and protective layer formation owing to adsorption of active sites on the rebar surface takes place simultaneously.
2. Addition of inhibitors to the pore solution yields gel type complexes with the Cl^- ions in the pore solution which gets adsorbed to the surface of the rebar.
3. The impregnation of gel on the rebar surface decreases the intrusion of chloride, oxygen and water consistently.

The polymers (natural) used contains the repeated heterocyclic pyrane moiety linkage as well as presence of heteroatoms get adsorbed on the cathodic sites and decreases the evolution of hydrogen. Lone pairs get adsorb on anodic sites and decreases the anodic metal dissolution. Similarly polyamide linkages of synthetic polymers is expected to adsorb on to the metal surface with near flat orientation of the entire molecule. Also, the adsorbed molecules would tend to arrange themselves parallel to each other covering the entire metal surface, thereby preventing the ingress of aggressive species to the metal surface[39-41]. The pictorial representation of mechanism of rebar corrosion is given in Fig.10.
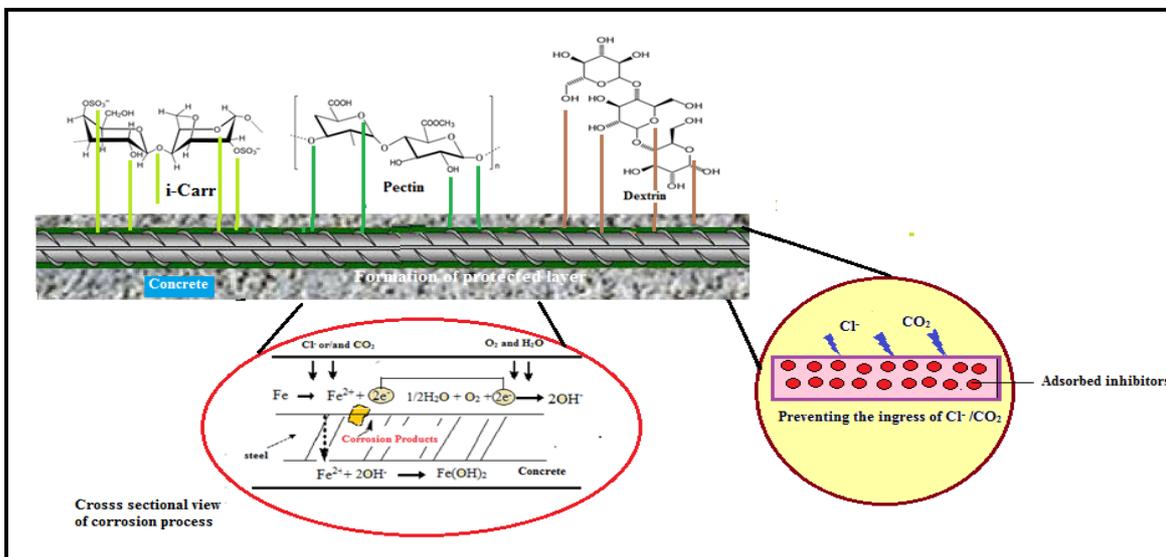

Fig.10 Pictorial representation of mechanism of rebar corrosion

Conclusions

The following conclusions could are drawn for corrosion of rebar in alkaline medium:

1. Natural polymers perform as effective inhibitor for corrosion of rebar in alkaline medium
2. Electrochemical impedance measurements prove the effective inhibiting property of inhibitors
3. Moreover, surface coverage values exhibited that when polymer concentration increases, the thickness of the protective layer also increases and accounting for the increase in inhibition efficiency.
4. Polarization studies performed prove that inhibitors are predominantly anodic in nature.

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