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Corrosion Potential Assessment of Eco-friendly Inhibitors Layered Reinforcement Embedded in Concrete Structures in Severe Medium

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Abstract

This research work experimentally investigated the use of inorganic inhibitors and Greener approach inhibitors to evaluate the assessment of corrosion potential using Mangifera indica resins paste extracts layered to reinforcing steel with coated thicknesses of 150µm, 250µm and 350µm. Examinations and assessments were done on concrete reinforced slab with the application of half cell potential, concrete resistivity and tensile strength mechanical properties of reinforcement surface condition after 119 days immersion in sodium chloride and with applied currents potential of -200 mV through 1200mV, with a scan rate of 1mV/s. Results recorded of half cell potential, concrete resistivity and tensile strength properties for non- inhibited concrete specimens on the mapping areas for the expedited periods designated 95% probability of corrosion and indicating a high or moderate probability of corrosion. the results recorded of potential $E_{corr,mV}$, and concrete resistivity of Mangifera indica inhibited specimen, the results indicated a 10% or uncertain probability of corrosion which indicates no corrosion presence or likelihood and concrete resistivity indicated a low probability of corrosion or no corrosion indication. Average percentile results of potential $E_{corr,mV}$, and concrete resistivity are 26.57% and 61.25% respectively. When compared to corroded samples, corroded has 70.1% increased values potential $E_{corr,mV}$ and 38.8% decreased values of concrete resistivity, yield stress against ultimate strength at summary and average state of corroded slab with nominal values of 100% and decremented in ultimate strength from 105.36% to 96.12%, weight loss versus cross-section diameter reduction decreased due to attack from sodium chloride from 64.8% to 44.45% and 46.76% to 86.43% respectively

Key Words: Corrosion, Corrosion inhibitors, , Concrete and Steel

Reinforcement

1.0 Introduction

Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the future. Environmental requirements are still being developed but some elements have been established (Uhlig, [1]). In general, EC50 values are lower than LC50 values because the former are the concentrations required to damage the species in some way without killing it. Some chemicals are excellent inhibitors, but are quite toxic and readily absorbed through the skin (Uhlig, [1]). Inorganic inhibitors and Greener approach inhibitors has shown highly and environmentally friendly, toxic free, generally, widely and inexpensive for future use, based on this properties, there is great demand of green inhibitors to organic ones due to their biodegradable properties. (Uhlig, [1]). In the past two decades, the research in the field of ‘‘green’’ corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or ‘‘zero’’ environmental impact (Moretti *et al.* [2]). The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products as corrosion inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by several authors (El-Etre, [3], [4]; Gunasekaran and Chauhan, [5]; Moretti *et al*, [2]; El-Etre *et al*, [6]; Sethuraman and Raja, [7], Ismail, [8]; Ashassi-Sorkhabi and Asghari, [9]; Raja and Sethuraman, [10], [11], [12], [13]; Oguzie, [14]; Okafor *et al.*, [15]; Radojcic *et al*, [16]; Zhang *et al*, [17]; Eddy, [18]; Ostovari *et al*, [19]; Satapathy *et al*, [20]; Solomon *et al*, [21; Olusegun and James, [22].

Rasheeduzzafar *et al.* [23] conducted seven years site exposure tests and evaluated the performance of corrosion resisting steels in chloride media concrete. Evaluation of bare mild steel, galvanized, epoxy-coated and stainless steel clad reinforcing steels examined by embedment process in concrete with three different levels of chloride content (0.6, 1.2 and 4.8% by weight of cement). Conclusion was drawn that bare mild steel bars suffer severe rust related damage in all the three chloride levels whereas the use of galvanized steel in concrete with high levels of chloride merely delay the concrete failure, while epoxy-coated bars offer good corrosion resistant properties in low chloride levels.

Kayyali and Yeomans [24] compared galvanized, black and epoxy-coated rebars were embedded in reinforced concrete beams of size 1500 × 160 × 320 mm by evaluating the bond and slip of coated reinforcement in concrete. The test results revealed that ultimate capacity in flexure of beams reinforced with ribbed, galvanized or epoxy coated bars was not statistically dissimilar to that of black steel reinforced beams from the specimens subjected to flexure test such that pure flexure occurred within the middle third of the beam. Furthermore, results from load-slip measurements were indicative of the variation in bond for the different bar coatings. It was found that loads at a slip of 0.05mm was close to the ultimate load and accordingly loads at lower slip levels such as 0.01 mm and 0.02 mm were considered for analysis.

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2.0 MATERIALS AND METHODS FOR EXPERINMENT

2.1 Aggregates

The fine aggregate was gotten from the river, washed sand deposit, coarse aggregate was granite a crushed rock of 12 mm size and of high quality. Both aggregates met the requirements of [25]

2.1.2 Cement

The cement used was Ordinary Portland Cement, it was used for all concrete mixes in this investigation. The cement met the requirements of [26]

2.1.3 Water

The water samples were clean and free from impurities. The fresh water used was gotten from the tap at the Civil Engineering Department Laboratory, University of Uyo, Uyo. Akwa - Ibom State. The water met the requirements of [27]

2.1.4 Structural Steel Reinforcement

The reinforcements are gotten directly from the market in Port Harcourt. [28]

2.1.5 Corrosion Inhibitors (Resins / Exudates) Mangifera indica

The study inhibitor Mangifera indica is of natural tree resin /exudate substance extracts. They are abundantly found in Rivers State bushes and they are sourced from plantations and bushes of Odioku communities, Ahoada West Local Government areas, Rivers State, from existed and previously formed and by tapping processes for newer ones.

2.2 EXPERIMENTAL PROCEDURES

2.2.1 Experimental method

2.2.2 Sample preparation for reinforcement with coated resin/exudates

Corrosion test was conducted on high tensile reinforcing steel bar of 12mm, specimens rough surface were treated with sandpaper and wire brush, washed with acetone to remore rust and dried to enable proper adhesion of coated / inhibitive materials. Coating was done by direct application on the ribbed reinforcement rough surface with 150µm, 250µm and 350µm coated thicknesses of Mangifera indica paste were polished and allowed to dry for 72 hours before embedded into concrete slab.

Mix ratio of 1:2:3 by weight of concrete, water cement ratio of 0.65, and manual mixing was adopted. The samples were designed with sets of reinforced concrete slab of 150mm thick x 350mm width x 900mm long, uncoated and coated specimens of above thicknesses were embedded into the concrete, spaced at 150mm apart. Fresh concrete mix batch were fully compacted to remove trapped air, with concrete cover of 15mm and projection of 150mm for half cell potential measurement and concrete resistivity tests. Slabs were demoulded after 72 hours and cured for 28 days with room temperature and corrosion acceleration ponding process with Sodium Chloride lasted for 119days with 14 days checked intervals for readings. The corrosion rates were quantified predicated on current density obtained from the polarization curve and the corrosion rate quantification set-up. The corrosion cell consisted of a saturated calomel reference electrode (SCE), counter electrode (graphite rod) and the reinforcing steel embedded in concrete specimen acted as the working electrode. The polarization test was performed utilizing scanning potential of -200 mV through 1200mV, with a scan rate of 1mV/s. The data were recorded for a fine-tuned duration of 1hr at ambient temperature. The polarization curve was obtained as the relationship between corrosion potential and current density.

2.3 Accelerated Corrosion Test

In order to test concrete resistivity and durability against corrosion, it was necessary to design an experiment that would accelerate the corrosion process and maximize the concrete's resistance against corrosion until failure. The accelerated corrosion test allows the acceleration of corrosion to reinforcing steel embedded in concrete and can simulate corrosion growth that would occur over decades. A laboratory acceleration process helps to distinguish the roles of individual factors that could affect chloride induced corrosion. An accelerated corrosion test is the impressed current technique which is an effective technique to investigate the corrosion process of steel in concrete and to assess the damage on the concrete cover. (Care and Raharinaivo [29] Reinforcement corrosion normally requires long exposure period of time, and usually by the first crack observed on the concrete surface. Therefore, for design of structural members and durability against corrosion as well as selection of suitable material and appropriate protective systems, it is useful to perform accelerated corrosion tests for obtaining quantitative and qualitative information on corrosion resistance in a relatively shorter period of time.

2.4 Corrosion Current Measurements (Half-cell potential measurements)

Half-cell potential measurements are indirect method of assessing potential bar corrosion, but there has been much recent interest in developing a means of performing perturbative electrochemical measurements on the steel itself to obtain a direct evaluation of the corrosion rate (Gowers and Millard [30]). Corrosion rates have been related to electrochemical measurements based on data first reported by Stern and Geary [31]. If the potential measurements indicate that there is a high probability of active corrosion, concrete resistivity measurement can be subsequently used to estimate the rate of corrosion. This was also stated from practical experience (Figg and Marsden [32] and Langford and Broomfield [33]. Classifications of the severity of rebar corrosion rates are presented in Table 2.1. However, caution needs to be exercised in using data of this nature, since constant corrosion rates with time are assumed.

Table 2.1: Dependence between potential and corrosion probability

Potential E_{corr}	Probability of corrosion
Ecorr < −350mV	Greater than 90% probability that reinforcing steel corrosion is occurring in that area at the time of measurement
$-350mV \le E_{corr} \le -200mV$	Corrosion activity of the reinforcing steel in that area is uncertain
$E_{corr} > -200mV$	90% probability that no reinforcing steel corrosion is occurring in that area at the time of measurement (10% risk of corrosion

2.5 Concrete Resistivity Measurement Test

In the study, the Wenner four probes method was used; it was done by placing the four probes in contact with the concrete directly above the reinforcing steel bar. Different readings were taken at different locations at the surface of the concrete. The mean values of the readings were recorded as the final readings of the resistivity in the study. The saturation level of the slabs was monitored through concrete electrical resistivity measurements, which are directly related to the moisture content of concrete. The electrical resistivity becomes constant once the concrete has reached saturation. Before applying water on the slabs, the concrete electrical resistivity was measured in the dry condition at the specified locations. Henceforth, these measurements will be referred to as the measurements in «dry» conditions. These locations were chosen at the side of the slabs, since concrete electrical resistivity measurements could be taken when water was on the top surface of the slab. Time limitation was the main challenge to perform all the experimental measurements, as the concrete saturation condition changes with time. After applying water on the surface of the slabs, the concrete resistivity was measured daily at the reference locations, looking for the saturation condition. Since each of the slabs had a different w/c, the time needed to saturate each of the slabs was not the same. Once one slab would reach the saturated condition, the water could be drained from that slab, while the other slabs remained ponded.

Table 2.2: Dependence between concrete resistivity and corrosion probability

Concrete resistivity ρ, kΩcm	**Probability of corrosion**
$\rho < 5$	Very high
$5 < \rho < 10$	High
$10 < \rho < 20$	Low to moderate
$\rho > 20$	Low

2.6 Tensile Strength of Reinforcing Bars

To ascertain the yield and tensile strength of tension bars, bar specimens of 12 mm diameter of non-corroded, corroded and coated were tested in tension in a Universal Testing Machine and were subjected to direct tension until failure; the yield, maximum and failure loads being recorded. To ensure consistency, the remaining cut pieces from the standard length of corroded and non-corroded steel bars were subsequently used for mechanical properties of steel.

3.0 Experimental results and discussion

The results of the half-cell potential measurements in table 3.1 were plotted against concrete resistivity of table 3.2 for easy interpretation. It is evident that potential E_{corr} if low (< -350mV) in an area measuring indicates a 95% probability of corrosion. In the other measuring points, potential E_{corr} is high ($-350\text{mV} \leq E_{\text{corr}} \leq -200\text{mV}$), which indicates a 10% or uncertain probability of corrosion.

Results of the concrete resistivity measurements are shown in Table 3.2. It used as indication of likelihood of significant corrosion ($\rho < 5$, $5 < \rho < 10$, $10 < \rho < 20$, $\rho > 20$) for Very high, High, Low to moderate and Low, for Probability of corrosion. Resistivity survey data gives an indication of whether the concrete condition is favorable for the easy movements of ions leading to more corrosion. Concrete resistivity is commonly measured by four-electrode method.

3.1 Non-corroded Concrete Slab Members

Results obtained from table 3.1 of half-cell potential measurements for and concrete resistivity for 7days to 119 days respectively indicated a 10% or uncertain probability of corrosion which indicates no corrosion presence or likelihood and concrete resistivity which indicated a low probability of corrosion or no corrosion indication.

Tables 3.1, 3.2 and tables 3.3 are the results of average values derived from randomly slab samples from A-I of control, corroded and coated specimens of 150µm, 250µm, 350µm summarized to A, B and C from ABC, DEF and GHI. Figures 3.1 and 3.2 are the plots representations of Concrete Resistivity ρ, kΩcm versus Potential $E_{corr,}{}^{mV}$ Relationship which showed average of 27.2% Potential $E_{corr,}{}^{mV}$ and 87.8% Concrete Resistivity. Figure 3.3 and 3.4 are the plots of yield stress and ultimate strength of mechanical properties of non-corroded specimens at 100.3% and 100.68%, while figures 3.5 and 3.6 are the plots of weight loss versus cross-section diameter reduction at 67.1% and 98.2% respectively.

3.2 Corroded Concrete Slab Members

Tables 3.1, 3.2 and 3.3 are the results recorded of potential $E_{corr,}{}^{mV}$ and concrete resistivity and tensile strength properties for non- inhibited concrete specimens on the mapping areas for the accelerated periods of 7days to 119 days which indicated 95% probability of corrosion and indicating a high or moderate probability of corrosion. Average results on comparison showed an increase of 70.1% against 27.2% non-corroded of Potential $E_{corr,}{}^{mV}$ and 87.8% to 38.8% a decrease values in Concrete Resistivity. Figures 3.1 and 3.2 are the plots representations of Concrete Resistivity ρ, kΩcm versus Potential $E_{corr,}{}^{mV}$ Relationship. Figures 3.3 and 3.4 are the plots of yield stress against ultimate vigor at summary and average state of corroded slab with nominal values of 100% and decremented in ultimate vigor from 100.68% to 96.12%, while figures 3.5 and 3.6 presented the weight loss versus cross-section diameter reduction decremented due to assail from sodium chloride from 67.1% to 48.5% and 98.2% to 94.82% respectively.

3.3 Mangifera indica Steel Bar Coated Concrete Cube Members

Tables 3.1 and 3.2 are the results recorded of potential $E_{corr,mV}$, and concrete resistivity of Mangifera indica inhibited specimen, the results indicated a 10% or uncertain probability of corrosion which indicates no corrosion presence or likelihood and concrete resistivity indicated a low probability of corrosion or no corrosion indication. Average percentile results of potential $E_{corr,mV}$, and concrete resistivity are 26.57% and 61.25% respectively. When compared to corroded samples, corroded has 70.1% increased values potential $E_{corr,mV}$ and 38.8% decreased values of concrete resistivity . Figures 3.1 and 3.2 are the plots representations of concrete resistivity ρ, kΩcm versus potential $E_{corr,}^{mV}$ relationship. Figures 3.3 and 3.4 are the plots of yield stress against ultimate vigor at summary and average state of corroded slab with nominal values of 100% and decremented in ultimate strength from 105.36% to 96.12%, while figures 3.5 and 3.6 presented the weight loss versus cross-section diameter reduction decreased due to attack from sodium chloride from 64.8% to 44.45% and 46.76% to 86.43% respectively

Table 3.1 : Potential $E_{corr,}$ after 28b days curing and 119 days acceleration Ponding

s/no	Inhibitor (resin/exudates) and controlled sample	**Potential $E_{corr,mV}$**								
		Time Intervals after 28 days curing								
		A (7days)	B (21days)	C (35days)	D (49days)	E (63days)	F (77days)	G (91days)	H (105 days)	I (119 days)
1	Control Concrete slab	-102	-102.2	-100.3	-101.2	-101.7	-100.8	-100.3	-101.4	-100.4
2	Non-inhibitor	-268.5	-294.7	-328.6	-367.7	-377.5	-384.5	-418.4	-425.6	-429.7
		150µm,			250µm,			`350µm,		
3	Mangifera indica	-129.5	-135.5	-128.6	-121.5	-124.8	-115.6	-125.6	-132.6	-138.7
Average values Potential $E_{corr,mV}$										

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		ABC = A	`DEF = B	GH1 = C
1A	Control Concrete slab	-101.5	-102.2	-100.7
2A	Non-inhibitor	-297.3	-393.5	-424.6
		150µm,	250µm,	`350µm,
3A	Mangifera indica	-131.2	-201.6	`-132.3

Table 3.2 : Results of Concrete Resistivity ρ, kΩcm Time Intervals after 28 days curing curing and 119 days acceleration ponding

s/no	Inhibitor (resin/exudates) and controlled sample	Concrete Resistivity ρ, kΩcm								
		Time Intervals after 28 days curing								
		A (7days)	B (21days)	C (35days)	D (49days)	E (63days)	F (77days)	G (91days)	H (105 days)	I (115 days)
1	Control Concrete slab	15.35	15.52	15.42	15.65	15.48	14.43	15.45	15.45	15.48
2	Non-inhibitor	6.77	6.91	7.74	8.05	8.22	8.38	9.12	9.55	9.59
		150µm,			250µm,			`350µm,		
3	Mangifera indica	13.88	14.02	14.36	14.47	14.5	14.67	14.84	14.92	14.65
Average values Concrete Resistivity ρ, kΩcm										
		ABC = A			`DEF = B			GH1 = C		
1B	Control Concrete slab	15.43			15.19			15.46		

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2B	Non-inhibitor	7.14	8.21	9.42
3B		150µm,	250µm,	`350µm,
	Mangifera indica	14.1	14.5	14.8

Table 3.3 : Mechanical properties of Non-Corroded, Corroded and Coated Beam

s/no	Inhibitor (resin/exudates) and controlled sample	**Yield Stress (N/mm^2)**								
		Time Intervals after 28 days curing								
		A (7days)	B (21days)	C (35days)	D (49days)	E (63days)	F (77days)	G (91days)	H (105 days)	I (119 days)
1	Control Concrete slab	410.4	410.1	410.3	410.0	410.3	410.7	410.0	410.5	410.4
2	Non-inhibitor	4.10.2	410.0	410.0	410.4	410.0	410.3	410.0	410.3	410.2
		150µm,			**250µm,**			**`350µm,**		
3	Mangifera indica	410.6	410.2	410.7	410.7	410.7	410.4	410.2	410.2	410.4
		Average values Yield Stress (N/mm^2)								
		ABC = A			`DEF = B			GH1 = C		
1C	Control Concrete slab	410.27			410.33			410.3		
2C	Non-inhibitor	410.01			410.23			410.17		
		150µm,			250µm,			`350µm,		
3C	Mangifera indica	410.45			410.60			410.27		
		Ultimate strength (N/mm$^{2)}$								

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1	Control Concrete slab	564.7	565.6	562.4	562.6	566.8	562.2	565.2	562.7	562.4
2	Non-inhibitor	584.7	585.8	586.8	582.8	586.8	582.8	585.4	582.6	588.4
		150µm,			**250µm,**			**`350µm,**		
3	Mangifera indica	560.9	566.4	568.4	568.7	569.5	568.7	568.5	568.9	569.5
	Average value of Ultimate strength (N/mm$^{2)}$									
		ABC = A			`DEF = B			GH1 = C		
1D	Control Concrete slab	564.23			563.87			563.43		
2D	Non-inhibitor	585.77			584.13			585.47		
		150µm,			250µm,			`350µm,		
3D	Mangifera indica	565.23			568.3			567.97		
		Weight Loss of Steel Loss (in grams)								
1	Control Concrete slab	7.25	7.37	7.33	7.25	7.26	7.45	7.28	7.18	7.35
2	Non-inhibitor	10.628	10.796	10.839	10.876	10.882	10.884	10.835	10.885	10.676
		150µm,			**250µm,**			**`350µm,**		
3	Mangifera indica	7.29	7.29	7.25	7.30	7.26	7.26	7.31	7.29	7.28
		Average values of Weight Loss of Steel Loss (in grams)								
		ABC = A			`DEF = B			GH1 = C		
1E	Control Concrete slab	7.32			7.33			7.27		
2E	Non-inhibitor	10.754			10.681			10.799		

		150µm,			**250µm,**			**`350µm,**		
3E	Mangifera indica	7.27			7.27			7.29		
		Cross- section Area Reduction (Diameter, mm)								
1	Control Concrete slab	12	12	12	12	12	12	12	12	12
2	Non-inhibitor	11.53	11.53	11.54	11.61	11.64	11.71	11.75	11.76	11.79
		150µm,			**250µm,**			**`350µm,**		
3	Mangifera indica	12	12	12	12	12	12	12	12	12
		Average Values of Cross- section Area Reduction (Diameter, mm)								
		ABC = A			`DEF = B			GH1 = C		
1F	Control Concrete slab	12			12			12		
2F	Non-inhibitor	11.587			11.563			11.662		
		150µm,			**250µm,**			**`350µm,**		
3F	Mangifera indica	12			12			12		

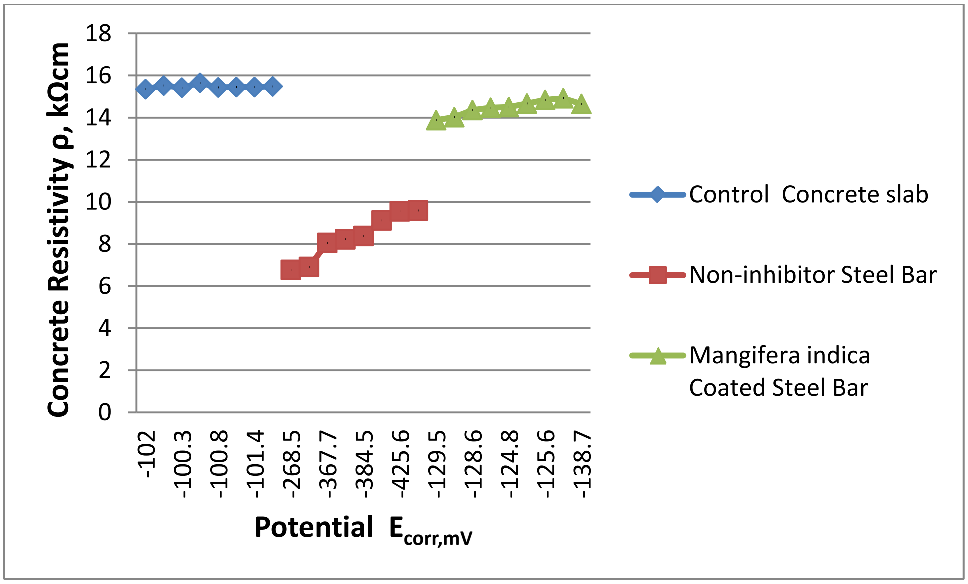

Figure 3.1: Concrete Resistivity versus Potential Relationship Concrete Resistivity ρ, kΩcm versus Potential $E_{corr,}$^{mV} Relationship

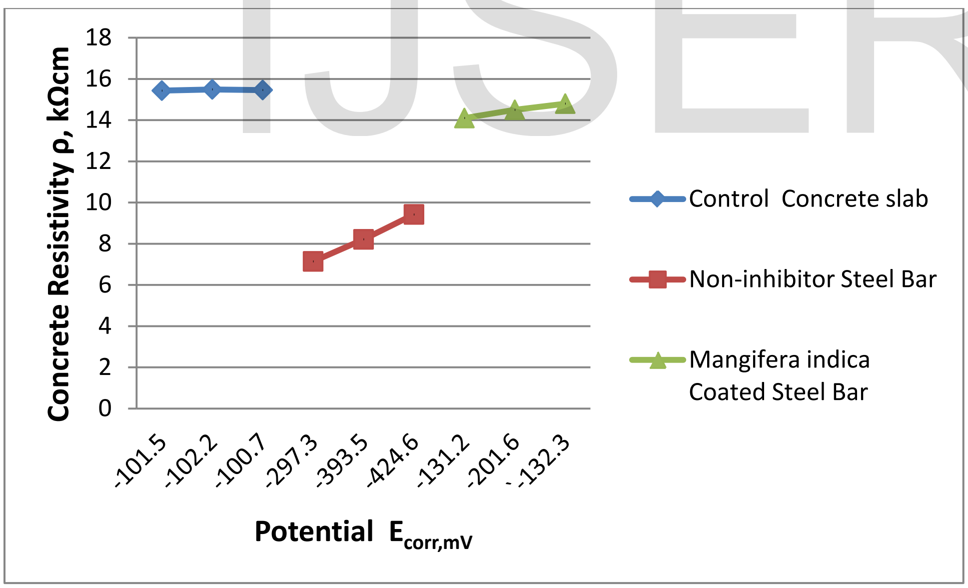

Figure 3.2: Average Concrete Resistivity versus Potential Relationship

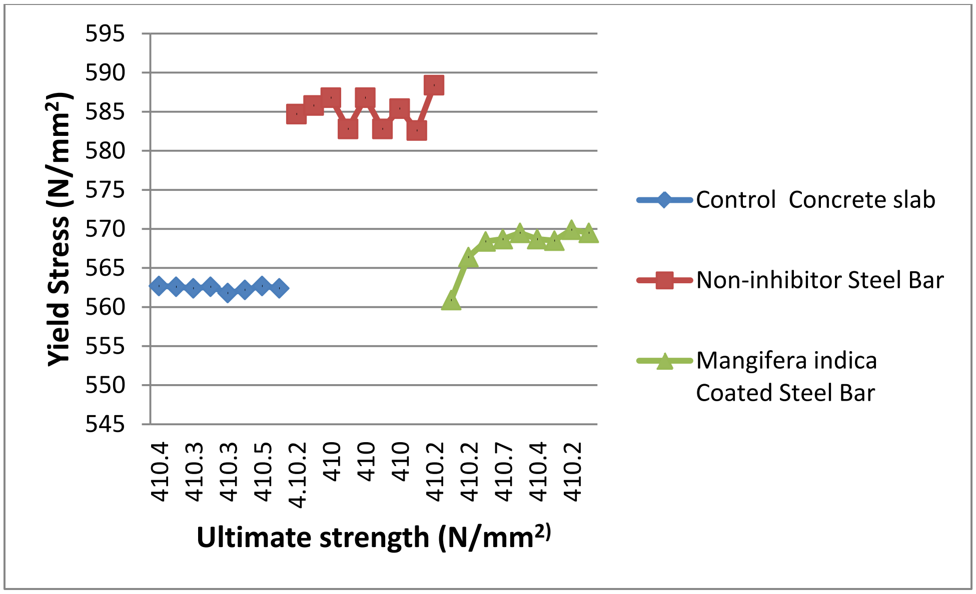

Figure 3.3: Yield Stress versus Ultimate strength

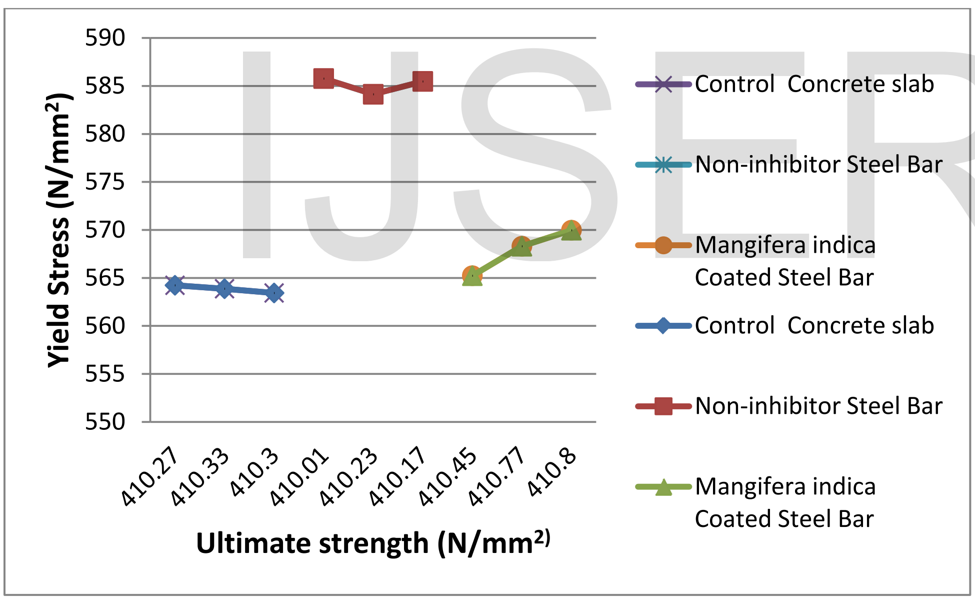

Figure 3.4: Average Yield Stress versus Ultimate strength.

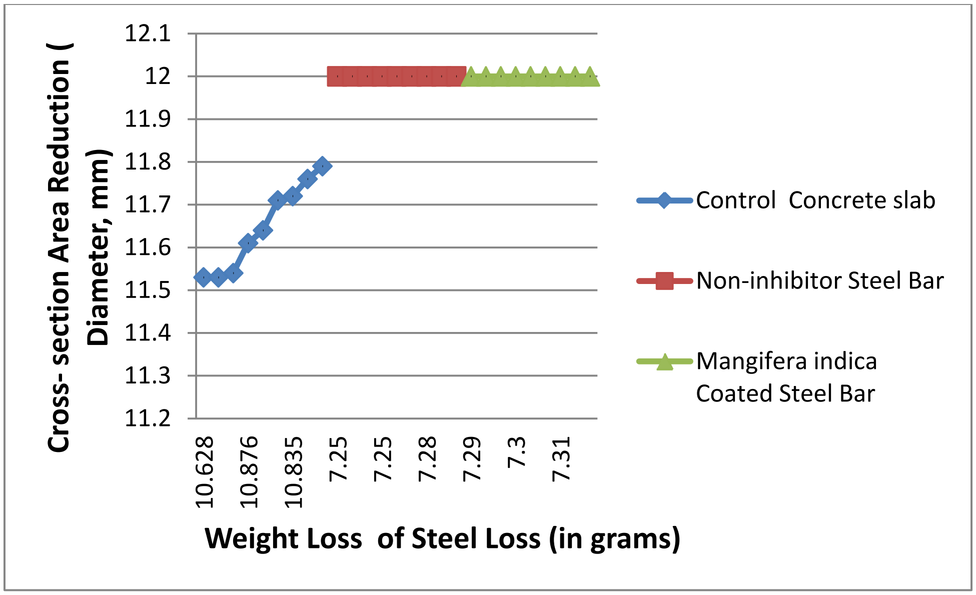

Figure 3.5: Weight Loss of Steel Loss versus Cross- section Area Reduction

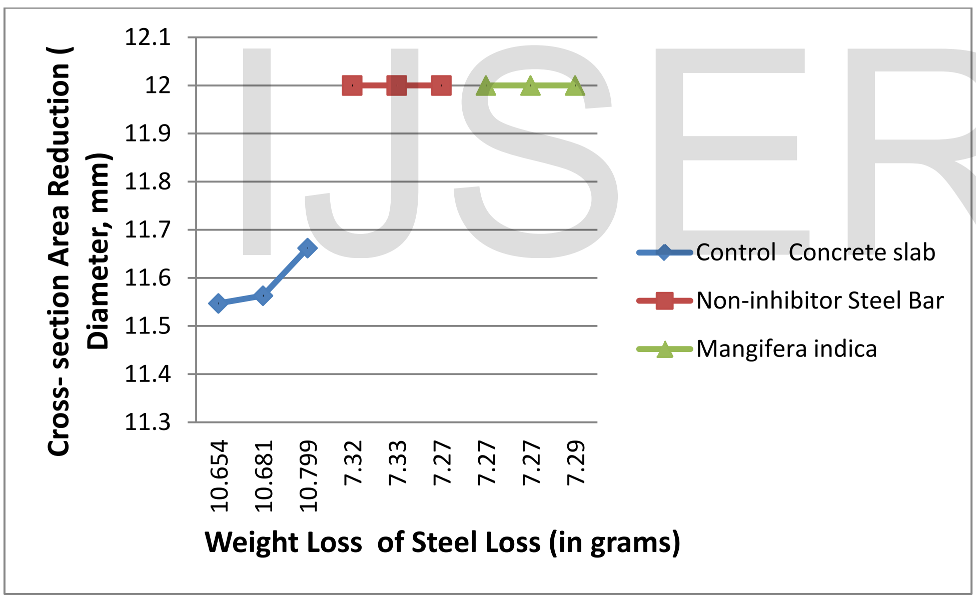

Figure 3.6: Average Weight Loss of Steel Loss versus Cross- section Area Reduction

4.0 Conclusion

Experimental results showed the following conclusions:

i. Corrosion potential was obtained from non-inhibited specimens

ii. Results justified the effective use of resins of trees extract as corrosion inhibitors

iii. Entire results showed higher values of non-corroded and coated to corroded specimens

iv. Tensile strength of inhibited reinforcement is higher compared to the corroded specimens.

v. Adhesion of resins to steel reinforcement was adequate and active

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