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Investigation of Corrosion Inhibitive Property of Chrysopogon Zizanioides + Mn^{2+} System in Aqueous Medium

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Abstract: This research work is concerned with the development of new ecofriendly inhibitor system which functions for the corrosion control of carbon steel in aqueous environment efficiently. 300 ppm of the extract obtained from the root of the plant Chrysopogon Zizanioides worked in conjunction with 100 ppm of Mn^{2+} ***ions in controlling the corrosion of carbon steel immersed in 180 ppm of chloride ion solution. A film is formed on the surface of the carbon steel immersed in the inhibitor system containing the root extracts of the plant Chrysopogon Zizanioides (CZRE) and*** Mn^{2+} ***ions. Inhibition was found to increase with increase in concentration of the extract. In order to investigate the nature of the protective film UV-visible spectroscopy, FTIR spectroscopy, Scanning Electron Microscopy, EDX. electrochemical studies, temperature studies, cyclic voltammetry and XRD have been used in the present study. Based on the results obtained from the mass-loss method, polarisaion studies, surface analysis, spectral studies, diffraction studies and electron dispersive x-ray spectra a suitable mechanism for the corrosion inhibition has been proposed.***

Keywords: Carbon Steel, Corrosion, Inhibitor, Inhibition Efficiency, Chrysopogon Zizanioides

I. INTRODUCTION

Corrosion is considered as a major industrial problem and has posed a serious concern. It is highly a complex phenomenon, and a wide range of physical, electrochemical and mechanical mechanism are involved. It is a constant and continuous problem, often very difficult to eliminate completely. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors which adsorb on the reacting metal surface. Green corrosion inhibitors (extracts from plant) which happen to be nontoxic organic compounds, displaying substantially improved environmental properties 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 and will be the inhibitors most widely used in the future. The present study investigates the role of *Chrysopogon Zizanioides* + Mn^{2+} as the corrosion inhibitor of carbon steel in aqueous medium. This is commonly called as Vettiver which belongs to the family, poaceae and the root system of this plant is finely structured, very strong and can grow 3 metres to 4 metres deep within. The chemical substances present in the CZRE are responsible for the formation of a protective layer that blankets the metal surface and retards the corrosion. The adsorptive property and the formation of protective layer is investigated through various techniques.

II. EXPERIMENTS AND METHODS

A. *Mass loss method*

1) *Determination of corrosion rate:* Polished specimens were initially weighed in an electronic balance. Weighed samples were immersed in 100 ml of the DD water with and without the different concentrations of the inhibitor for various intervals of time. They were then taken out and washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed.

From the change in weight of specimens, the corrosion rate was calculated using the following relationship.

$$\text{Corrosing rate} = \frac{W}{A \times T} \text{ (mdd)}$$

W = Loss in weight in mg
A = Surface area of the specimen (dm^2)

T = Period of immersion (days)

Corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100\,[1 - (W_2 / W_1)]\%$$

where W_1 = corrosion rate in the absence of the inhibitor and
W_2 = corrosion rate in the presence of the inhibitor.

Table 1

Inhibition efficiency (IE) of carbon steel in aqueous environment (Cl^- = 180 ppm) in the presence of different concentrations of the inhibitor system by the mass-loss method

Inhibitor system: *Chrysopogon Zizanioides*+Mn^{2+} Immersion period: 1 day

S. No	CZRE, ppm	Mn^{2+}, ppm	Corrosion rate, mdd	Inhibition Efficiency,%
1	0	0	39	-
2	0	100	35.81	8.17
3	50	100	34.79	10.79
4	100	100	29.38	24.66
5	150	100	23.71	39.2
6	200	100	18.73	51.97
7	250	100	12.57	67.76
8	300	100	7.39	81.08

From the Table1, it is observed that IE (81.08%) is maximum for 300 ppm concentration of the root extract with 100 ppm of Mn^{2+}. It clearly states that corrosion rate is minimum for this composition of the inhibitor system and ensures that the inhibition efficiency increases[1] as the concentration of the inhibitor increases which is shown in Figure 1.

Figure 1 Inhibition Efficiency of carbon steel with different concentrations of CZRE

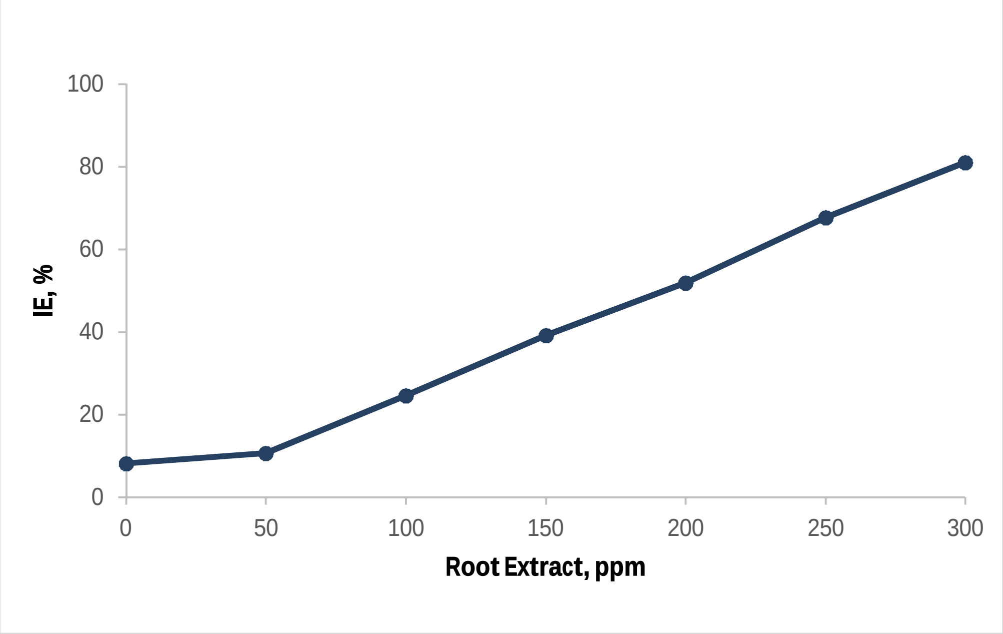


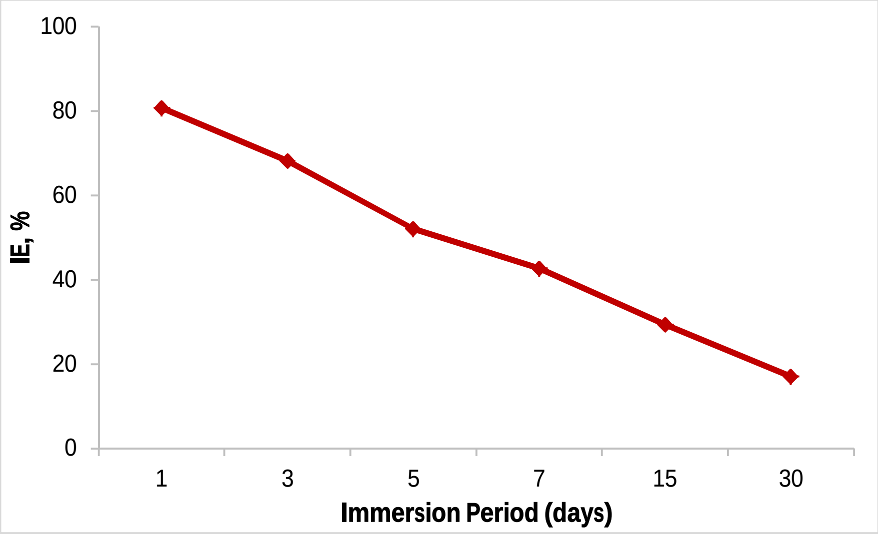
Table 2 Effect of duration of immersion on the IE of CZRE+Mn^{2+} system on Carbon steel

Corrosion rates and inhibition efficiency of carbon steel in aqueous environment (Cl^- = 180 ppm) in the presence of the inhibitor system for various number of immersion period by the mass-loss method.

S.No	CZRE (ppm)	Mn^{2+} (ppm)	Immersion period (days)	Corrosion rate (mdd)	Inhibition Efficiency (%)
1	300	100	1	7.53	80.69
2	300	100	3	12.39	68.23
3	300	100	5	18.69	52.07
4	300	100	7	22.34	42.71
5	300	100	15	27.52	29.43
6	300	100	30	32.31	17.15

The corrosion rates of carbon steel in the presence of the inhibitor system in 180 ppm Cl^- ion solution for different durations of immersion are tabulated in Table 2 and the IE as a function of immersion period are shown in Figure 2.

Figure 2 Inhibition efficiency of carbon steel of CZRE - $Mn^{2+}$for different immersion period.



From the Table 2 and Figure 2, it is clear that the IE decreases from 80.69 % to 52.07 % from the first day to the third day of immersion. On the fifteenth day it is found to be only 29.43%. This indicates that the aggressive chloride ions are finally able to destroy the film, formed on the surface. The film is not able to sustain their attack for a long time. It is obvious that the inhibitor system protects the carbon steel for only one day.

The decrease in IE with time may be due to the fact that the molecules are physically adsorbed on the surface and as the activation energy for desorption is less for physical adsorption. Therefore the molecules are easily desorbed from the surface after some days and hence the inhibition efficiency decreases on increasing the period of immersion[2].

B. *Effect of pH on the IE of CZRE+Mn^{2+} System*

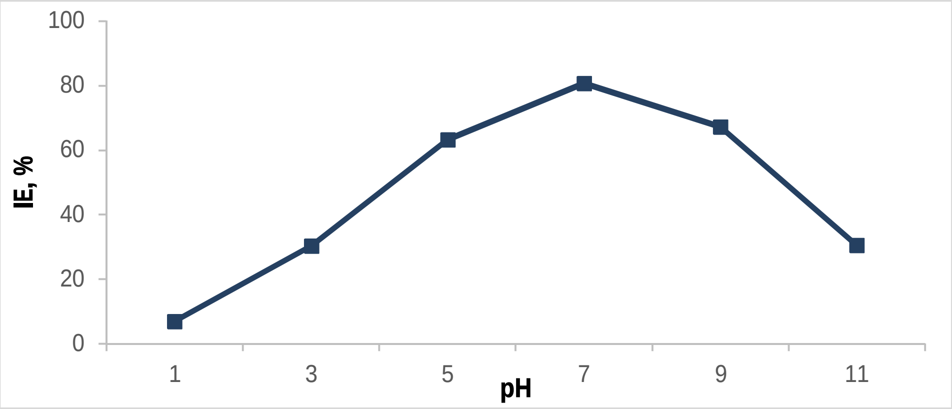
Corrosion rates of carbon steel in aqueous environment (Cl^- = 180 ppm) in the presence of the inhibitor system at different pH and the inhibition efficiencies obtained by the mass-loss method are tabulated and given in Table 3.

Table3 Effect of pH on the IE of CZRE+Mn^{2+} system on carbon steel in aqueous medium

S.No.	CZRE (ppm)	Mn^{2+} (ppm)	pH	Corrosion rate (mdd)	Inhibition efficiency (%)
1	300	100	1	36.29	6.94
2	300	100	3	27.16	30.35
3	300	100	5	14.31	63.3
4	300	100	7	7.48	80.8
5	300	100	9	12.75	67.3
6	300	100	11	27.10	30.5

IE as a function of pH is shown in Figure 3. It is found from the Table 3 that the inhibition efficiency increases with increase in the pH, reaches maximum value at pH = 7 and then decreases. The IE at pH 5 is found to be 63.3% and at pH 7, it is 80.8%. This is the highest IE obtained. This may be due to the ionization of the phytoconstituents at pH 7, resulting in the availability of the COO$^-$ ion, for the interaction with Mn^{2+} ions. At higher pH due to the precipitation of Mn^{2+} as Mn(OH)$_2$ a slight reduction in IE is noticed. The amount of Mn^{2+} ions for the transport of phytoconstituents to the surface of the carbon steel is less[3]. Hence a reduction in the IE is noted.

Figure 3 Inhibition efficiency of carbon steel of CZRE + Mn $^{2+}$ for different pH



C. Temperature Studies

The dependence of corrosion rate (CR) on the temperature is given by the Arrhenius equation: CR=A exp (-Ea / RT) where A is the pre exponential factor, Ea is the activation energy, R is the gas constant and T is the temperature. A graph is plotted between log CR and 1/T and is shown in Figure 9 indicates that as the temperature increases, the rate of corrosion increases[14].

Figure 9 Arrhenius plots in the absence and presence of different concentrations of CZRE

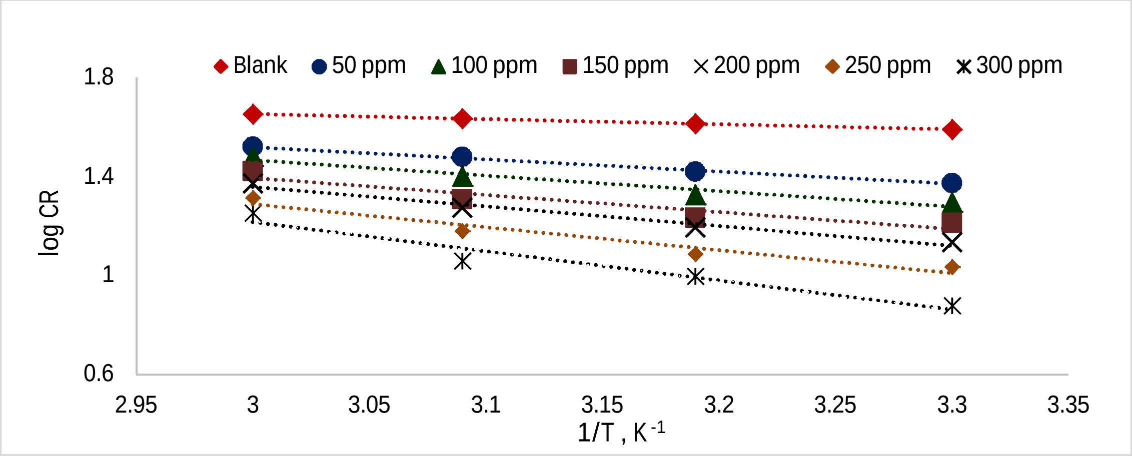
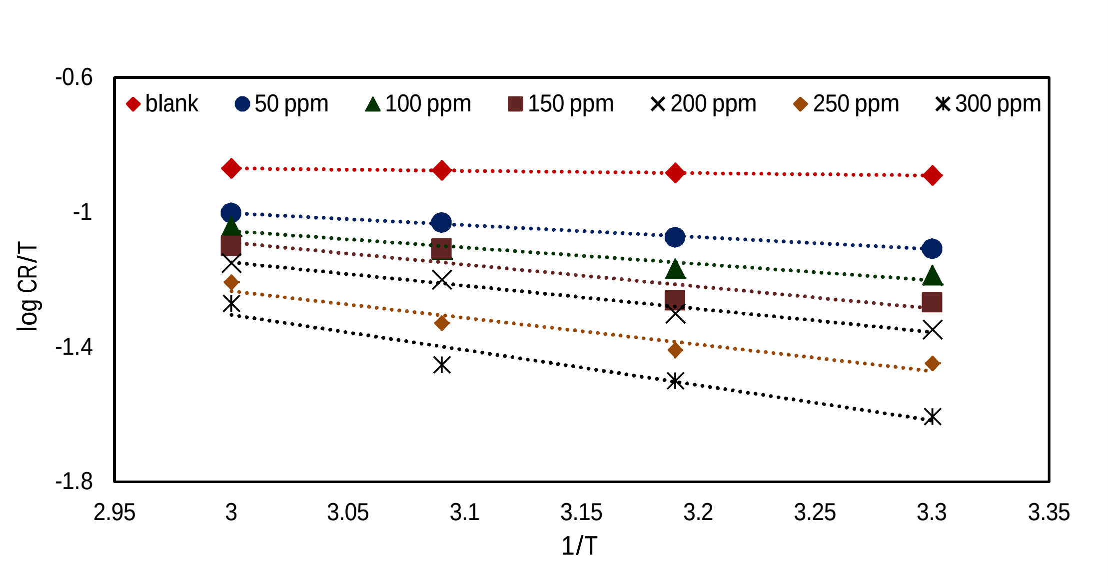


Table 7 Kinetic parameters for the Arrhenius equation for different concentration of the inhibitor

Conc, ppm	E_a, KJ/MOL	R^2
0	3.955	0.9991
50	9.5	0.9957
100	11.94	0.9932
150	13.29	0.8974
200	15.06	0.9771
250	17.72	0.9444
300	22.63	0.9425

The activation energy (E_a) for the system is found out from the slope of the Arrhenius plot of log CR versus 1/T. Here the slope is equal to E_a/2.303R where R is the gas constant and T is the temperature in Kelvin. These values ranges from 3.95 – 22.63 KJMol^{-1}. The E_a is higher for the inhibited system than the uninhibited system. This is an indication of spontaneous adsorption of the CZRE on the metal surface and is attributed to physical adsorption. They are lower than the threshold value of -80 KJ Mol $^{-1}$ which is required for the chemical adsorption[15]. This tells us that the adsorption of CZRE on carbon steel is physisorption.

Figure 10 Transition state plot for carbon steel in the absence and presence of CZRE



The entropy and enthalpy of the corrosion process are calculated from the transition state equation CR=RT/Nh exp ΔS^0/R exp -ΔH/RT where h is the Planck's constant, N Avogadro number, R is the gas constant, ΔH^0 is the enthalpy of activation and ΔS^0 is the entropy of activation. A graphical representation of log (CR/T) versus 1/T will give straight line with a slope equal to ΔH/2.303 RT and intercept equal to [log(RT/Nh) +(ΔS^0/2.303R)]. From this ΔH^0 and ΔS^0 are calculated and is given in Table 8.

Table 8 Kinetic parameters for the transition state equation for different concentrations of the inhibitor CZRE on carbon steel

Conc, ppm	ΔH^0, KJ/Mol	$-\Delta S^0$ J/Mol/K	R^2
0	1.346	-210.16	0.9995
50	6.684	-196.15	0.9941
100	9.2805	-189.94	0.9266
150	12.55	-180.76	0.8296
200	13.2	-179.93	0.9745
250	15.12	-175.79	0.9289
300	20.08	-162.28	0.9288

The enthalpy has positive sign which implies that the corrosion inhibition process is endothermic and the value of ΔH^{0} increases as the concentration of CZRE increases. This tells us that corrosion rate decreases and is controlled by parameters of activation. ΔH^{0} value is lower than -80 KJ/Mole, which points to the physisorption process.

Negative value of entropy of activation ΔS^{0}, shows that the rate determination step is the formation of activated complex and represents an association rather than dissociation meaning that a decrease in disorderliness. ΔS^{0} has lower negative values in the presence of the CZRE. The decrease of ΔS^{0} with the increase in the concentration of CZRE, implies that adsorption process has happened efficiently.

D. Adsorption Isotherms

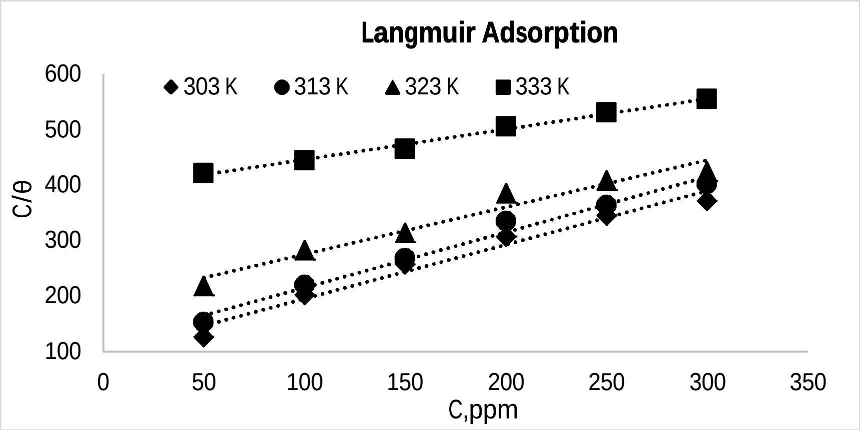
Adsorption isotherms values are important in explaining the mechanism of corrosion, and in the inhibition of organo electro chemical reactions. The degree of surface coverage θ which is calculated, gives information about the metal-inhibitor interactions. The observed surface coverage θ could be due to the adsorption of its molecules on the surface of the steel making a barrier between the metal and the environment.

The data obtained from the degree of surface coverage θ for different temperatures were used for the evaluation of different adsorption isotherms like Langmuir, Frumkin, Frendlich.

E. Langmuir Adsorption Isotherm

For the testing the Langmuir adsorption isotherm a graph is plotted between the C/θ and C for different temperatures and different concentration of the inhibitor CZRE.

Figure 11 Langmuir adsorption isotherm for CZRE on carbon steel at different temperatures



It is found that as the concentration of CZRE increases, surface coverage θ also increases. A straight line is obtained and the linear correlation co efficient values are almost equal to one which indicates that the CZRE on carbon steel obeys Langmuir adsorption isotherm. The decrease in K_{ads} value with increase in temperature states that the adsorption has not been favoured at high temperatures[16] and the results are presented in Table 9.

Table 9 Thermodynamic parameters for the inhibition of the corrosion of carbon steel by CZRE

Temp, K	K_{ads}	ΔG^{0}_{ads}(KJ/Mol)	R^{2}
303	10.16	-15.961	0.9716
313	8.62	-15.546	0.9839
323	5.23	-14.287	0.9574
333	2.55	-12.478	0.9921

The free energy of adsorption ΔG^{0}_{ads} at various concentration of inhibitor at different temperatures is calculated using the following relation: ΔG^{0}_{ads} = - RTln(55.55 K) where R is the gas constant, T is the temperature in Kelvin. The values of ΔG^{0}_{ads} at different temperatures are negative and found to be less than – 40 KJ/Mol which signifies that the reaction is spontaneous and indicates physisorption and the inhibition is due to the electrostatic interaction between the charged molecules and the charged metal surface.

F. Freundlich Adsorption Isotherm

Freundlich proposed an empirical relationship between amount of gas adsorbed by unit mass of adsorbent and pressure at a particular temperature. Following equation was proposed for Freundlich adsorption isotherm:

$$\mathbf{x/m= k.\ p^{1/n}\ (n > 1)}$$

This model is expressed using the relation $\log \theta = \log K + n \log C$.

This is obtained by plotting log θ against log C.

The value of n is used to describe the ease of adsorption and relates to the adsorption intensity and it varies with the heterogeneity of the material. It is a constant that depends on the characteristics of the adsorbed molecules and has values between 0 and 1. It is clear that the degree of surface coverage of an inhibitor is proportional to its adsorption process. The values of n, K_{ads} and $\Delta G^{\mathbf{0}}_{ads}$ are tabulated in Table10.

Figure 12 Freundlich adsorption isotherm for CZRE on carbon steel at different temperatures

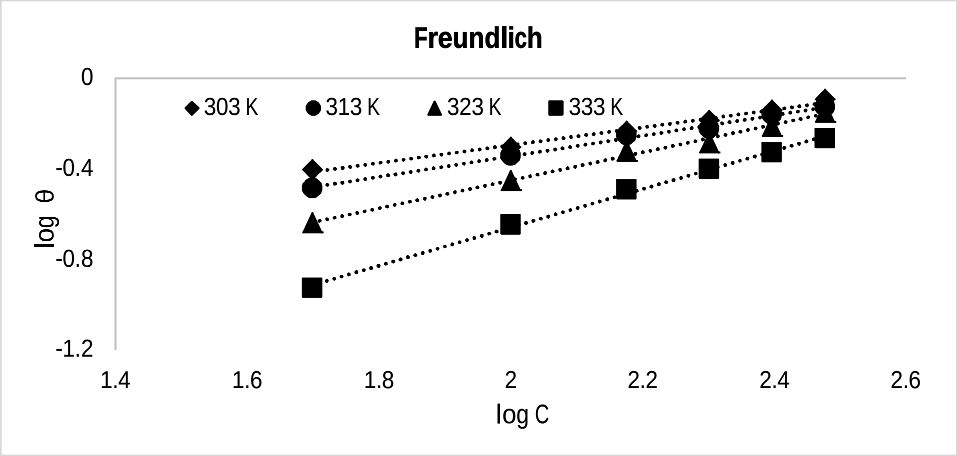


Table 10 Thermodynamic parameters for the inhibition of the corrosion of carbon steel by CZRE

Temp K	K_{ads}	ΔG^{0}_{ads}	n	R^2
303	82.3	-21.241	0.394	0.9904
313	55.6	-20914	0.454	0.9948
323	20.8	-18.941	0.614	0.9941
333	4.48	-15.276	0.845	0.9975

From the calculated values of n presented in the Table 10, it is clear that it indicates a favorable adsorption process and its average value reaches to 0.6. Negative sign of $\Delta G^{\mathbf{0}}_{ads}$ indicates that this process is spontaneous and it slows down with increase in the temperature. The K_{ads} values too decrease with increase in temperature ensures that the adsorption process is unfavorable at higher temperatures. Straight lines obtained and the values of R which are closer to 1 indicate that the adsorption of the inhibitor onto the surface of the carbon steel can be approximated by Freundlich isotherm[17].

G. Frumkin Adsorption Isotherm

The Frumkin approach applied to the adsorption of corrosion inhibitors on metal surfaces has been explained by the relation $\log[(\theta/1-\theta) x\ C] = \log K + 2\alpha\theta/2.303$ where α is the interaction parameter that describes about the interaction between adsorbate and the adsorbent. It can have either positive or negative values. When α is less than zero there is repulsion otherwise there will be attraction.

A graph is plotted against $\log[(C\ x(\theta/1-\theta)]$ and θ , and a straight line is obtained. From that K_{ads} and α values and $\Delta G^{\mathbf{0}}_{ads}$ are calculated which is presented in Table 11.

Figure 13 Frumkin adsorption isotherm for CZRE on carbon steel at different temperatures

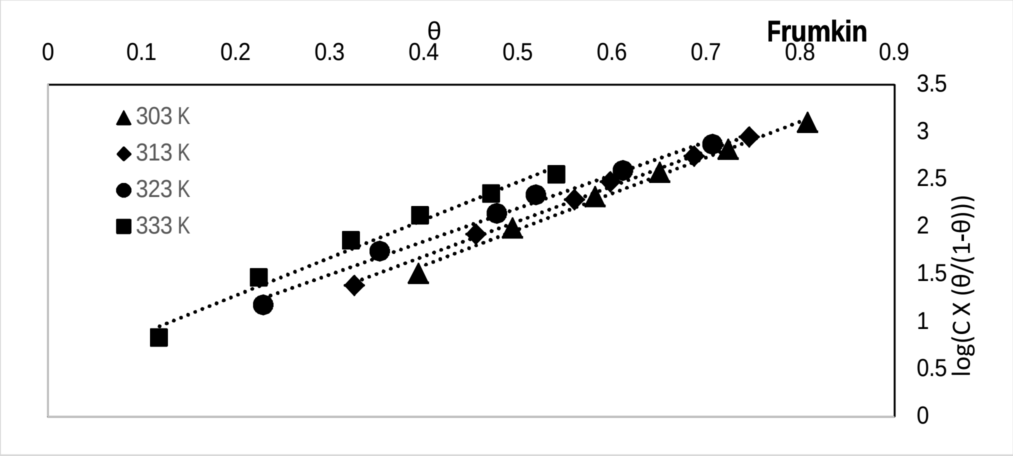


Table 11 Thermodynamic parameters for the inhibition of the corrosion of carbon steel by CZRE

Temp, K	α	K_{ads}	ΔG^0_{ads}	R^2
303	1.89	1.19×10^3	-27.964	0.9948
313	1.85	1.618×10^3	-29.687	0.9967
323	1.75	2.768×10^3	-32.078	0.9907
333	1.99	3.023×10^3	-33.315	0.9789

From the positive α values it is obvious that the increased adsorption energy with increased surface coverage θ is the result of molecular interactions. The positive and greater values of α at different temperatures imply that there is attraction between adsorbent and adsorbate. The values of K_{ads} show that the inhibitor molecules have got adsorbed well on the surface and negative ΔG^0_{ads} values indicates the spontaneity of the process and it is physisorption as the value ranges below -40 $KJMol^{-1}$. The coefficient of variation is approximately equal to one which ensures that the values obey Frumkin adsorption isotherm well.

H. Analysis of the Results of Potentiodynamic Polarization Studies

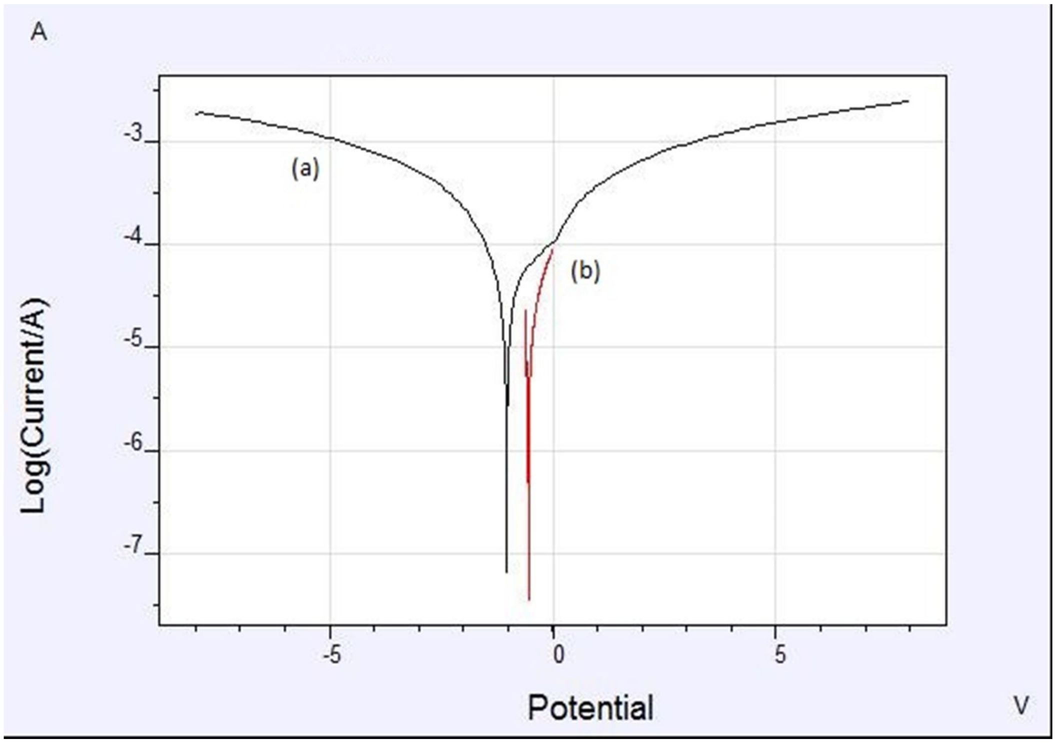
The potentiodynamic polarization curves of carbon steel immersed in 180 ppm chloride ion in the presence of Mn^{2+} and CZRE are given in Figure 4. The corrosion parameters of carbon steel immersed in 180 ppm Cl^- ion solution in the presence and absence of Mn^{2+} and CZRE are given in Table 4.

When carbon steel is immersed in 180 ppm Cl^- ion solution, the corrosion potential (Ecorr) is -0.7786 mV and the corrosion current is 1.923×10^{-5} A/cm^2. When immersed in inhibited system, the corrosion potential is found to be –1.0306 mV and the corrosion current is 4.018×10^{-6} A/cm^2. The decrease in the corrosion current and the change in the corrosion potential on the addition of the inhibitor system to 180 ppm of chloride ion solution indicate that the formulation reduces anodic dissolution and cathodic hydrogen evolution reaction of carbon steel immersed in 180 ppm of chloride ion solution. The anodic slope changes from 1.459 mV/dec to 9.062 mV/dec and the change in cathodic slope from 0.385 mV/dec to 7.823 mV/dec shows that the shift in the anodic slope is higher than the shift in cathodic slope. This indicates the modification of both anodic and cathodic reaction mechanism is inhibited by the inhibitor. This tells that CZRE acts as a mixed inhibitor and the corrosion rate decreases which indicates the adsorption of inhibitor system on the metal surface that blocks the active sites and retards the corrosion[4,5].

Table 4 Results of potentiodynamic polarization studies

S. NO	SYSTEM	E_{Corr} (mV)	b_a (mV/dec)	b_c (mV/dec)	R_p $\Omega(Cm^2)$	I_{corr} (A/cm^2)	Corrosion rate mm/y
1	180 ppm of chloride ion	-671.9	1.459	.385	6877	1.923×10^{-5}	3.492
2	180ppm of Cl^- +CZRE+Mn^{2+}	-592.8	9.062	7.823	5404	4.018×10^{-6}	.2693

Figure 4
Polarization curves for carbon steel for inhibited and uninhibited system



1) Chloride ion solution (180 ppm) in DD water
2) CZRE + Mn^{2+} + 180 ppm Chloride ion in DD water

III. EIS MEASUREMENTS

A. *Analysis of the Results of Electrochemical Impedance Spectroscopy*

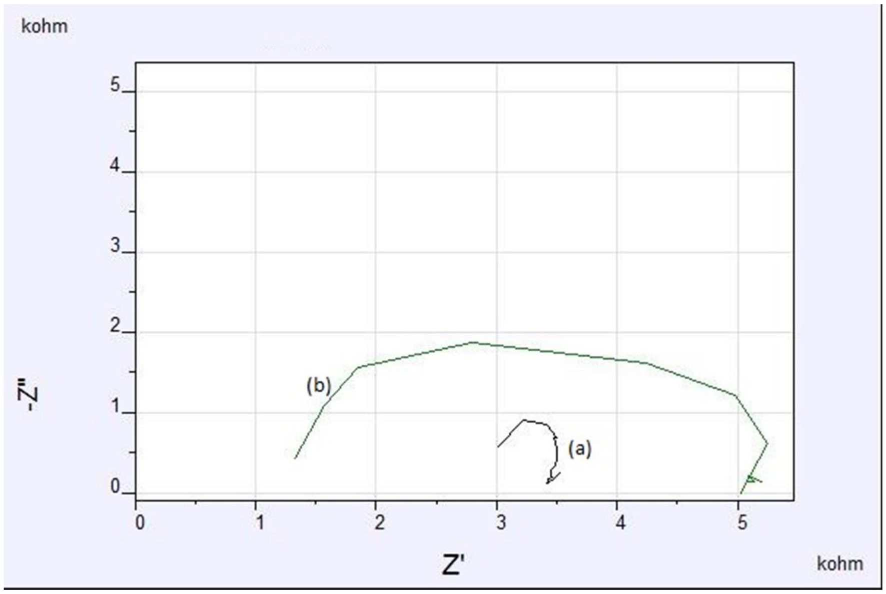
The AC impedance spectra have been used to detect the formation of film on the metal surface. It provides a rapid and convenient method to evaluate the performance of the organic coating on the metal and has been used for the corrosion studies. The AC impedance spectra of carbon steel immersed in 180 ppm chloride solution and solution containing the inhibitor formulation are shown in Figure 5. The AC impedance parameters namely charge transfer resistance and the double layer capacitance are given in Table 5. It shows clearly that in the presence of inhibitor the R_{ct} value increases and hence inhibition efficiency increases. The decrease in C_{dl} value can be attributed to the increase in the electrical double layer at the metal solution interface by the adsorption process. Further the decrease in the C_{dl} value indicates the replacement of water molecules by inhibitor molecules by the process of adsorption with an increase in surface coverage. The increase in R_{ct} values with the concentration of inhibitor tells that the charge transfer process is controlling the corrosion process. The increased R_{ct} values and decreased C_{dl} values from impedance studies justify the good performance of the extract with Mn^{2+} as corrosion inhibitor in chloride ions in DD water. This behavior means that the film obtained acts as a barrier to the corrosion process and proves the existence and the formation of the film[6,7].

R_{ct} value is used to calculate the percentage of inhibition efficiency using the equation $\%IE = [(R_{ct} - R^*_{ct}) / R_{ct}] \times 100$ where R_{ct} and R^*_{ct} indicates the charge transfer resistances with and without the inhibitor.

Table 5 AC Impedance results for carbon steel for inhibited and uninhibited system

Environment in DD water	R_{ct}(Ohm.cm^2)	C_{dl}(µF/cm^2)	Inhibition Efficiency%
180 ppm of Chloride ion in DD water	4.02×10^2	3.70×10^{-7}	89.13
Cl^- + CZRE+ Mn^{2+}	3.7×10^3	2.39×10^{-8}	

Figure 5 AC Impedance curves for carbon steel for inhibited and uninhibited system

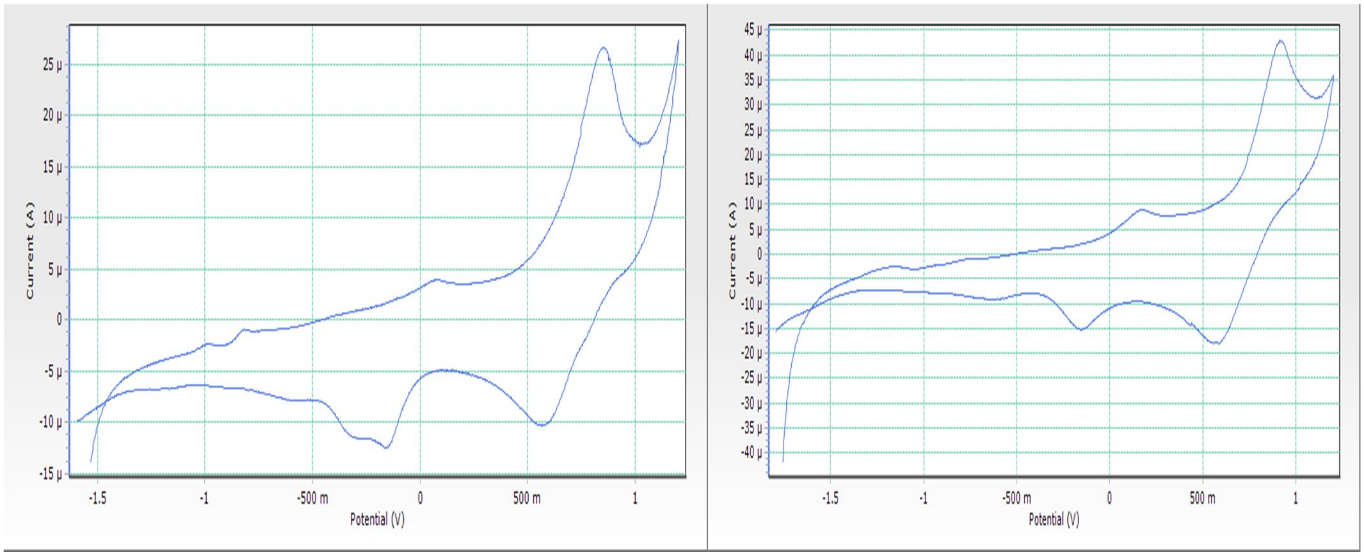


1) Chloride ion solution (180 ppm) in DD water
2) CZRE + Mn^{2+} + 180 ppm Cl^- ion in DD water

B. *Cyclic Voltammetry*

The cyclic voltammetry is used to analyze the adsorption process of CZRE at the surface of carbon steel in aqueous medium. Cyclic voltammetry is an excellent technique for surface characterizations. The peak potential, peak multiplicity, and the relative intensity of peaks can provide information about any change in the surface composition and reversibility of the electrochemical reactions that take place at the surface of the metal.

Figure 6a, 6b Cyclic Voltammogram for carbon steel for uninhibited and inhibited system



6a 6b

Table 6 Results for carbon steel for inhibited and uninhibited system of Cyclic Voltammetry studies

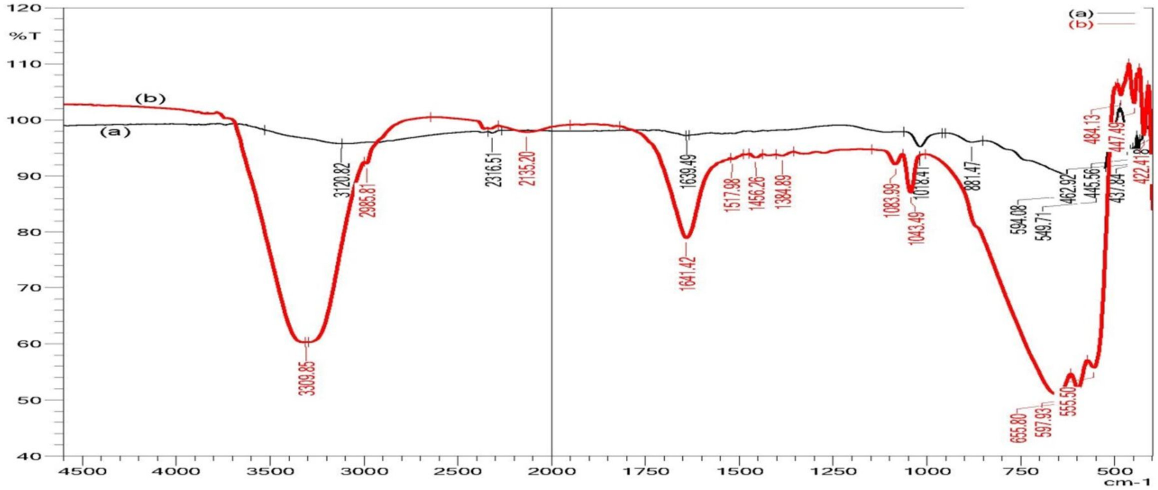
Sample	EPc, mV	PEAK E	Current, A	Area, μc
Blank	860	564.95	27	75.991
Inhibitor System	900	558.20	43	149.959

The cyclic voltammogram of carbon steel electrode, are shown in Figure 6a and Figure 6b. It is observed that during the anodic sweep, dissolution of metal does not take place. This indicates that the protective film is stable and compact. Electrons are not transferred from the metal surface, and a passive region is observed[8]. During the cathodic sweep, the peak corresponding to reduction of pitting corrosion product appears at 860 mV and for the inhibited system appears at 900 mV and the intensity of current is increased from 27 A to 43 A which ensures the protective film is formed. When the electrode is immersed in the inhibitor medium the area of the peak E gets decreased from 564.95 to 558.20 which tells that a film is found on the metal surface in the presence of inhibitors. When the peaks of inhibited and uninhibited system is compared, the area of the inhibited is increased from 75.991 to 149.95 µC implies that the extract shows higher antioxidant capacity. The reduction in the peak intensity tells that the oxidation of the carbon steel which releases electrons is prevented in the presence of inhibitor system[9,10]. The presence of OH groups of the inhibitor that show high antioxidant power is responsible for the low oxidation potential due to electro oxidation.

C. Spectroscopic Studies

1) *Analysis of FTIR Spectra:* Figure 7 shows the FTIR spectrum of the thin film formed on the surface of the carbon steel immersed in 180 ppm of chloride ion solution containing the inhibitor system. The -OH frequency of the extract at 3120 cm^{-1} is shifted to 3309cm^{-1} with a sharp peak. The bands at 2316 cm^{-1} and 2135 cm^{-1} are due to the C≡C stretching and 1639 cm^{-1} is due to the –C=C stretching is shifted to 1641 cm^{-1}in the thin film. The band at 1083 is due to the C-O stretch. The band at 881cm-1 which is due to CH stretching is merged to form a broad peak. A notable band at 1018cm^{-1} can be assigned to C-O stretching and the band appeared at 655 cm^{-1} revealed the presence of aromatic ring present in the extract. The shifting of the bands in the thin film indicates that the carboxylate anion and the ring oxygen present in the phytoconstituents are responsible for the interaction between the phytochemicals present in the extract of the roots of Chrysopogon Zizanioides and iron present in the carbon steel. It could be seen that certain additional peaks had appeared and some had shifted to higher frequency region, providing information that some interaction/adsorption over metal surface had taken place. The absorption bands at 594 and 462 cm$^{−1}$ are due to C≡C and Fe–N stretching vibration are merged to a broader peak. The above results suggested the presence of inhibitor complex with Fe^{2+} on the surface[11]. There is an increase in absorbance after carbon steel is immersed in the CZRE. This reveals the formation of a complex between the Fe^{2+} and the phytoconstituents of the root extract. Formation of this complex may be responsible for the observed deviation in the frequency and its intensity value and this may be responsible for anti-corrosion activity[12].

Figure 7 FTIR spectrum (a) pure CZRE and (b) thin film formed on the surface of the carbon steel immersed in 180 ppm Cl$^-$ ion containing inhibitor system



D. UV-Visible Spectral Study

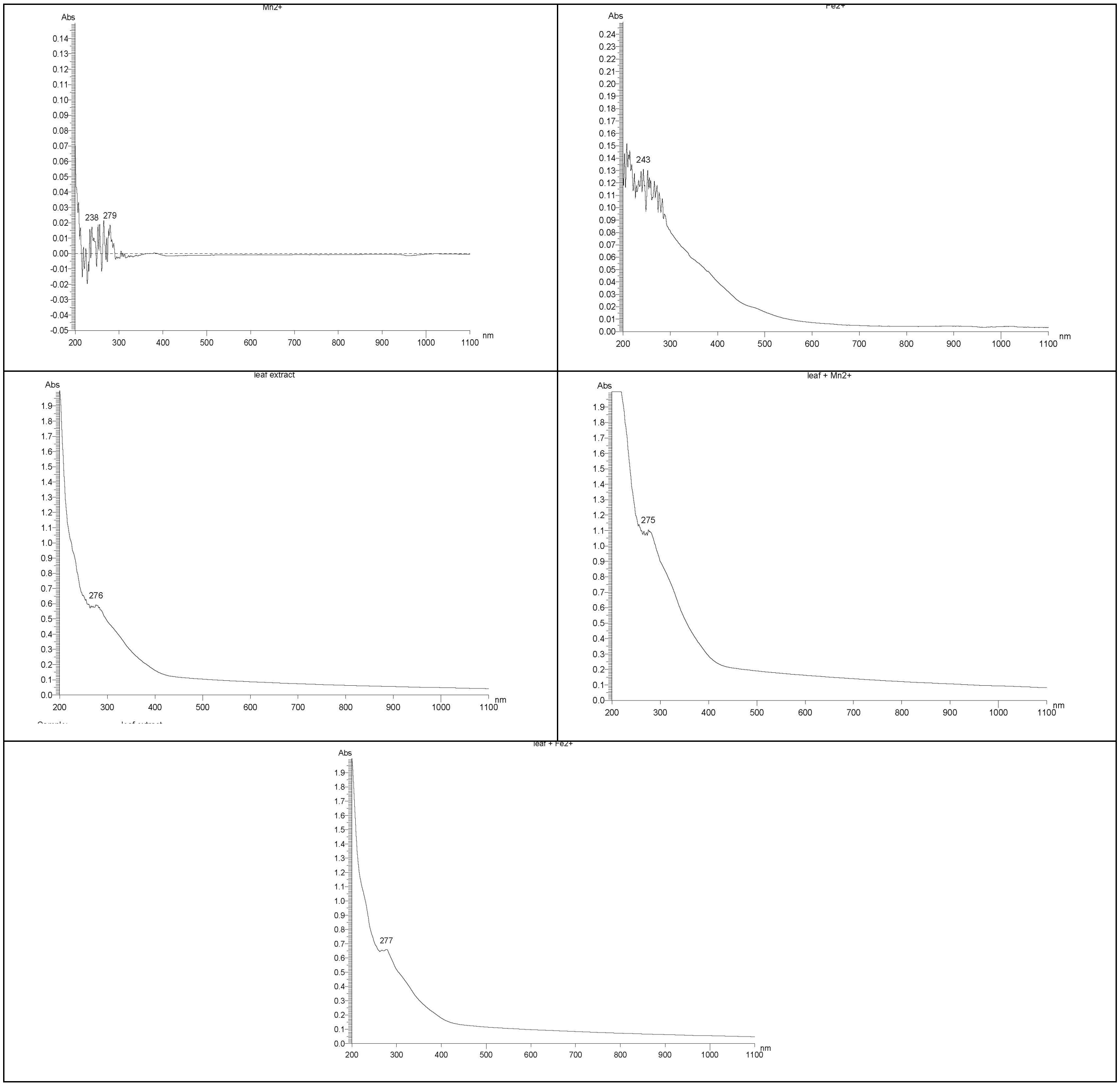
The UV-Visible spectrum of Mn^{2+}, Fe^{2+}, CZRE, Mn^{2+} in the presence of CZRE, and Fe^{2+} in the presence CZRE in 180 ppm Cl- ion solution are given in Figure 8 a-e. The absorbance of CZRE at 276 nm is found to be 0.58 (Figure 8c). The absorbance of Mn^{2+} ion is found to be 0.025 at 279 nm (Figure 8a).

The addition of 100 ppm of Mn^{2+} to 300 ppm of CZRE changes the absorbance value. The absorbance is found to be 0.58 at 276 nm and it increases to 1.08 at 275 nm (Figure 8d). The change in the value of absorbance in Mn^{2+} + CZRE constituents indicates the existence of strong interaction between Mn^{2+} and phytoconstituents present in CZRE.

UV-visible spectrum of Fe^{2+} (Figure 8b) shows that at 243 nm the solution has an absorbance of 0.13. When Fe^{2+} added to CZRE the absorbance is found to be 0.65 at 277 nm (Figure 8e) then increases gradually. This clearly proves the existence and formation of a complex between Fe^{2+} and phytoconstituents present in CZRE.

From the figures, the deviation is shown in absorbance values and their intensities and there is an increase in absorbance after carbon steel immersion in CZRE. This reveals the formation of a complex between the Fe ions and the phytoconstituents of the green inhibitor. Formation of the complex may be responsible for the observed deviation in the absorbance and its intensity value and this may be responsible for anticorrosion activity. It is also noted that there was significant difference in the shape of the spectra before and after the immersion of specimen[13] showing the possibility of forming thin inhibitor layer over the carbon steel surface (Physisorption).

Figure 8 UV-Visible absorption spectra of the test solutions in 180 ppm Cl^- ion
(a) Mn^{2+}, (b) Fe^{2+} ion, (c) CZRE, (d) CZRE +Mn^{2+}, and (e) CZRE + Fe^{2+}



E. SEM

The texture and pore structure of the inhibited and uninhibited surface of the carbon steel immersed in chloride ion solution in aqueous medium in the presence and absence of the inhibitor system are shown in Figure 14a,b,c,d.

Figure 14 a SEM image of carbon steel in 180 ppm Cl^- ion

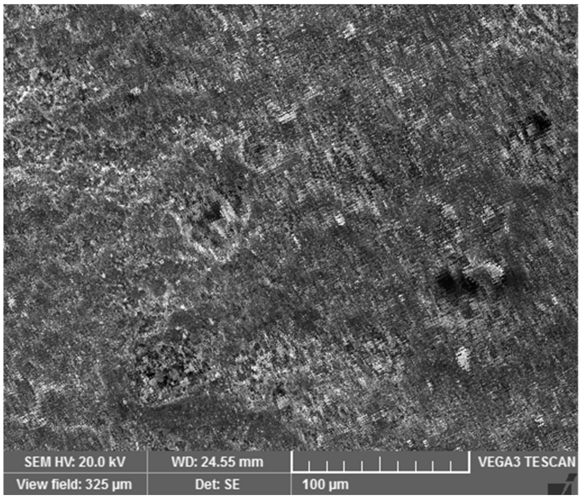
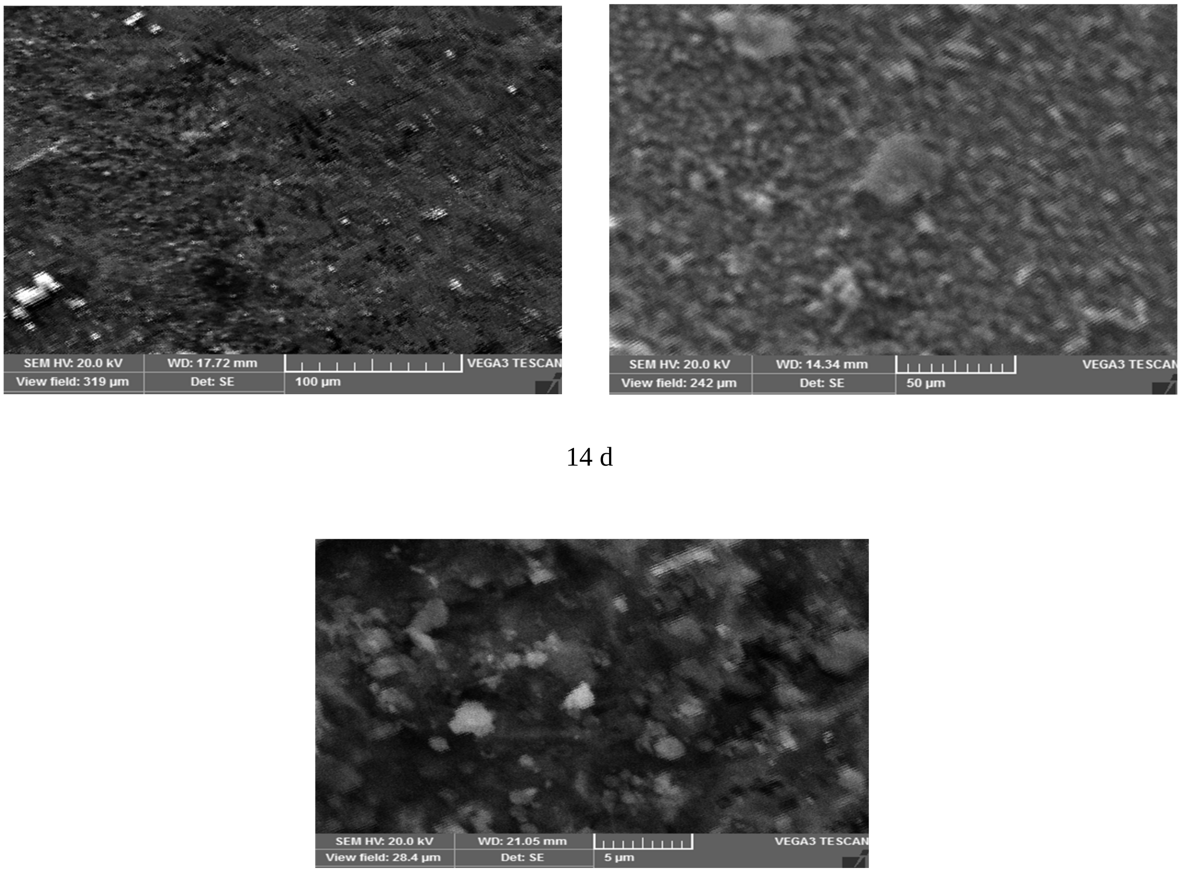


Figure 14 b, c, d Carbon steel in 180 ppm Cl^- ion + CZRE + Mn^{2+}



14 b

14 c

14 d

SEM image 14 a clearly implies that the carbon steel surface is highly damaged with pitted areas in the absence of inhibitor system. But figure 14 b, c, d shows a clear, smooth deposition of CZRE on the surface of the specimen after the immersion in the inhibitor system. On viewing the images it is seen that the pits disappear and carbon steel is free from corrosion. This is because of the formation of a layer of the CZRE on the surface of carbon steel. This is also confirmed by the FTIR spectral analysis. Thus this has retarded and resisted further corrosion by forming a protective layer[18] on the carbon steel.

F. XRD

The X-ray diffraction (XRD) represents the method of choice for the analysis of corrosion products, as it is the only analysis method that readily provides information about the phase-composition of solid materials. Analysis can be used not only for identification of crystalline phases in corrosion products but also for their quantitative phase analysis on measuring the intensity of a single diffraction line or even all the lines in the pattern. Compositional analysis and identification of the products formed on carbon steel surface in aqueous media in the absence and presence of the inhibitor are given with the application of X-ray diffraction studies and the recorded diffraction patterns are presented in Figure 15 a, b respectively.

Figure 15 a Carbon steel in 180 ppm Cl^- ion

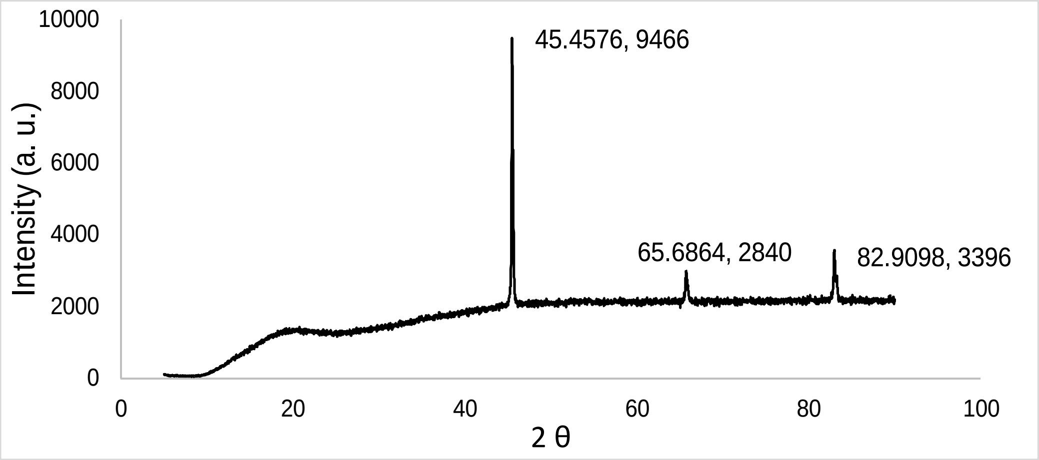
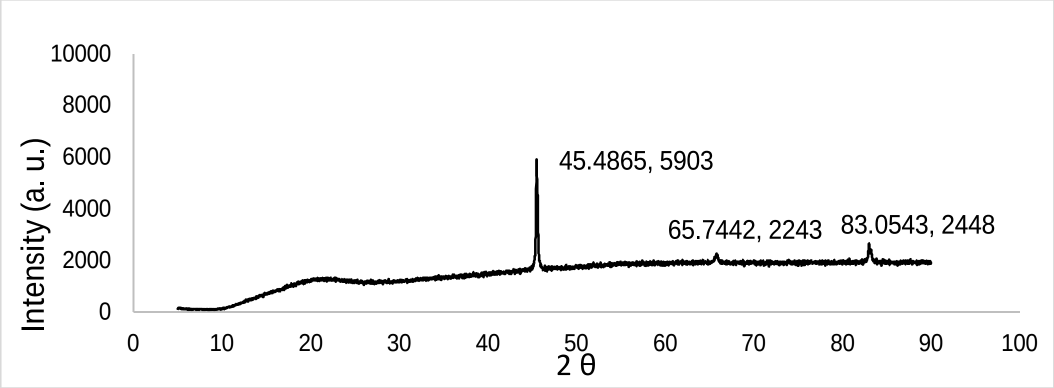


Figure 15 b Carbon steel in 180 ppm Cl^- ion + CZRE + Mn^{2+}



In the absence of inhibitor, the XRD pattern Figure15 a reveals the presence of a large proportion of goethite (α-FeOOH) as indicated from its characteristics peaks at 2θ and it is the expected product of corrosion of carbon steel in chloride environment. The pattern also shows the presence of a small amount of $FeCl_2$ at 2θ which is equal to 65.68. The XRD pattern of inhibited surface Figure15b also shows the same two main peaks observed in uninhibited surface but the intensity of the peaks becomes extremely weak[19] to those seen in the absence of inhibitor. It has got reduced to a greater extent. It can be noted from the peaks shown in Figure15b that the addition of the inhibitor leads to a decrease in the height of the characteristic peaks of both goethite and $FeCl_2$. The decrease in the height of the peak can be considered as an indication of the retardation of the corrosion process and hence gives good evidence for the excellent inhibitive effect of the inhibitor for carbon steel corrosion in aqueous media.

G. Energy Dispersive X-ray Spectroscopy (EDX)

The EDX spectra are used to determine the elements present on the surface of carbon steel to get a clear idea regarding the elements present. EDX spectra of the surfaces of carbon steel are recorded in order to observe changes occurred during corrosion process in absence and presence of the inhibitor. The EDX spectra of the carbon steel specimen, uninhibited specimen and inhibited specimen with the inhibitor CZRE are given in the following Figures 16 a, b, c.

Figure 16 a Carbon steel

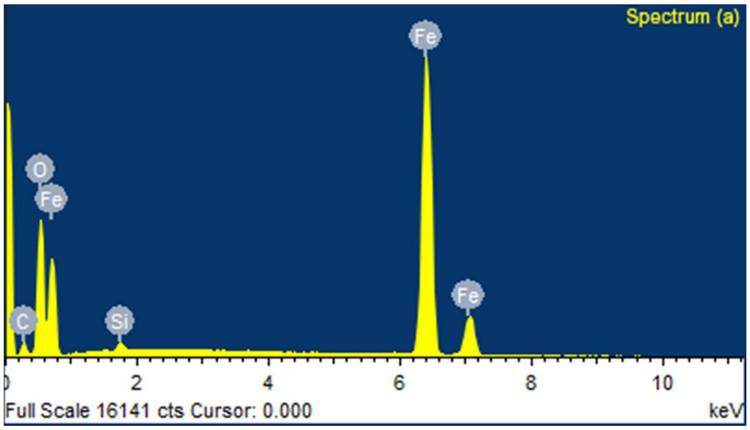


Figure 16 b Carbon steel in 180 ppm Cl^- ion

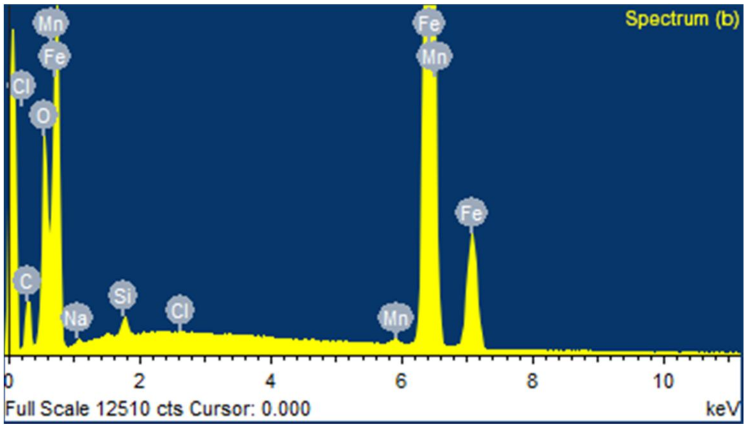
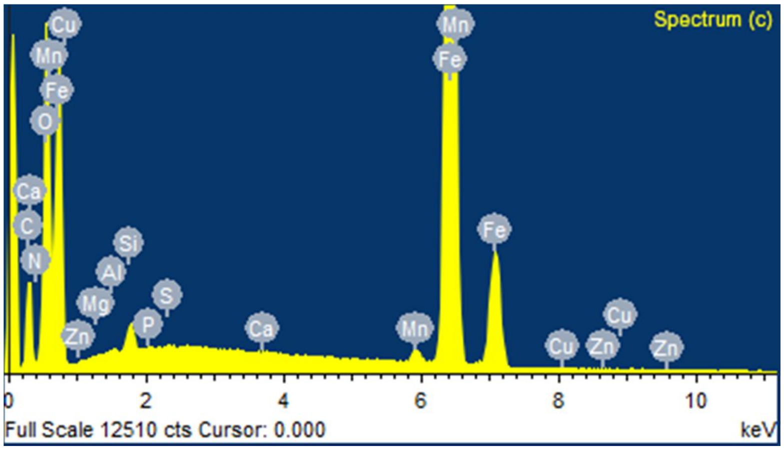


Figure 16 c Carbon steel in 180 ppm Cl^- ion + CZRE + Mn^{2+}



The EDX spectra show the characteristics peaks of some of the elements constituting the carbon steel, carbon steel sample that was immersed in 180 ppm of chloride ion environment without inhibitor and in the presence of the inhibitor. The EDX spectrum of inhibited specimen show the presence of calcium, magnesium, aluminium, zinc, phosphorus, and sulphur. Their presences are due to the phytoconstituents that are adsorbed on the surface of the specimen.[20] There is suppression in iron peaks because of the overlying inhibitor film whereas the uninhibited specimen shows the absence of most of the elements, except Cl. All these confirm the presence of thin layer on the surface of inhibited specimen and CZRE to be a good and efficient, green inhibitor.

IV. SUMMARY AND CONCLUSION

Analysis of the results of the mass-loss method shows that the formulation consisting of 300 ppm extract of the roots of *Chrysopogon Zizanioides* and 100 ppm Mn^{2+} offers 81.02 % IE in controlling the corrosion of carbon steel immersed in 180 ppm Cl^- ion solution. A synergistic effect exists between Mn^{2+} and the phytoconstituents present in the extract of *Chrysopogon Zizanioides* root extract. The inhibition of corrosion of carbon steel in aqueous chloride ion solution in the presence of the inhibitor system is due to the interaction between the lone pair of electrons on oxygen atoms present in the active constituents of the extract with the positively charged metal surface. The IE of the inhibitor formulation depends on the ability of the inhibitor to form complex with Mn^{2+} and the ability of Fe^{2+} to react with Mn^{2+} complex to form iron complex on the surface of the specimen.

Results of polarization studies show that this inhibitor controls both anodic and cathodic reactions and behaves as mixed inhibitor. AC impedance spectra reveals the formation of protective film on the metal surface. Cyclic voltammetry confirms the protective nature of the film formed on the metal surface, in the presence of inhibitor. The temperature studies tells that the rate of corrosion increases as the temperature is increased and the and the transition studies implies that the adsorption process is physisorption and is poor at higher temperatures . The different adsorption isotherms explains the interaction between inhibitor and the carbon steel and the spontaneity of the reaction. The FTIR spectra confirm the presence of active constituents on the metal surface and also the change in nature of the active constituents. The UV-visible absorption spectra indicate the possibility of formation of a film with the extract and the iron ions. The SEM micrographs confirm the formation of protective layer on the metal surface. The XRD and EDX analysis confirms the presence of a layer and the reduction in intensity of peaks and reveals the existence of other ions in the inhibited specimen and confirms the adsorption of extract molecules on the carbon steel surface.

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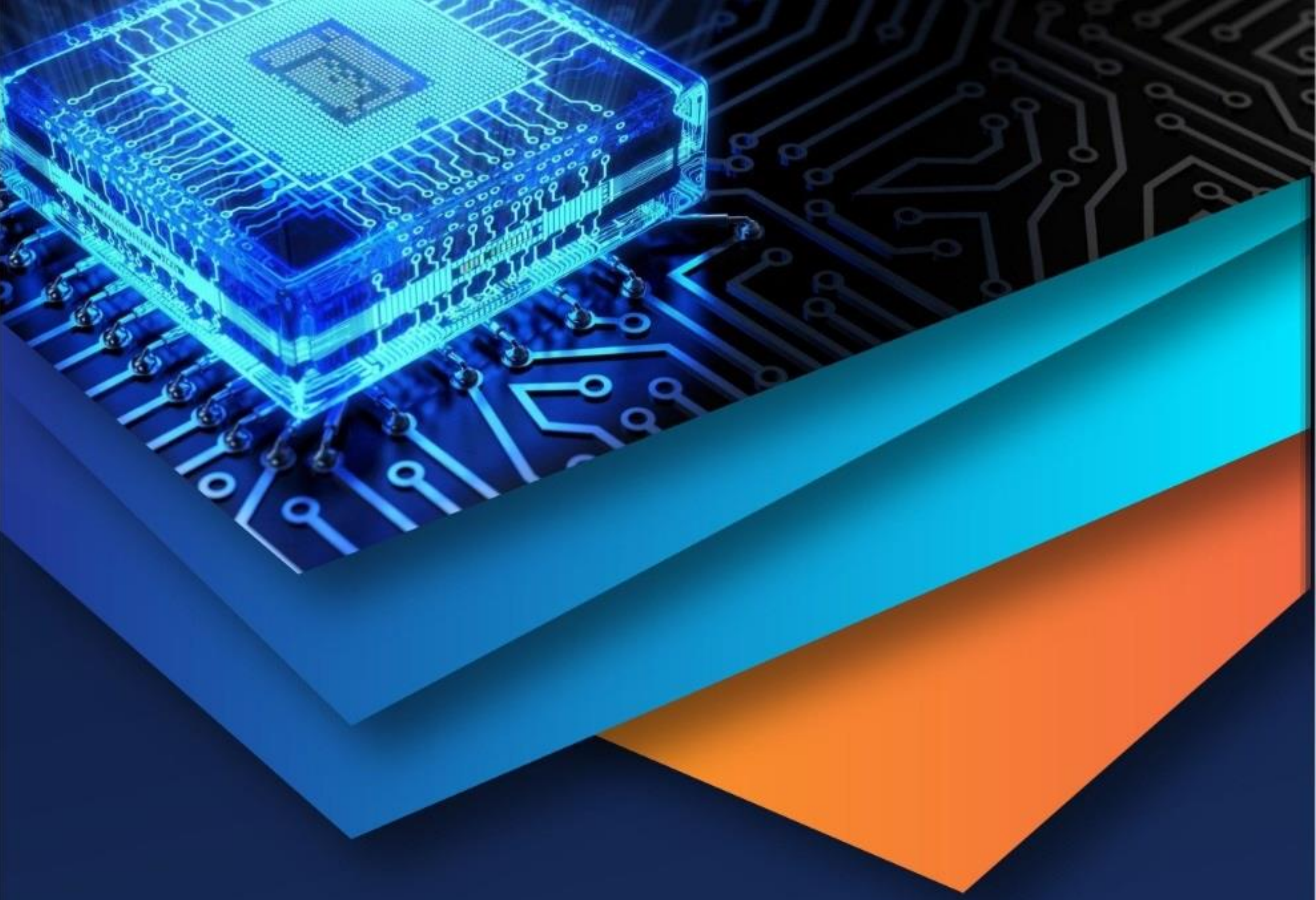

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