

Inhibitive action of malachite green-Zn²⁺ system

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The inhibition efficiency (IE) of malachite green- (MG) Zn²⁺ system in controlling corrosion of carbon steel in well water containing 665 ppm of Cl⁻ (model corrosion medium) has been evaluated by weight loss method. Weight loss study reveals that the formulation consisting of 30 ppm of MG and 25 ppm of Zn²⁺ has 95% inhibition efficiency in controlling corrosion of carbon steel immersed in well water (model corrosion medium). Synergistic parameters suggest that a synergistic effect exists between MG and Zn²⁺. Polarization study reveals that this system functions as cathodic type inhibitor controlling cathodic reaction predominantly. AC impedance spectra reveals that a protective film is formed on the metal surface. The FTIR spectra reveals that the protective film consists of Fe²⁺-MG complex. This is further confirmed by UV-visible spectra and fluorescence spectra. The colour of the dye can be removed by electrolysis using platinised titanium as anode and graphite as cathode.

Keywords : Carbon steel, corrosion inhibition, malachite green, F-Test, synergism parameter

INTRODUCTION

Several compounds such as nitrates [1,2] phosphates [3,4] silicates [5] sodium salicylate [6] sodium cinnamate [7] molybdates [8,9] phosphonic acids [10,12] polyacrylamide [13] and caffeine [14,15] have been used as corrosion inhibitors. Talati and Gandhi have studied the effect of some dyes as corrosion inhibitors for B26S aluminium in hydrochloric acid [16,18]. The inhibition efficiency (IE) of triphenylmethane dyes such as Victoria blue, fast green, light green, malachite green, fuchsine base, fuchsine acid, crystal violet and methyl violet 6B in controlling corrosion of aluminium in phosphonic acid has been studied by Talati and Daraji using mass and polarization studies [19]. Several dyes such as Nile blue, indigo carmine organic dyes [20], crystal violet [21], congo red [22], methylene blue [23], basic yellow 13 [24], fluorescein [25], methyl orange [26], and eriochrome black-T [27] have been used as corrosion inhibitors. The present work is undertaken to investigate (i) the inhibition efficiency of malachite green in controlling corrosion of carbon steel immersed in well water (model corrosion medium) (Table 1) in the absence

Table 1: Physico –chemical parameters of well water (model corrosion medium)

Parameter	Well Water
pH	8.38
Conductivity	3110 μ mhos/cm
Total dissolved solids	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

and presence of zinc ions; (ii) the influence of pH and immersion period on the inhibition efficiency and (iii) the protective film by UV-visible reflectance, FTIR and fluorescence spectra.

MATERIALS AND METHODS

Preparation of the specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and rest iron) of the dimensions 1.0 \times 4.0 \times 0.2 cm were polished to a mirror finish, degreased with trichloroethylene, and used for the weight-loss method and surface examination studies.

Mass-loss method

Determination of surface area of the specimens

The length, breadth and the thickness of carbon

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steel specimens and the radius of the holes were determined with the help of vernier calipers of high precision and the surface areas of the specimens were calculated.

Weighing the specimens before and after corrosion

All the weighing of the carbon steel specimens before and after corrosion were carried out using Shimadzu Balance-AY62.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2\text{)} \times \text{period of immersion (days)}}$$

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

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

where W₁ is the corrosion rate in absence of inhibitor; W₂ is the corrosion rate in presence of inhibitor.

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimen was analyzed by surface analysis technique, namely, FTIR, UV-visible reflectance and fluorescence spectroscopy.

The UV-Visible Spectra

The UV-visible reflectance spectra were recorded using Hitachi U-3400 spectrophotometer. The same instrument was used for recording UV-visible absorption spectra of aqueous solutions also.

Luminescence spectra

The luminescence spectra of solution and the film formed on the metal surface were recorded using Hitachi 650-10 S fluorescence spectrophotometer equipped with 150 W Xenon lamp and a Hamamatsu R 928 F photomultiplier tube.

Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out using CHI electro chemical impedance analyzer, model 660 A. A three electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as a reference electrode and a rectangular platinum foil was used as the counter electrode.

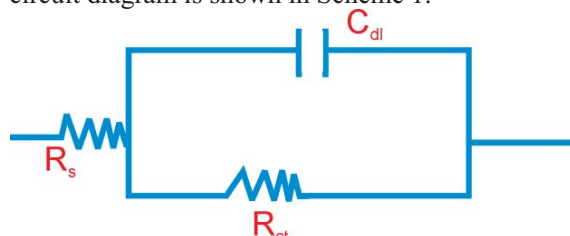
Determination of corrosion rate

The weighed specimen in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml various test solutions and after 24 hours of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimen, corrosion rates were calculated using the following relationship.

The working electrode and platinum electrode were immersed in well water (model corrosion medium) in the absence and presence of inhibitor saturated calomel electrode was connected with the test solution through a salt bridge. Potential (E) vs log current (I) plots were then recorded. Corrosion potential (E_{corr}) and Tafel slopes b_a and b_c were determined from E vs log I plots.

AC impedance measurements

A CHI electrochemical impedance analyzer (Model 660A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to reach the stable open circuit potential. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. Equivalent circuit diagram is shown in Scheme 1.



Scheme 1: Equivalent circuit diagram

Synergism parameters

Synergism parameters are indications of synergistic effect existing between two inhibitors.

Synergism parameters were calculated using the relation

$$S_I = \left| 1 - \theta_{1+2} / 1 - \theta'_{1+2} \right|$$

- where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2)$;
- θ_1 = surface coverage of substance 1;
- θ_2 = surface coverage of substance 2;

-where θ_{1+2} = combined surface coverage of substance 1 & 2.

Analysis of variance (F-Test)

F-test was carried out to investigate whether the synergistic effect between CAE and Zn²⁺ was statistically significant.

Analysis of the results of the mass loss method

The calculated inhibition efficiencies (IE) of malachite green in controlling the corrosion of carbon steel immersed in well water (model corrosion medium) both in the absence and presence of zinc ion have been tabulated in Table 2 and 3. The calculated values indicate the ability of malachite green to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of zinc ion. The formulation consisting of 30 ppm of MG and 25 ppm of Zn²⁺ offers 95% inhibition efficiency.

Table 2: Corrosion rates (CR) of carbon steel in well water (model corrosion medium) in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method. Inhibitor system: Malachite green (MG) + Zn²⁺. Period of immersion: 1 day

MG ppm	Zn ²⁺ ppm	CR mdd	IE %
0	0	42.72	--
10	0	16.36	61
30	0	15.45	63
50	0	8.18	80
70	0	7.27	82
90	0	2.72	93

Table 3 : Corrosion rates (CR) of carbon steel in well water (model corrosion medium) in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method. Inhibitor system : Malachite green (MG) + Zn²⁺. Period of immersion: 1 day

MG ppm	Zn ²⁺ ppm	CR mdd	IE %
0	25	18.18	17
10	25	4.54	75
30	25	2.14	95
50	25	2.72	85
70	25	2.72	85
90	25	0.90	80

Influence of immersion period on the corrosion inhibition of carbon steel in well water (model corrosion medium) by MG + Zn²⁺ system

The corrosion rates of carbon steel in the presence of the inhibitor system in well water (model corrosion medium) for different durations of immersion are tabulated in Table 3.

The IE of 30 ppm MG–25 pm Zn²⁺ system is found to decrease as the immersion period

Table 4: Corrosion rates (CR) of carbon steel in well water (model corrosion medium) in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method. Inhibitor system: Malachite green (MG) + Zn²⁺. Period of immersion: 1 day

MG ppm	Zn ²⁺ ppm	CR mdd	IE %
0	50	9.09	23
10	50	5.45	40
30	50	4.54	50
50	50	3.63	60
70	50	2.72	70
90	50	0.90	90

increases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl⁻ ion (665 ppm) present in well water (model corrosion medium). There is a competition between the formation of FeCl₂ (and also FeCl₃) and Fe²⁺-MG complex on the anodic sites of the metal surface. Analysis of results suggests that the formation of FeCl₂ is more favoured than the formation of Fe²⁺-MG complex. Similar observation has been made by Selvaraj et al., [28], while studying corrosion behaviour of carbon steel in presence of polyvinyl pyrrolidone.

Table 5 : Influence of immersion period on the inhibition efficiency of the MG (30 ppm) - Zn²⁺ (25 ppm) Corrosion rates of carbon steel in well water (model corrosion medium) in the presence and absence of the inhibitor system and the inhibition efficiencies obtained by the mass loss method

Inhibitor system : MG (30 ppm) + Zn²⁺ (25 ppm).

MG ppm	Zn ²⁺ ppm	Immersion period days	Corrosion Rate mdd	Inhibition efficiency %
0	0	1	42.72	--
30	25	1	0.90	95
0	0	3	47.31	--
30	25	3	4.73	90
0	0	5	49.25	--
30	25	5	5.42	89
0	0	7	54.01	--
30	25	7	9.18	83

Influence of pH on inhibition efficiency of malachite green Zn²⁺ system

Corrosion rates of carbon steel in well water (model corrosion medium) in the presence of the inhibitor system at different pH values and the IE are tabulated in Table 6.

At pH 8, the IE of MG Zn²⁺ system is 90%. When the pH is lowered to 6 (by the addition of

dil.H₂SO₄), the IE decreases to 88 due to the attack of H⁺ ion present in the acid, on protective film formed on the metal surface. When the pH decreased from 8 to 7 (by addition of diluted H₂SO₄). The IE decreases from 90 to 83. This is due to the fact that the protective film formed on the metal surface is broken by the attack of H⁺ ion [29]. The IE at pH 6 is found to be greater than that at pH 7. This is explained as follows: The inhibitor contains amino groups. When acid is added (pH = 6), protonation of amines takes place. Nitrogen atom attains positive charge. This positive charge and the (Fe²⁺) positive charge on the metal are coordinated through the chloride ions (665 ppm) which are also present on the metal surface. Thus, when acid is added (pH=6), inhibition efficiency increases.

Table 6: Influence of pH on the inhibition efficiency of MG (30 ppm) - Zn²⁺ (25 ppm). Corrosion rates of carbon steel in well water (model corrosion medium) at different pH and the inhibition efficiencies obtained by the mass loss method. Inhibitor system : MG (30 ppm) – Zn²⁺ 25 ppm. Immersion period: 1 day.

MG ppm	Zn ²⁺ ppm	pH	Corrosion Rate mdd	IE %
0	0	7	30.27	--
30	25	7	5.15	83
0	0	8	42.72	--
30	25	8	1.82	90
0	0	6	32.78	--
30	25	6	3.93	88

Influence of CTAB, SDS on the IE of MG + Zn²⁺ system

Influence of CTAB

The corrosion rates of carbon steel in well water (model corrosion medium) containing Zn²⁺ – MG inhibitor formulation for various concentrations of N-Cetyl–N,N,N-trimethyl ammonium bromide (CTAB) are tabulated in Table 7.

Table 7: Influence of CTAB on the IE of MG + Zn²⁺ system. Corrosion rates of carbon steel in well water (model corrosion medium) in the presence and absence of the inhibitor system and the inhibition efficiencies obtained by mass loss method
Inhibitor system : MG + Zn²⁺ + CTAB

MG ppm	Zn ²⁺ ppm	CTAB ppm	CR mdd	IE %
30	25	0	2.14	95
30	25	5	6.36	73
30	25	10	0.15	34
30	25	15	9.09	61
30	25	20	9.09	61
30	25	25	4.54	80

It is seen that as the concentration of CTAB (a cationic surfactant) increases, the IE increases and

then decreases and again increases. The decrease in IE at a given concentration of CTAB is due to the fact, that at this concentration of CTAB, monomers are formed. Hence more number of CTAB molecules are adsorbed on metal surface. Hence IE increases, at higher concentrations of CTAB [30]. Similar observations have been made by. CTAB is a biocide [31]. It can control the corrosion caused by bacteria. The present study reveals that the formulation consisting of MG, Zn²⁺ and CTAB has excellent corrosion inhibitor efficiency. This formulation may find application in cooling water systems, provided the experiments are carried out at high temperature and under dynamic condition.

Influence of SDS on the IE of MG + Zn²⁺ system

The corrosion rates of carbon steel in well water (model corrosion medium) containing Zn²⁺ + MG

Table 8: Influence of SDS on the IE of MG + Zn²⁺ system. Corrosion rates of carbon steel in well water (model corrosion medium) in presence and absence of the inhibitor system and the inhibition efficiencies obtained by the mass loss method. Inhibitor system : MG + Zn²⁺ + SDS

MG ppm	Zn ²⁺ ppm	SDS	CR mdd	IE %
30	25	0	2.14	95
30	25	5	12.73	53
30	25	10	9.09	66
30	25	15	8.18	70
30	25	20	5.45	80
30	25	25	4.54	83

inhibitor formulation for various concentrations of sodium dodecyl sulphate (SDS) are tabulated in Table 8.

When various concentrations of an anionic surfactant, SDS, were added to the inhibitor system, the inhibition efficiency decreased and reached a minimum and then increased. A micelle would have been formed at the minimum efficiency concentration. Afterwards the micelles would have been converted into monomer, which improved the inhibition efficiency. When more amount of SDS is added, SDS exists as monomer. These monomers are easily adsorbed on the metal surface. A protective film is formed. This prevents corrosion of metal SDS is a biocide [32]. This formulation may find application in cooling water systems, provided the experiments are carried out at high temperature and dynamic condition.

Synergism parameters

Synergism parameters have been calculated to evaluate the synergistic effect existing between two inhibitors [33–37]. There is synergistic effect when

the value of the synergism parameter is greater than 1.

The synergism parameters are given in Table 9. It is observed that the value of synergism parameter is greater than 1. This suggests that a synergistic effect exists between MG and Zn²⁺. It is also interesting to note that the values of S_i are slightly smaller in the case of 50 ppm of Zn²⁺, when compared with 25 ppm of Zn²⁺ (Fig.1). This is in agreement with inhibition efficiencies obtained by weight loss method. Thus the values of synergism parameter give a quantitative picture of synergism existing between two inhibitors.

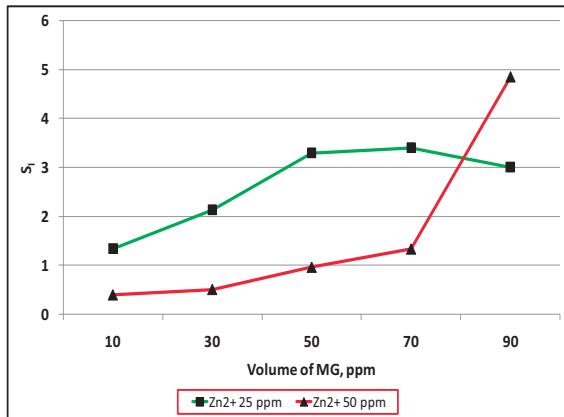


Fig. 1. Synergism parameters as a function of concentration of MG.

Table 9: Synergism parameters derived from inhibition efficiencies (surface coverage, θ) of MG-Zn²⁺ system

MG ppm	Zn ²⁺		S _i
	0 ppm	25 ppm	
0	--	17	--
10	61	75	1.345
30	63	95	2.142
50	80	85	3.293
70	82	85	3.404
90	93	80	3.01

Table 10 : Synergism parameters derived from inhibitor efficiencies (surface coverage, θ)of MG-Zn²⁺

MG ppm	Zn ²⁺		S _i
	0 ppm	50 ppm	
0	-	23	-
10	61	40	0.399
30	63	50	0.510
50	80	60	0.965
70	82	70	1.338
90	93	90	4.861

Analysis of variance (ANOVA)

F-test was carried out to find out whether the influence of Zn²⁺ on the inhibition efficiencies of MG is statistically significant [38-40]. The results are given in Tables 11 and 12.

In Table 11, the influence of 25 ppm of Zn²⁺ on the inhibition efficiencies of 7, 10, 30, 50, 70 and 90 pm MG is investigated. The obtained F-value 0.1071 is statistically insignificant, since it is less than the critical F-value 5.32, for 1,8 degrees of freedom at 0.1071 level of significance. Therefore, it is calculated that the influence of 25 ppm of Zn²⁺ on the inhibition efficiencies of various concentration of MG is not statistically significant.

In Table 12, the influence of 50 ppm of Zn²⁺ on the inhibition efficiencies of 10 ppm, 30 ppm, 50 ppm, 70 ppm, 90 ppm of MG is investigated. The obtained F-value 0.4052 is statistically insignificant

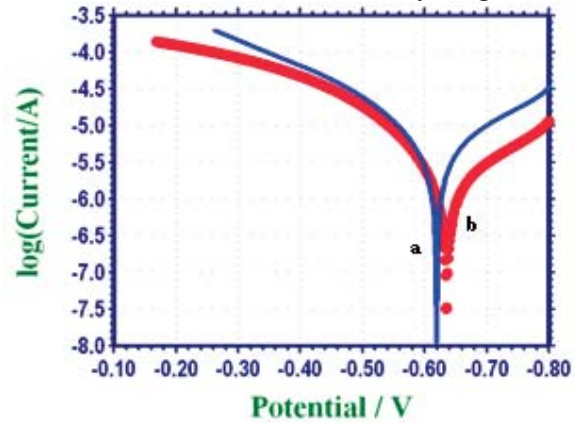


Fig. 2. Polarization curves of carbon steel immersed in various test solutions. (a) -Well water (model corrosion medium). (b) -Well water (model corrosion medium) + MG 30 ppm + Zn²⁺ 25 ppm.

since it is less than the critical F-value 5.32, for 1,8 degrees of freedom at 0.4052 level of significance. Therefore, it is concluded that the influence of 50 ppm of Zn²⁺ on the inhibition efficiencies of various concentrations of MG is not statistically significant.

Table 11: Distribution of F-value between the inhibition efficiencies of various concentrations of MG (0 ppm of Zn²⁺) the inhibition efficiencies of MG is the presence of 25 ppm of Zn²⁺

Source of variance	Sum of squares	Degree of freedom	Mean square	F	Level of significance of F
Between	168.1	1	168.1	0.1071	p<0.05
Within	12547.232	8	1568.404		

Table 12: Distribution of F-value between the inhibition efficiencies of various concentrations of MG (0 ppm of Zn²⁺) and the inhibition efficiencies of MG is the presence of 50 ppm of Zn²⁺

Source of variance	Sum of squares	Degree of freedom	Mean square	F	Level of significance of F
Between	476.1	1	476.1	0.4052	p < 0.05
Within	9398.84	8	1174.85		

Analysis of polarization curves

Polarization study has been used to detect the formation of protective film on the metal surface [41–45]. When a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current (I_{corr}) decreases. The potentiodynamic polarization curves of carbon steel immersed in various test solutions are shown in Fig.2. The corrosion parameters namely, corrosion potential (E_{corr}), Tafel slopes (b_c =cathodic; b_a =anodic), linear polarization

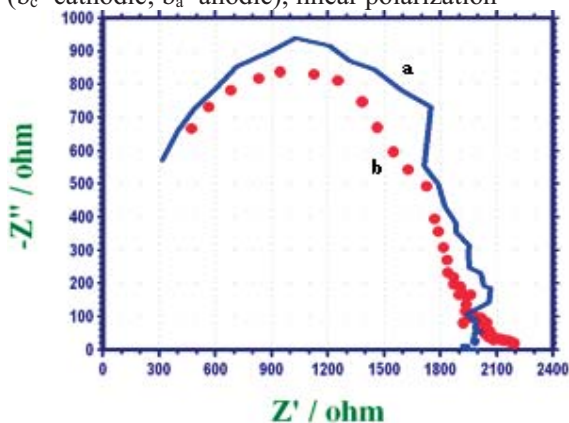


Fig. 3 : AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots). (a) - Well water (model corrosion medium); (b)- Well water (model corrosion medium) + MG 30 ppm + Zn²⁺ 25 ppm

resistance (LPR) and corrosion current (I_{corr}) are given in Table 13. When carbon steel is immersed in an aqueous solution containing well water (model corrosion medium) (665 ppm), the corrosion potential is -619 mV vs SCE. The formulation consisting of 30 ppm of malachite green solution (MG) and 25 ppm of Zn²⁺ shifts the corrosion potential to -635 mV vs SCE. This suggests that the cathodic reaction is controlled predominantly. The LPR value increases from 7.454×10^3 to 16.71×10^3 ohm cm². This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from 4.858×10^{-6} A/cm² to 2.029×10^{-6} A/cm². The IE calculated from corrosion current is 58%. This value is lower than the IE obtained by weight loss method (95%). The discrepancy may be explained by the fact that in electrochemical processes, the instantaneous corrosion current is measured.

Analysis of AC impedance spectra

AC impedance spectra have been studied to detect the formation of film on the metal surface. If a protective film is formed, the charge transfer

resistance increases and double layer capacitance value decrease [46–50]. The AC impedance spectra of carbon steel immersed in various solutions are shown in Figs.3 and 4. The AC impedance parameter, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) (derived from Nyquist plot) are given in Table 14.

Table 13. Potentiodynamic polarization curves of carbon steel immersed in various test solution

System	E_{corr} mV vs SCE	b_c mV/ deca	b_a mV/d ecade	LPR ohm cm ²	I_{corr} A/cm ²
Well water (model corrosion medium)	-619	193	147	7.454×10^3	4.858×10^{-6}
Well water (model corrosion medium) + MG 30 ppm + Zn ²⁺ 25 ppm	-635	192	132	16.71×10^3	2.029×10^{-6}

However, in the case of the weight loss method, IE is calculated after a long time. The protective film formed is strengthened as the duration of immersion increases.

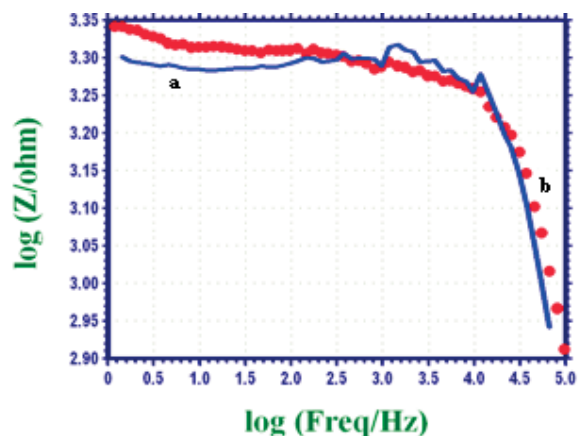


Fig. 4a. AC impedance spectra of carbon steel immersed in various test solutions (impedance – Bode plots). (a) - Well water (model corrosion medium); (b) - Well water (model corrosion medium) + MG 30 ppm + Zn²⁺ 25 ppm.

When carbon steel is immersed in aqueous solution containing well water (model corrosion medium). The R_t value is 1710 ohm cm² and C_{dl} value is 2.98×10^{-9} F/cm².

When MG and Zn²⁺ are added, the R_t value increases from 1710 ohm cm² to 1748 ohm cm² and C_{dl} value decrease from 2.98×10^9 F/cm² to 2.92×10^{-9} F/cm². This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of MG Zn²⁺ system. Further there is increase in impedance, log (z/Ohm), value

from 3.909 to 3.343 (derived from Bode plot shown in Fig.4).

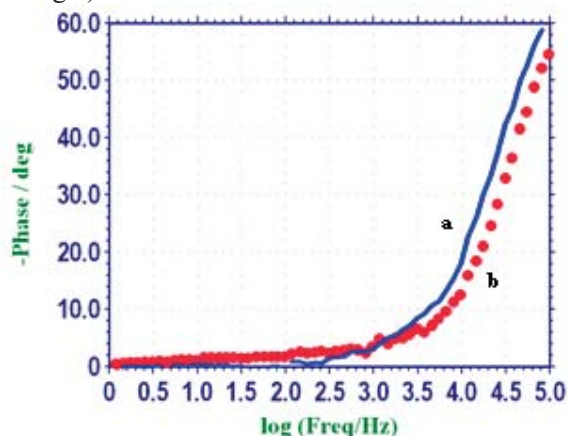


Fig. 4b. AC impedance spectra of carbon steel immersed in various test solutions (-phase – Bode plots).(a)-Well water (model corrosion medium) (b) -Well water (model corrosion medium) + MG 30 ppm + Zn²⁺ 25 ppm.

In electrochemical studies, instantaneous corrosion rate is measured. But in weight loss method corrosion rate is measured after a longer period in the present study after one day. After a longer period the protective film becomes more compact and stable. This accounts for the discrepancy in IE, obtained from AC impedance spectra and from weight loss method.

Table 14: AC impedance parameters of carbon steel immersed in various test solution.

System	R _t ohm cm ²	C _{dl} F/cm ²	Impedance Value log(z/ohm)
Well water (model corrosion medium)	1710	2.98 × 10 ⁻⁹	3.309
MG (30 ppm) + Zn ²⁺ 25 ppm	1748	2.92 × 10 ⁻⁹	3.343

Analysis of UV visible spectra

The UV-visible absorption spectrum of an aqueous solution of MG and Fe²⁺ (freshly prepared FeSO₄ solution) is shown in Fig. 5. Peaks appear at 202, 313, 423 and 615 nm. This is due to the Fe²⁺-MG complex formed in solution [51,52].

The UV-visible reflectance spectrum of the film formed on the metal surface after immersion in the solution containing well water (model corrosion medium), 30 ppm of MG and 25 ppm of Zn²⁺ is shown in Fig. 6. Peaks appear at 202, 313, 423 and 615 nm.

These peaks match with those of the Fe²⁺-MG complex in solution. Hence it is confirmed that the protective film consists of the Fe²⁺-MG complex [53, 54].

Analysis of luminescence spectra

Fluorescence spectra were used to confirm the formation of a protective film on the metal surface during corrosion inhibition studies [55,56].

The luminescence spectrum (λ_{ex}=300 nm) of an aqueous solution of malachite green (MG) and freshly prepared Fe²⁺ (FeSO₄.7H₂O) is shown in Fig. 7(a). Peaks appear at 336 nm, 364 nm, 410 nm, 441 nm and 521 nm. This spectrum is due to the formation of a MG-Fe²⁺ complex in the solution.

The luminescence spectrum (λ_{ex}=300 nm) of the film formed on the metal surface after immersion in an aqueous solution containing well water (model corrosion medium), 30 ppm of MG, and 25 ppm of Zn²⁺ is shown in Fig. 7(b). Peaks appear at 335 nm, 364 nm, 410 nm, 440 nm and 520 nm. These peaks match with the peaks of the Fe²⁺-MG complex formed in solution, which confirms that the protective film formed on the metal surface consists of the Fe²⁺-MG complex.

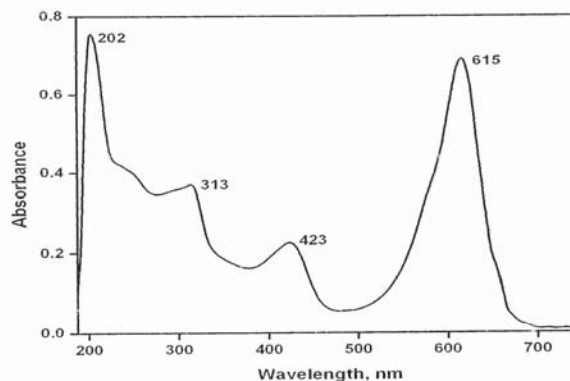


Fig.5. UV-visible absorption spectrum of an aqueous solution of MG + Fe²⁺.

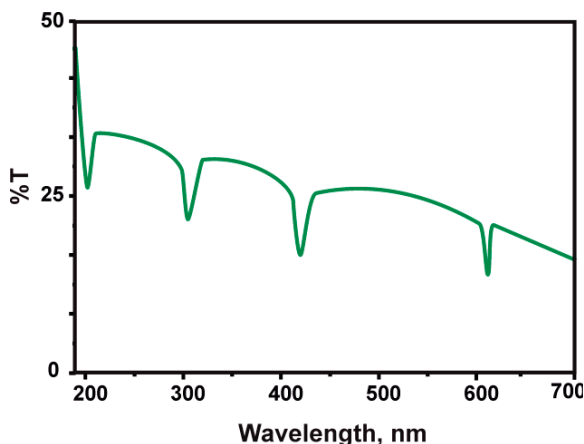


Fig. 6. The UV-visible reflectance spectrum of the film formed on metal after immersion in the solution containing Well water (model corrosion medium) + MG 30 ppm + Zn²⁺ 25 ppm/

Analysis of FTIR spectra

The structure of MG is shown in Scheme 2. The FTIR spectrum (KBr) of pure MG is shown in Fig. 8(a). The peak at 1616 cm⁻¹ corresponds to aromatic -C=C- stretching frequency. The peak at 1319 cm⁻¹ corresponds to -N stretching frequency. Thus the structure of MG, namely,

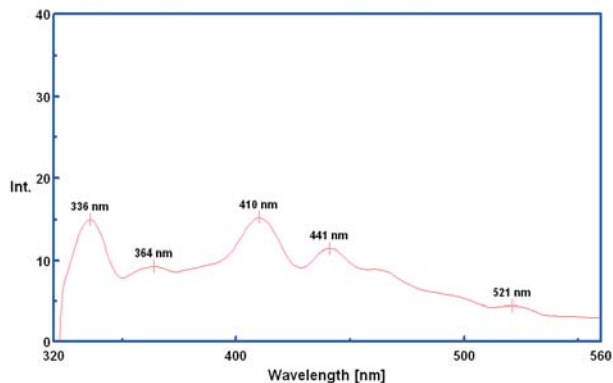


Fig.7a. The luminescence spectrum of an aqueous solution containing MG and Fe²⁺.

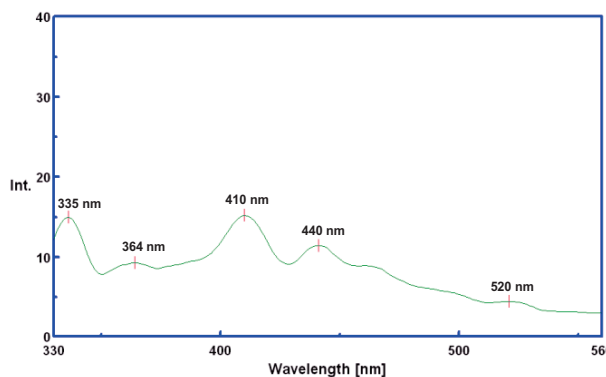


Fig.7b. The luminescence spectrum of the film formed on the metal surface after immersion in aqueous solution containing well water (model corrosion medium), 30 ppm of MG and 25 ppm of Zn²⁺.

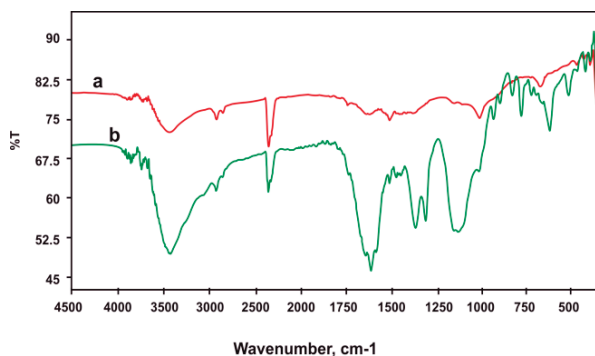
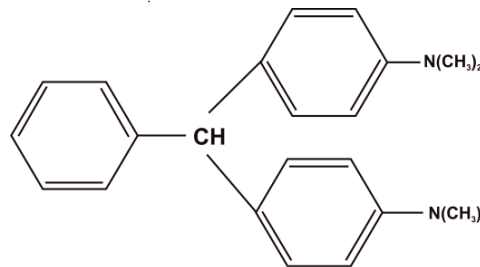


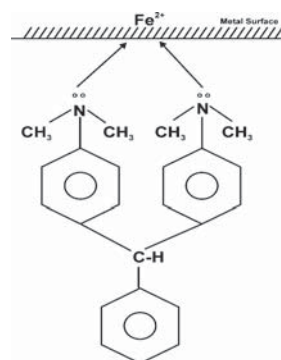
Fig.8: FTIR spectra. (a) pure MG; (b) - film formed on the carbon steel surface after immersion in a solution containing well water (model corrosion medium) + MG (30 ppm) + Zn²⁺ (25 ppm).

4-[(4-dimethylaminophenyl)-phenylmethyl-N,N-dimethyl aniline] is confirmed by FTIR [57].

The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the well water (model corrosion medium) containing 25 ppm of Zn²⁺ and 30 ppm of MG is shown in Fig.8b. It is found that the disappearance of tertiary nitrogen confirms the co-ordination through the -N atom. It is interesting to note that



Scheme 2. Structure of Malachite Green



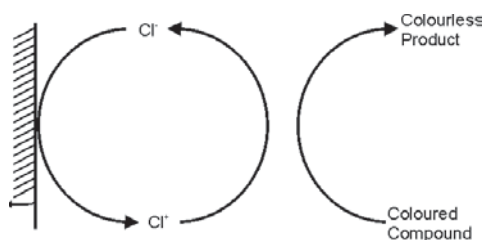
Scheme 3. Adsorption of MG on metal surface.

the aromatic π electron peak at 1616 cm⁻¹ does not disappear in the FTIR spectrum of the protective film. It appears at 1616 cm⁻¹ without shift, which indicates that the aromatic π -electrons do not participate in the coordination with Fe²⁺ on the metal surface. Thus, it is confirmed that the Fe²⁺-MG complex on the metal surface is formed through coordination of electrons of nitrogen atoms and Fe²⁺ on the metal surface. The aromatic π -electrons do not participate in Fe²⁺-MG complex formation. The probable structure of this complex is shown in Scheme 3.

Parallel coordination is not possible due to steric hindrance. Hence, perpendicular coordination takes place. The peak at 1350 cm⁻¹ is due to zinc hydroxide. Thus, it follows from the FTIR spectral study that the protective film consists of the Fe²⁺-MG complex.

Decolourisation process

Platinized titanium anode and graphite cathode were immersed in 100 ml of the solution to be decolorized. Current was passed for 10 minutes without addition of NaCl. Potential was 2 V; current density was 0.25 A/cm². There was no discoloration. When 1 g of NaCl was added (1% solution supporting electrolyte), partial discoloration took place after passing current for 10 minutes, due to the low concentration of sodium hypochlorite produced. However, it is very interesting to note that when 2 g of NaCl were added (2% solution), the solution was completely discolored within a few seconds. Hence this formulation, namely 2% solution of NaCl, platinized titanium anode, graphite cathode, current density of 0.125 A/cm² and potential of 2 V may be used for a few seconds to discolor the solution of MG (20 ppm). The supporting electrolyte plays an important role in the oxidation process [58,59]. When NaCl solution is electrolysed, the active species produced is Cl⁺ which oxidizes the colored product into a colorless one (Scheme 4).



Scheme 4. Mechanism of decolourisation.

The optical density value for coloured solution before decolourisation was 0.38 and after decolourisation was 0.01. Hence the efficiency of decolourisation is 96%.

The optical density of the colored solution before discoloration was 0.38 and after discoloration - 0.01. Hence, the efficiency of discoloration is 96%.

The main objection for using dyes as corrosion inhibitors in cooling water systems is the color of dye.

The present study offered a method of discoloration of the colored inhibitor solutions.

Table 15: The decolourising efficiency

System	Current Density A/cm ²	Potential volts	NaCl g	OD	Efficiency %
MG before electrolysis	--	--	--	0.38	--
MG after electrolysis	0.125	2	2	0.01	96

CONCLUSION

The inhibition efficiency (IE) of the malachite green (MG)-Zn²⁺ system in controlling corrosion of carbon steel in well water containing 665 ppm of Cl⁻ (model corrosion medium) was evaluated by the mass-loss method. The present study leads to the following conclusions:

- The mass-loss study reveals that the formulation consisting of 30 ppm of MG and 25 ppm of Zn²⁺ has 95% inhibition efficiency in controlling corrosion of carbon steel immersed in well water (model corrosion medium).
- The values of the synergistic parameters point to a synergistic effect between MG and Zn²⁺.
- The polarization study reveals that the formulation functions as a cathodic type inhibitor predominantly controlling the cathodic reaction.
- It follows from the AC impedance spectra that a protective film is formed on the metal surface.
- The FTIR spectra show that the protective film consists of the Fe²⁺-MG complex, which is further confirmed by the UV-visible spectra and fluorescence spectra.
- The colour of the dye can be removed by electrolysis using platinized titanium as anode and graphite as cathode.

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ИНХИБИРАЩО ДЕЙСТВИЕ НА СИСТЕМАТА Zn²⁺ -МАЛАХИТОВО ЗЕЛЕНО

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(Резюме)

Ефективността на инхибиране (IE) на системата Zn²⁺ - малахитово зелено (MG) при корозията на въглеродна стомана е оценена по метода за загуба на теглото. Използвана е моделна среда, съдържаща 665 ppm хлоридни йони. Изследванията показват, че препаратът, съдържащ 30 ppm от MG и 25 ppm от Zn²⁺ има инхибираща ефективност от 95% при използваната моделна среда. Има данни за синергизъм на MG и Zn²⁺. Поляризационните изследвания показват, че системата работи като инхибитор от катоден тип, т.е. контролираща предимно катодната реакция. АС-импедансните спектри показват, че върху металната повърхност се образува защитен филм. FTIR-спектрите показват, че този филм се състои от комплекс между Fe²⁺ и багрилото. Този резултат е потвърден UV-Vis и флуоресцентна спектроскопия. Оцветяването може да се отстрани чрез електролиза при анод от платинизиран и графит като катод.