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The prevention of corrosion in mild steel when exposed to groundwater through the use of an aqueous solution of trisodium phosphate

ABSTRACT

An aqueous solution of trisodium phosphate has been utilized to mitigate the corrosion of mild steel in groundwater. The weight loss method has been employed to assess the corrosion rate of mild steel and to determine the corrosion inhibition efficiency of the inhibitor. It has been noted that the inhibitor molecules adhere to the metal surface. The adsorption process follows the Langmuir adsorption isotherm. The mechanism of corrosion inhibition has been investigated through electrochemical studies, including polarization studies and AC impedance spectra. The surface morphology of the protective film has been examined using SEM (scanning electron microscopy) images and FTIR spectra (KBr). The FTIR spectra indicate that the protective film is composed of an iron phosphate complex formed on the anodic sites of the metal surface. The examination of contact angle measurements across different surfaces indicates that when an inhibitor system is present, the contact angle rises, wettability diminishes, hydrophobicity escalates, and corrosion resistance improves. Examination of different AFM images of various surfaces indicates that, when an inhibitor system is present, AFM parameters such as average roughness, RMS roughness, and peak-to-valley height show a reduction. Consequently, the surface attains a smoother texture.

Examination of Vickers Hardness across different surfaces indicates that, when an inhibitor system is present, the hardness improves. This suggests that the protective film is both stable and more robust. Consequently, the resistance to corrosion is enhanced. These findings could be applicable in cooling water towers where groundwater may serve as the coolant.

Keywords: corrosion inhibition, ground water, cooling water towers, trisodium phosphate, SEM, FTIR, electrochemical studies, adsorption isotherm, contact angle measurements, AFM images, Vickers Hardness.

INTRODUCTION

Protection of cooling tower metals

Corrosion inhibitors protect cooling tower metals by forming thin protective films that reduce anodic and cathodic reactions, preventing metal loss and extending equipment life.

Corrosion in Cooling Towers

Cooling towers are prone to corrosion due to water chemistry, oxygen content, and microbial activity. Common corrosion types include uniform corrosion, pitting, crevice corrosion, and microbiologically influenced corrosion (MIC). Corrosion can reduce heat transfer efficiency, cause leaks, and shorten the lifespan of heat exchangers and piping. Open recirculating systems are particularly susceptible because water is exposed to the atmosphere, increasing oxygen and contaminant levels.

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Types of Corrosion Inhibitors

Corrosion inhibitors are chemicals that passivate metal surfaces and slow down electrochemical reactions. They are generally classified as:

Anodic inhibitors: Form insoluble salts with metal ions, increasing anodic polarization and reducing metal dissolution. They are effective in small-volume systems but require careful dosing to avoid localized attack.

Cathodic inhibitors: Slow the reduction reaction at the cathode, reducing overall corrosion rates. Zinc is a common cathodic inhibitor, often combined with phosphates for multi-metal protection.

Mixed inhibitors: Contain both anodic and cathodic agents to provide broad-spectrum protection for steel, copper, and other metals.

Common Chemical Treatments

Phosphate-based inhibitors: Form a protective phosphate layer on metal surfaces, preventing rust and scaling. Orthophosphates act mainly as anodic inhibitors, while polyphosphates provide cathodic protection.

Zinc-based programs: Effective against pitting corrosion, especially in aggressive waters with low hardness or high chlorides. Often combined with phosphates or phosphonates.

Molybdate-based inhibitors: Environmentally friendly alternatives to phosphates, forming protective barriers on metals and preventing localized corrosion.

Organic inhibitors: Include tolyltriazole (TTA) or benzotriazole (BZT) for copper alloys, forming adsorbed films that prevent dezincification and corrosion.

Proprietary blends: High-performance formulations like FlexPro® combine multiple chemistries for multi-metal protection and sustainability.

Integrated Cooling Water Treatment

Effective corrosion control often combines inhibitors with scale control, pH adjustment, and biocides. For example, CWT-500M is a commercial product that inhibits calcium scaling and oxygen-induced corrosion, suitable for high-hardness, high-alkalinity waters in HVAC and evaporative cooling systems. Maintaining proper pH (typically 6.5–7.5) and controlling microbial growth are essential to maximize inhibitor performance.

Key Considerations

Select inhibitors based on metal types, water chemistry, and system design.

Monitor dosage and water quality to prevent under- or over-treatment.

Consider environmental regulations, especially for zinc or phosphate discharge.

Combine with scale and biocide programs for comprehensive system protection.

Using the right corrosion inhibitor program ensures longer equipment life, reduced maintenance costs, and improved heat transfer efficiency in cooling tower systems.

Several corrosion inhibitors have been used in cooling water towers [1-10].

The Effect of the Concentration of a Nitrite-Based Inhibitor and Chloride Ions on the Corrosion Behavior of FCD-500 in a Simulated Marine Engine Cooling Water System has been investigated by Jeon and Jung [1].

Galanin et al. [2] have investigated the Use of Inhibitors to Prevent Oxidation in Cooling Systems of Nuclear Power Plants. Selection of the Optimal Water Chemistry Regime Using a Model Unit.

Vignesh et al. have synthesised a novel N-substituted tetrabromophthalic and used as corrosion inhibitor. This inhibitor has been used to control microbial influenced corrosion in cooling water system [3].

Pramudita et al. [4] have explored the Synergistic ability of Terminaliacatappa leaves extract as bio-corrosion inhibitor by adding KI to mild steel in demineralized water.

Anandkumar et al. [5] have investigated the Synergistic enhancement of corrosion protection of carbon steels using corrosion inhibitors and biocides.

Molecular adsorption studies, DFT calculations and long-term corrosion performance evaluation have been employed in this study.

AlSalhi et al. have undertaken a study on characterization of plants and seaweeds based corrosion inhibitors. They have been used to prevent microbially influenced corrosion in a cooling tower water environment [6].

Kokilaramani et al. [7] have undertaken an evaluation of crude methanolic mangrove leaves extract for antibiofilm efficacy against biofilm-forming bacteria on a cooling tower wastewater system [7].

Preethi et al. [8] have synthesized silver nanoparticles. They have been used as a green corrosive inhibitor for mild steel in re-circulating cooling water system.

Weberski et al. [9] have undertaken a study of Next Generation Closed Loop Corrosion Inhibitors. They have investigated the Increasing Reliability and Decreasing Environmental Impact.

Demadis et al. [10] have undertaken an investigation on Corrosion control using inhibitor systems based on phosphonates and metal phosphonate materials. Several phosphonates have been used as corrosion inhibitors [10].

The present work is undertaken to investigate the use of trisodium phosphate [11,12] as corrosion inhibitor to control corrosion of mild steel pipelines carrying ground water in cooling water towers. Weight loss method has been employed. Langmuir adsorption isotherm has been used. Mechanistic

aspects of corrosion inhibition have been investigated by polarisation study and AC impedance spectra. The surface morphology has been analysed using SEM and FTIR spectral analysis.

EXPERIMENTAL

In the present investigation, pure (trisodium phosphate) Na_3PO_4 , has been used as corrosion inhibitor to control corrosion of mild steel in ground water, whose composition is given in Table 1.

Table 1. Composition of ground water Water Quality Analysis (As per BIS 10500:2012)

Parameter	Observed Value	Unit	Requirement (Desirable Limit)	Permissible Limit	Remarks
pH	7–7.5	-	6.5–8.5	No relaxation	Within limit
Electrical Conductivity	1153.62	$\mu\text{S}/\text{cm}$	Not specified	Not specified	-
Chloride	119.96	mg/L	250	1000	Within limit
Alkalinity	570	mg/L	200	600	Within permissible limit
Total Hardness	244	mg/L	200	600	Within permissible limit
Calcium (Ca^{2+})	76	mg/L	75	200	Slightly above desirable
Magnesium (Mg^{2+})	168	mg/L	30	100	Above permissible
TDS	550	mg/L	500	2000	Within permissible
TSS	0	mg/L	Not specified	Not specified	-
Total Solids	5350	mg/L	Not specified	Not specified	-
Dissolved Oxygen	2.83	mg/L	≥ 6	Not specified	Below required
Sulphate	14.48	mg/L	200	400	Within limit
Nitrate	-	mg/L	45	No relaxation	Not detected

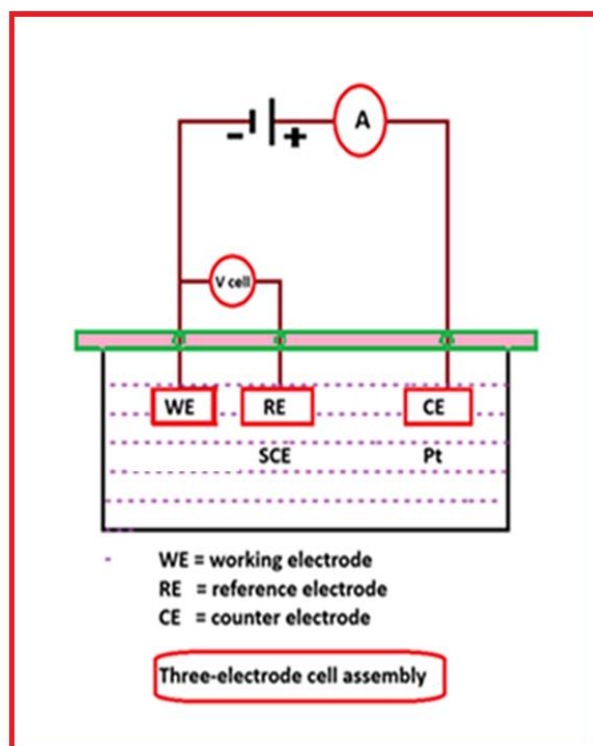


Figure 1. Three-electrode cell assembly

Weight loss method

Inhibitor solution

1g of pure (trisodium phosphate) Na_3PO_4 , was dissolved in 100 ml of double distilled water and this solution was used as corrosion inhibitor.

Mild steel specimen were polished to mirror finish, degreased with trichloroethylene (or acetone) and dried in a desiccator. Three mild steel specimens were immersed in various test solutions for a period of one day in the absence and presence of inhibitor system. Weights of the specimen were determined before and after immersion.

Electrochemical studies

Electrochemical investigations, including polarization studies and AC impedance spectroscopy, have been extensively employed in the examination of corrosion inhibition [13-22].

The electrochemical studies were carried out in a Three-electrode cell assembly (Figure 1).

Polarization study

In the current study, the corrosion resistance of mild steel submerged in groundwater was assessed through potentiodynamic polarization analysis and AC impedance spectra. The

experiments were conducted at ambient temperature. Polarization investigations were performed using a CHI electrochemical workstation equipped with an impedance model 660A, which included an iR compensation feature.

A three-electrode cell configuration was employed, utilizing a mild steel as the working electrode, platinum as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a and cathodic = b_c and linear polarization resistance (LPR) value were calculated.

AC Impedance spectra

AC impedance spectra have been employed to examine the development of a protective layer during the corrosion protection process.

In the current investigation, the identical apparatus and cell configuration employed for the polarization study were utilized to capture AC impedance spectra as well. A duration of 5 to 10 minutes was allowed for the system to reach a stable open circuit potential. The real component (Z') and the imaginary component ($-Z''$) of the cell impedance were recorded in ohms across a range of frequencies.

Charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were calculated.

Table 2. Corrosion rates and inhibition efficiencies (IE, %), offered by various concentrations of inhibitor system (sodium phosphate solution, ml)

Concentration of inhibitor, ppm	Corrosion rate, mdd	Inhibition efficiency, %	Surface coverage, θ	C/ θ
0	17.86	-	-	0.0
200	3.22	82	0.82	2.44
400	3.21	86	0.86	4.65
600	1.79	90	0.90	6.67
800	1.07	94	0.94	8.51
1000	0.36	98	0.98	10.24

$$R_t = (R_s + R_l) - R_s$$

Where R_s = solution resistance.

C_{dl} values were calculated using the relationship

$$C_{dl} = 1 / 2\pi f_{max} R_t$$

Where f_{max} = frequency at maximum imaginary impedance.

Analysis of surface morphology

The nature of protective film formed on the metal surface are analysed by SEM image analysis and FTIR spectral analysis.

RESULTS AND DISCUSSION

Analysis of results of weight loss method

The corrosion rates of mild steel, immersed in ground water (blank) for one day, in the absence and presence of various concentration of inhibitor solution (trisodium phosphate), are given in Table 2. The corrosion inhibition efficiencies (IE, %), the surface coverage θ , are also given in Table 2, and Figure 2.

It is observed that as the concentration of the inhibitor increases, the corrosion rate (mdd: mg/dm².day) decreases, the corrosion inhibition efficiencies (IE, %) increase and the surface coverage θ (θ = IE, %/100) increases.

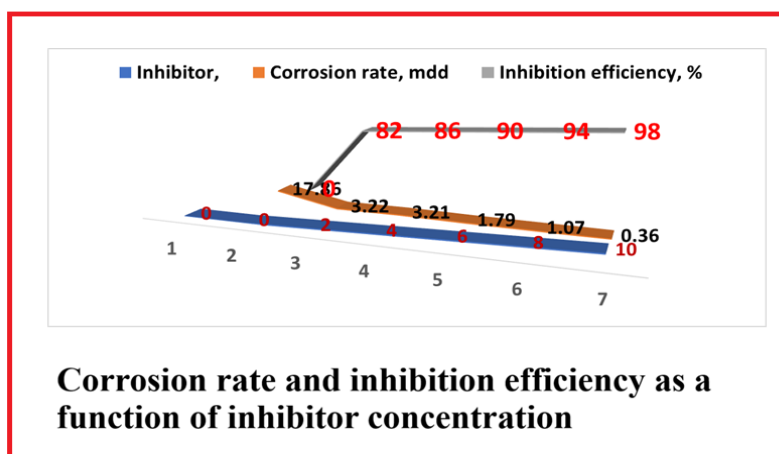


Figure 2.. Corrosion rate and inhibition efficiency as function of inhibitor concentration (ml)

Langmuir adsorption isotherm

Langmuir adsorption isotherms have been used in corrosion inhibition studies.

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is used to describe the equilibrium between adsorbate and adsorbent system, where the adsorbate adsorption is limited to one molecular layer at or before a relative pressure of unity is reached. There are the three assumptions of the Langmuir isotherm. They are the adsorption consists entirely of a monolayer at the surface; (2) there is no interaction between molecules on different sites and each site can hold only one adsorbed molecule; (3) the heat of adsorption does not depend on the number of sites and is equal for all sites.

Mild steel immersed in inhibitor system

A plot of C vs C/θ gives a straight line (Table 3, Figure 3). This indicates that Langmuir adsorption isotherm is obeyed. The R^2 value is very high (0.9959). The adsorption consists entirely of a monolayer of the inhibitor on the metal surface.

Table 3. Data for adsorption isotherm

C, ml of inhibitor	C/ θ
0	0.0
2	2.44
4	4.65
6	6.67
8	8.51
10	10.24

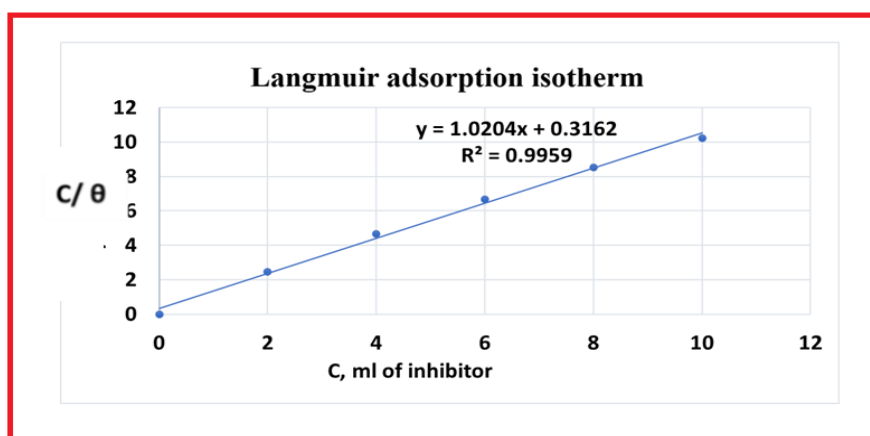


Figure 3. Langmuir adsorption isotherm

Analysis of results of Electrochemical studies

Electrochemical studies have been used in corrosion inhibition studies [13-22].

Polarisation study

Corrosion parameters of polarisation study are given in Table 4. The Tafel plots are shown in Figures 4 and 5.

Table 4.. Corrosion parameters derived from polarisation curves

System	E _{corr} , mV vs SCE	LPR, Ohmcm ²
water	-363	920
Water + inhibitor	-214	1308

It is observed that in the presence of inhibitor system the corrosion potential shifts to the anodic side. This indicates that the anodic reaction of metal dissolution is controlled predominantly.

In the presence of inhibitor, the corrosion potential is shifted to the anodic side. So the

inhibitor system functions as anodic type of inhibitor.

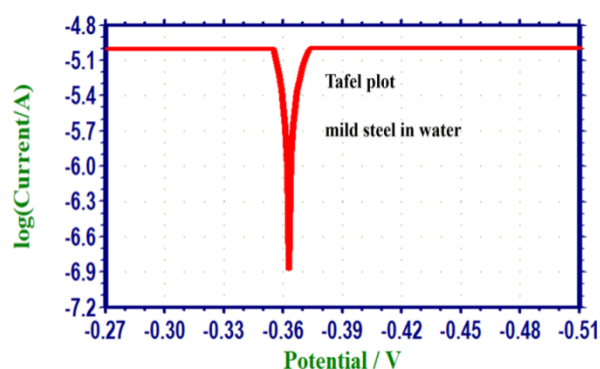


Figure 4. Tafel plot of mild steel immersed in water

Further it is noticed that in the presence of inhibitor system the linear polarisation resistance value increases. This indicates that the corrosion resistance of mild steel increases in the presence of inhibitor system. The electron flow in the electron

is restricted. The corrosion of mild steel is retarded. This is in agreement with the results of the weight loss method.

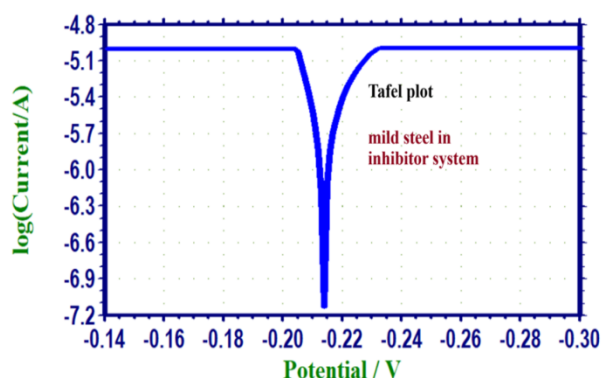


Figure 5. Tafel plot of mild steel immersed in water + inhibitor system

Analysis of AC impedance spectra

The corrosion parameters derived from AC impedance spectral analysis are given in Table 5. The AC impedance spectra are shown in Figures 6-9. The Nyquist plots are shown in Figures 6 and 8. The Bode plots are shown in Figures 7 and 9.

Table 5. Corrosion parameters derived from AC impedance spectra (Electrochemical Impedance Spectra, EIS)

System	Rt, Ohmcm ²	C _{dl} , F/cm ²	Impedance, Log (Z/ohm)	Phase angle,
water	112	4.554×10^{-8}	2.412	18.25
Water + inhibitor	486	1.049×10^{-8}	2.955	29.53

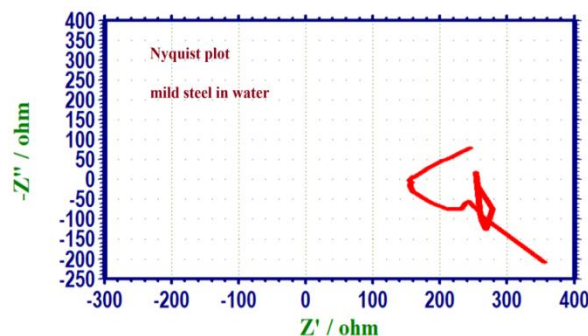


Figure 6. Nyquist plot of mild steel immersed in water

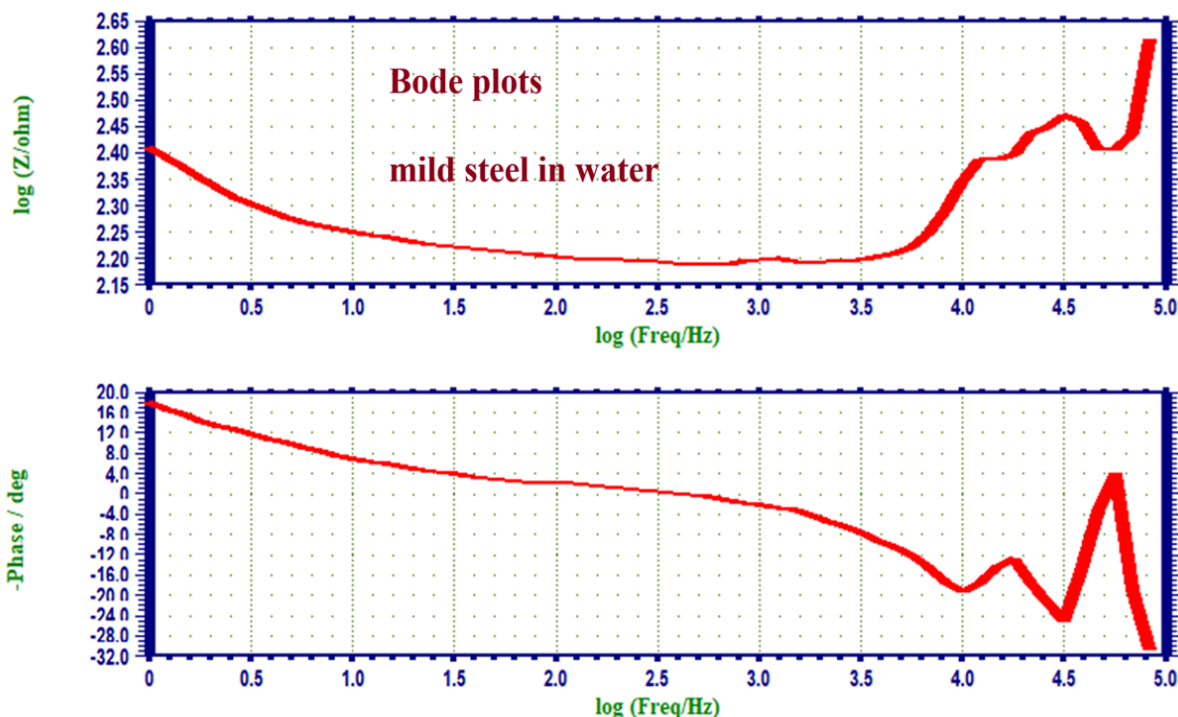


Figure 7. Bode plots of mild steel immersed in water system

Analysis of SEM images

Analysis of SEM images has been widely used in corrosion inhibition studies [23-27]. The SEM images of polished mild steel, mild steel immersed in water (blank), and polished metal in inhibitor solution are shown in Figure 10. In image of polished mild steel, some particles are noticed. They are due to oxides of iron formed on polished metal, during experimental procedure. In image of the blank system, cracks are noticed.

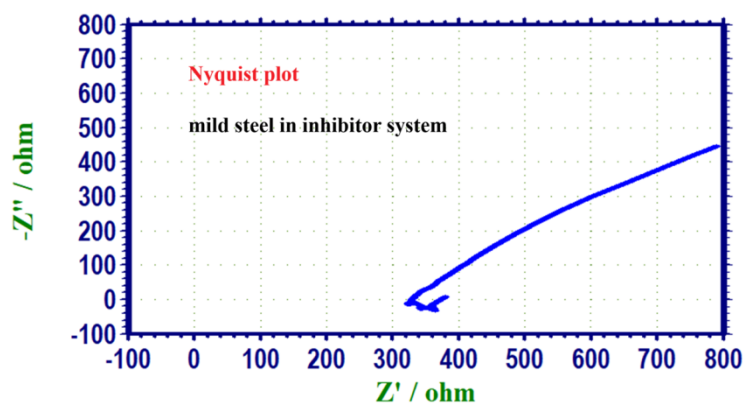


Figure 8. Nyquist plot of mild steel immersed in water + inhibitor system

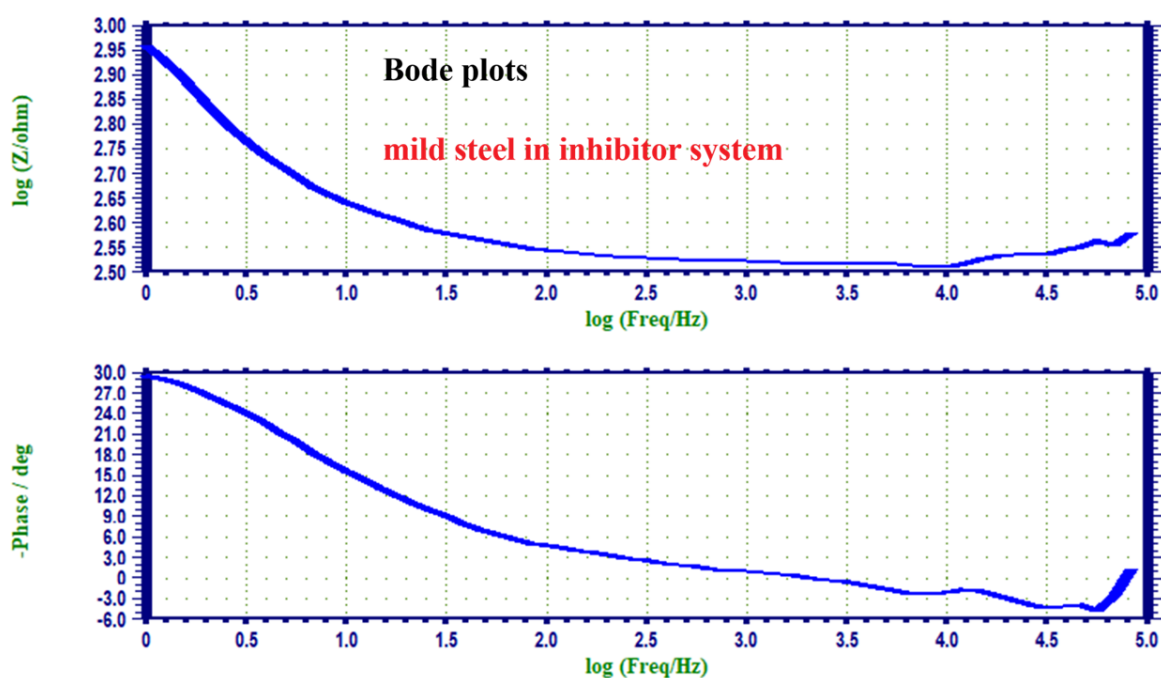


Figure 9. Bode plots of mild steel immersed in water + inhibitor system

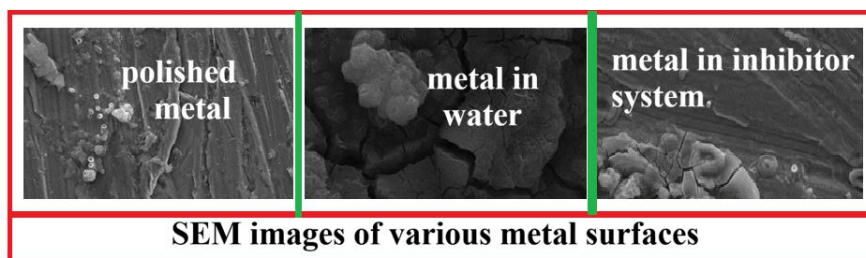


Figure 10. SEM images of various metal surfaces

The particles present on the surface are due to oxides of iron. In the SEM image of the polished metal, immersed in inhibitor system, the inhibitor films are noticed on the metal surface.

Analysis of FTIR spectra

Analysis of FTIR spectra has been widely used in corrosion inhibition studies [28-30]. The FTIR spectrum of pure (trisodium phosphate) Na_3PO_4

(KBr method) is shown in Figure 11. The P-O stretching frequency appears at 980.623 cm^{-1} .

The FTIR spectrum (KBr method) of film formed on the metal surface after immersion in ground water for one day, is shown in Figure 12. Oxides of iron are noticed on the metal surface. The stretching frequency at 471.51 cm^{-1} , is due to FeOOH . The stretching frequency at 2930.31 cm^{-1} , is due to Fe_3O_4 (magnetic oxide of iron). The iron-oxygen bond in general appears at 682.677 cm^{-1} . The peak at 3322.75 cm^{-1} , indicate that the

magnetic particles of iron are present in the nanoparticle scale.

The FTIR spectrum (KBr method) of film formed on the metal surface after immersion in ground water and inhibitor system for one day, is shown in Figure 13. The P-O stretching frequency has disappeared. This indicates that the oxygen atom of phosphate group has coordinated with the Fe^{2+} ion, resulting in the formation of iron-phosphate complex on the anodic sites of the metal surface (Figure 14). This film protects the metal from corrosion.

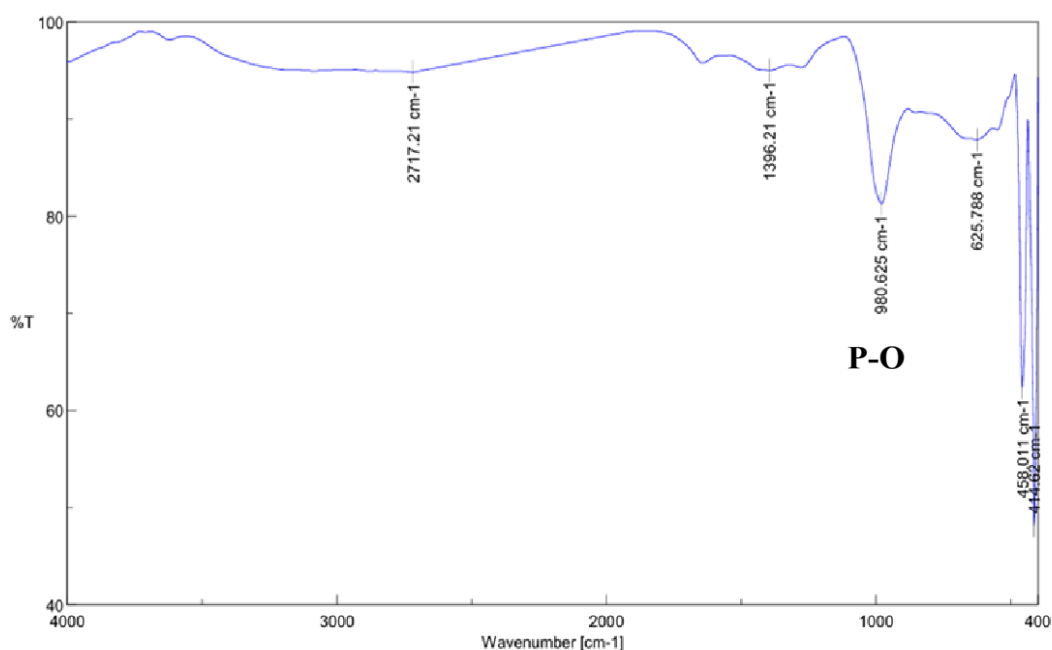


Figure11. FTIR spectrum (KBr) of pure trisodium phosphate

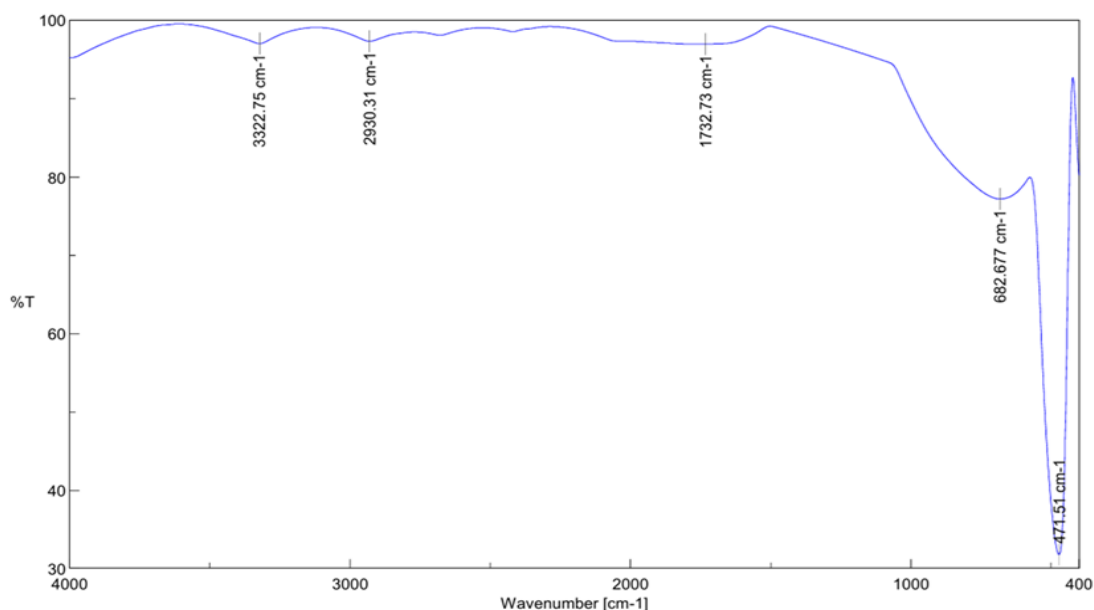


Figure 12. FTIR spectrum (KBr) of film formed on metal surface after immersion in water after one day (blank)

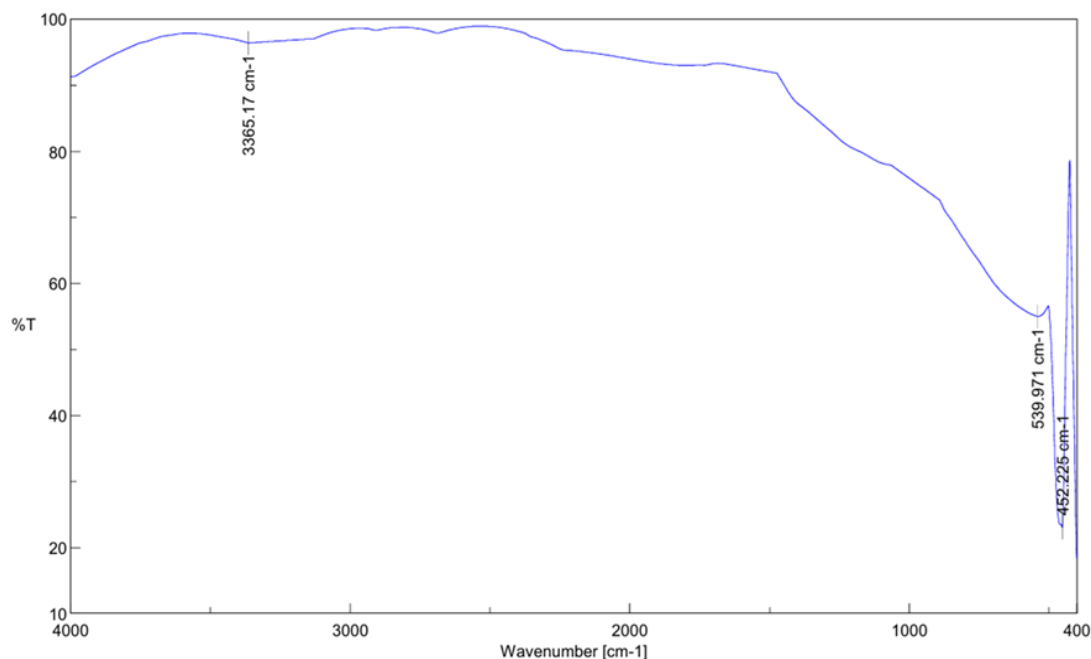


Figure 13. FTIR spectrum (KBr) of film formed on metal surface after immersion in water containing inhibitor system after one day

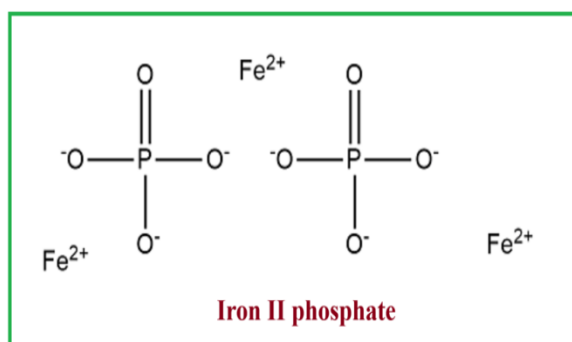


Figure 14. Structure of iron II phosphate

Analysis of contact angle measurements

Contact angle measurements have been employed in research related to corrosion inhibition [26-30,31-35]. When a surface undergoes corrosion or its protective properties weaken, the contact angle of that surface diminishes. This leads to enhanced wettability and a decrease in hydrophobicity, resulting in a reduced ability to repel water. In contrast, when a surface is free from corrosion or retains a significant level of protection, the contact angle rises. This causes a reduction in wettability and an increase in hydrophobicity.

A review of these facts, in conjunction with an assessment of Figure 15, suggests that the inhibitor system provides corrosion protection for mild steel submerged in groundwater.

This finding aligns with the outcomes derived from electrochemical investigations, including polarization analysis and AC impedance spectra.

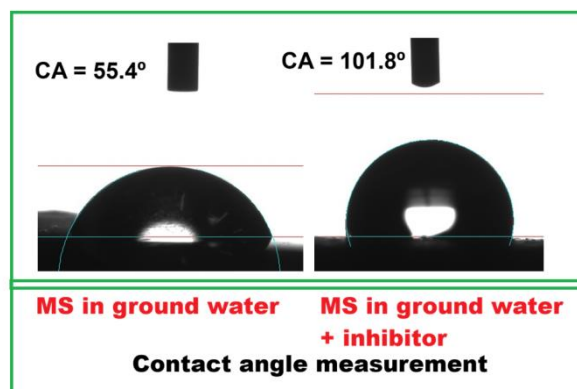


Figure 15. Contact angles of various surfaces

Analysis of AFM images

The analysis of AFM images has been widely employed in research related to corrosion inhibition [36-40]. Various AFM parameters, namely Average Roughness (Sa) (nm), RMS Roughness (Sq) (nm), and Maximum peak-valley height (Sy) (nm), are detailed in the Table 6. The AFM images are depicted in the Figure 16.

Typically, in systems designed to resist corrosion, the parameters of the AFM are generally lower. In contrast, in environments with higher

levels of corrosion, the AFM parameters are increased. This results in a greater surface roughness. Based on these principles, it can be inferred that the inhibitor system provides corrosion protection for mild steel submerged in groundwater.

This conclusion aligns with the findings derived from the electrochemical investigations, including the polarization analysis and AC impedance spectra.

Table 6. AFM parameters calculated from area roughness for various systems

System	Average Roughness, (S_a) (nm)	RMS Roughness (S_q) (nm)	Maximum peak - valley height, (S_y) (nm)
Mild steel in ground water	336.5	426.8	3.20 μ m
Mild steel in ground water + inhibitor	92.1	110.2	789.34
Observation	decreases	decreases	decreases
Inference	Inhibitor system offers corrosion protection to mild steel in ground water		

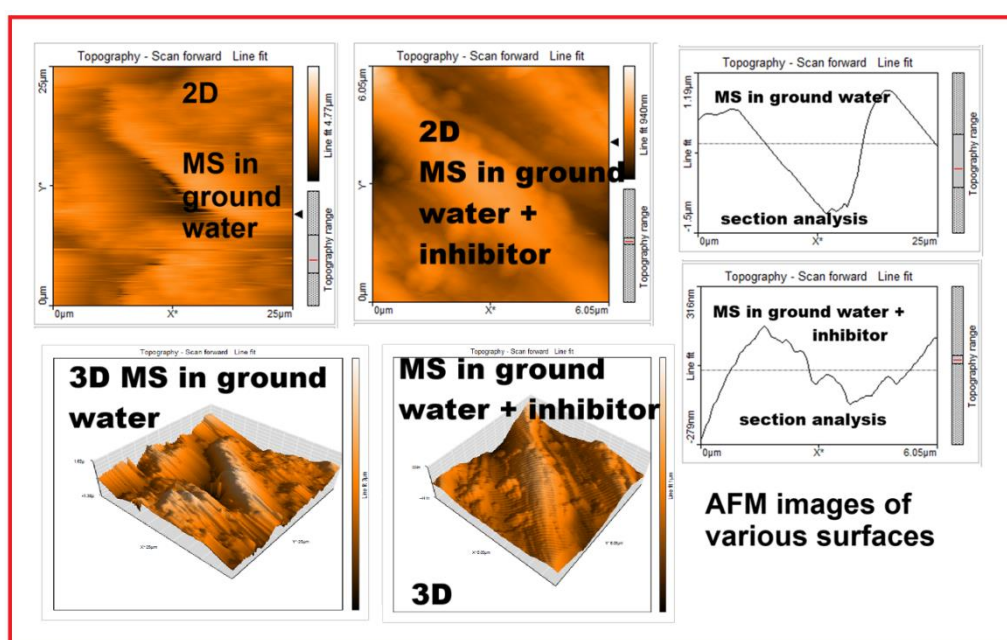


Figure 16. AFM images of various surfaces

Vickers Hardness Number (HV)

The Vickers hardness test evaluates a material's ability to withstand plastic deformation by employing a diamond-shaped pyramidal indenter, with hardness determined by the dimensions of the resulting indentation.

Table 7. Vickers Hardness of various surfaces

System	Load	L1	L2	HV
Mild steel in ground water	100 g	55.94	57.12	58.0
Mild steel in ground water + inhibitor	100 g	40.28	42.11	109

The Vickers hardness test has been widely applied in studies concerning corrosion inhibition

[41-45]. When the metal is placed in a corrosive environment (blank), the Vickers hardness is low. However, when corrosion protection is provided by an inhibitor system, there is an increase in Vickers hardness. Based on these principles and an examination of Table, it is evident that the inhibitor system provides effective corrosion protection for mild steel submerged in groundwater.

SUMMARY AND CONCLUSIONS

- An aqueous solution of trisodium phosphate has been used to control the corrosion of mild steel in ground water.
- Weight loss method has been used to measure the corrosion rate of mild steel and to evaluate the corrosion inhibition efficiency of the inhibitor.

- It is observed that the inhibitor molecules are adsorbed on the metal surface.
- The adsorption obeys Langmuir adsorption isotherm.
- The mechanism of corrosion inhibition has been evaluated by electrochemical studies such as polarisation study and AC impedance spectra.
- The surface morphology of the protective film has been analysed by SEM (scanning electron microscopy) images FTIR spectra (KBr).
- The FTIR spectra reveal that the protective film consists of iron phosphate complex formed on the anodic sites of the metal surface.
- The examination of contact angle measurements across different surfaces indicates that when an inhibitor system is present, the contact angle rises, wettability diminishes, hydrophobicity escalates, and corrosion resistance improves.
- Examination of different AFM images of various surfaces indicates that, when an inhibitor system is present, AFM parameters such as average roughness, RMS roughness, and peak-to-valley height show a reduction. Consequently, the surface attains a smoother texture.
- Examination of Vickers Hardness across different surfaces indicates that, when an inhibitor system is present, the hardness improves. This suggests that the protective film is both stable and more robust. Consequently, the resistance to corrosion is enhanced.
- These findings may be used in cooling water towers where ground water can be used as the coolant.

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IZVOD

SPREČAVANJE KOROZIJE MEKOG ČELIKA KADA JE IZLOŽEN PODZEMNIM VODAMA UPOTREBOM VODENOG RASTVORA TRINATRIJUM FOSFATA

Vodeni rastvor trinatrijum fosfata je korišćen za ublažavanje korozije mekog čelika u podzemnim vodama. Metoda gubitka težine je korišćena za procenu brzine korozije mekog čelika i za određivanje efikasnosti inhibitora u inhibiciji korozije. Primećeno je da se molekuli inhibitora lepe za površinu metala. Proces adsorpcije prati Langmirovu izotermu adsorpcije. Mehanizam inhibicije korozije je istražen elektrohemijskim studijama, uključujući studije polarizacije i spektre AC impedanse. Površinska morfologija zaštitnog filma je ispitana korišćenjem SEM (skenirajuće elektronske mikroskopije) slika i FTIR spektara (KBr). FTIR spektri pokazuju da je zaštitni film sastavljen od kompleksa gvožđe fosfata formiranog na anodnim mestima površine metala. Ispitivanje merenja kontaktnog ugla na različitim površinama pokazuje da kada je prisutan sistem inhibitora, kontaktni ugao raste, kvasivost se smanjuje, hidrofobnost se povećava i otpornost na koroziju se poboljšava. Ispitivanje različitih AFM slika različitih površina ukazuje da, kada je prisutan sistem inhibitora, AFM parametri kao što su prosečna hrapavost, RMS hrapavost i visina od vrha do dna pokazuju smanjenje. Shodno tome, površina postiže gladu teksturu.

Ispitivanje Vickersove tvrdoće na različitim površinama ukazuje da, kada je prisutan sistem inhibitora, tvrdoća se poboljšava. Ovo sugerise da je zaštitni film i stabilan i robusniji. Shodno tome, otpornost na koroziju je poboljšana. Ovi nalazi bi mogli biti primenljivi u rashladnim tornjevima gde podzemne vode mogu služiti kao rashladno sredstvo.

Ključne reči: inhibicija korozije, podzemne vode, rashladni tornjevi, trinatrijum fosfat, SEM, FTIR, elektrohemijske studije, izoterma adsorpcije, merenja kontaktnog ugla, AFM slike, Vickersova tvrdoća.

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