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The Use of Molybdate, Chromate and Tungstate Anions as Corrosion Inhibitors for Steel in Sulfide Polluted Salt Water

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The inhibiting effect of molybdate, chromate, and tungstate salts on the corrosion of steel used in sanitation plants was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM) techniques. The sulfide polluted salt water was simulated by a 3.5 %

NaCl and 16 ppm Na₂S solution. The results revealed that these inorganic anions are very good inhibitors. Potentiodynamic polarization curves indicated an anodic-type inhibition. The increased concentration of inorganic compounds increases the inhibition; at 250 ppm concentration the inhibition efficiency reached to 95 %, 91.6 %, and 87.5 % for MoO₄²⁻, CrO₄²⁻, and WO₄²⁻, respectively. The adsorption of the inhibitors on the metal surface basically obeys the Langmuir adsorption isotherm equation. Results of EIS measurements suggested that the dissolution of the steel occurs under activation control, and a passive film is probably formed on the metal surface. The electrochemical kinetic parameters calculated from EFM spectra confirm the polarization data.

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1. Introduction

The use of inhibitors is one of the most practical method for protection against corrosion. Inhibitors are often easy to apply and offer the advantage of in-situ application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor: (i) cost of the inhibitor can be sometimes very high when the reagent involved is expensive or when the amount needed is huge, (ii) toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species, (iii) avail-

ability of the inhibitor will determine the selection of it and if the availability is low, the inhibitor becomes often expensive, and (iv) the inhibitor should be environmental friendly. The cost of the inorganic inhibitors is low, but most of them are toxic such as chromate, molybdate, nitrite, arsenate compounds. Molybdate and tungstate salts were reported as corrosion inhibitors since 1939 [1, 2]. Robertson [3] first studied the mechanism of the inhibitive effect of molybdate and tungstate on the corrosion of carbon steel in neutral solution. Pryor and Cohen [4] extended Robertson's work to study the inhibitive mechanism of

molybdate. Because molybdate compounds may be less poisonous or non-poisonous [5], molybdate-based treatment for open recirculating cooling systems has become popular since the early 1980s as an alternative to the toxic and ecologically unacceptable chromate-based inhibitors [6,7]. Obviously, most molybdate-based inhibitors were used in neutral or quasi-neutral media [8, 9] and the effect of inhibition was significant when the concentration of molybdate was very high (thousands of mg/L) [10]. The corrosion inhibition of tungstate was more explored, but most of the studies were in neutral or quasi-neutral solutions, too [11]. The mechanism of inhibitive action of MoO_4^{2-} has received the attention of researchers [9] who take into consideration the interaction of the MoO_4^{2-} anions with the charged metal surface.

The aim of the present work is to investigate the effect of some inorganic anions, as corrosion inhibitors for the steel, namely molybdate, chromate, and tungstate. The experiments were performed in a 3.5 % NaCl and 16 ppm Na_2S solution which simulate sulfide polluted salt water.

2. Experimental

2.1. Material composition of the sample

The steel material used is steel which was provided from a bridge in a Talkha sanitation plant, Egypt. The samples have the following chemical composition (wt %): 0.20% C, 0.005% Si, 0.248% Mn, 1.832% Zn, and the remainder is iron.

2.2. Aggressive solutions

The aggressive solution of 3.5% NaCl and 16 ppm Na_2S was prepared by dissolving the required amount of salts in bidistilled water. All chemicals were analytical-grade reagents. The experiments

were carried out under non-stirred and naturally aerated conditions.

2.3. Inhibitors

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ high-grade reagents were used as inhibitors. The corresponding solutions having 50-250 ppm inhibitor were prepared by dissolving 5-25 mg of each salt in 100 mL of double distilled water.

2.4. Electrochemical measurements

For electrochemical measurements, the steel cylindrical rods were welded with Cu wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active surface of 1 cm^2 geometric area exposed to the test solution. Prior to each experiment, the surface was first abraded with emery paper up 1200 grit size, washed with bi-distilled water, degreased with absolute ethanol and then dried. A conventional electrochemical cell of capacity 100 mL was used; it contains three compartments for working electrode, a platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. The measurements were carried out in 3.5% NaCl with 16 ppm Na_2S solution in the presence of various concentrations of the investigated compounds, as environmentally-friendly corrosion inhibitors. For each run, a freshly prepared solution as well as a cleaned set of electrodes were used. Each run was carried out in aerated stagnant solutions at the required temperature ($25 \pm 1^\circ\text{C}$), using a water thermostat.

The potentiodynamic polarization curves were recorded at a scan rate of 1 mVs^{-1} starting from -1.7 V up to -0.1 V (SCE). Before polarization, the open circuit potential of the working electrode was measured as a function of time during 30

min, the time necessary to reach a quasi-stationary value. Impedance measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open-circuit potential in the frequency range 100 kHz and 0.2 Hz. In electrochemical frequency modulation (EFM) measurements two sine excitation waves (2 and 5 Hz frequencies) were applied to the cell simultaneously; in the intermodulation spectra the current response contained supplementary harmonic components. The causality factors (CF-2 and CF-3) were used to validate the data.

All electrochemical measurements were performed using a potentiostat/galvanostat/ZRA analyzer Gamry PCI300/4 (version 3.20). A personal computer with DC105 software for potentiodynamic polarization, EIS300 software for EIS, and EFM140 software for EFM measurements, respectively, as well as Echem Analyst 5.21 were used for data fitting and calculating.

3. Results and Discussion

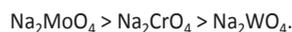
3.1. Potentiodynamic polarization measurements

Figures 1-3 show the potentiodynamic polarization curves of steel in sulfide polluted salt water without and with different concentrations of inorganic anions at 25°C. The obtained electrochemical parameters: cathodic and anodic Tafel slopes (β_c and β_a), corrosion potential (E_{corr}), corrosion current density (i_{corr}) and corrosion rate (C.R.) are listed in Tables 1-3. The degree of surface coverage, θ , and the inhibition efficiency, IE (%), were calculated by equation (1):

$$IE = \theta \times 100 = [1 - (i_{corr(inh)}/i_{corr(free)})] \times 100 \quad (1)$$

where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities by working with uninhibiting and

inhibiting solutions, respectively. Addition of inorganic anions reduces the steel corrosion, meaning that the desorption rate of the inhibitor is lower than its adsorption rate [12]. So, it could be concluded that these anions act as anodic inhibitors ($\beta_c < \beta_a$) for steel in 3.5 % NaCl + Na₂S medium by adsorption on the anodic sites of the steel. This kind of inhibitory action was found in different researches [13, 14]. The obtained results of inhibition efficiency listed in Tables 1-3 show that molybdate, chromate, and tungstate are efficient inhibitors in 3.5 % NaCl + Na₂S medium. Due to the oxidizing power of molybdate, tungstate and chromate, where the latter is the most oxidizing one, they have the ability for oxidizing ferrous ions, even in acid solution [3]. In addition, molybdate, chromate and tungstate form insoluble complex with the oxidized metal ion (Fe²⁺). Qualitative evidence indicates that the effects are closely associated with adsorption of the inhibitor ions at the metal interface and this determines inhibitor efficiency rather than homogeneous chemical properties, such as oxidation ability. The singly charged Cl⁻ ions, having a low sphere of hydration, move into the metal / electrolyte interface displacing the inhibitor ions and, in the case of steel, the formed soluble complex accelerates the corrosion; the effect may be counteracted by raising the inhibitor concentration. The adsorption characteristics depend on the competing factors of ion-dipole interaction in the water phase and the solubility of the complex formed by the metal ions at the surface, as well as the chemical nature of inhibitor ions. The solubility constants for compounds of the type FeWO₄ and FeMoO₄ are unknown, but in general all molybdates and tungstates are classed as insoluble compounds. According to the results, the inhibition efficiency of the studied anions can be arranged in the following order:



Tab. 1: The effect of Na_2MoO_4 concentration on the electrochemical parameters calculated by using potentiodynamic polarization for corrosion of steel in sulfide polluted salt water at 25°C.

Conc., ppm	$-E_{\text{corr}}$ V vs SCE	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_{\text{c}}$ mV dec^{-1}	β_{a} mV dec^{-1}	C.R., mmy^{-1}	θ	IE, %
blank	1.056	11470	265	209	133.19	-----	-----
50	1.126	5699	250	188	66.17	0.503	50.3
100	1.112	3625	238	175	42.09	0.684	68.4
150	1.136	2258	230	155	26.22	0.803	80.3
200	1.125	1170	226	142	13.58	0.898	89.8
250	1.112	574	221	133	6.67	0.950	95.0

Tab. 2: The effect of Na_2CrO_4 concentration on the electrochemical parameters calculated by using potentiodynamic polarization for corrosion of steel in sulfide polluted salt water at 25°C.

Conc., ppm	$-E_{\text{corr}}$ V	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_{\text{c}}$ mV dec^{-1}	β_{a} mV dec^{-1}	C.R., mmy^{-1}	θ	IE, %
blank	1.056	11470	265	209	133.19	-----	-----
50	1.156	6515	259	191	75.65	0.432	43.2
100	1.142	4209	245	186	48.87	0.633	63.3
150	1.166	2455	237	167	28.51	0.786	78.6
200	1.155	1560	225	142	18.11	0.864	86.4
250	1.142	963	218	133	11.18	0.916	91.6

Tab. 3: The effect of Na_2WO_4 concentration on the electrochemical parameters calculated by using potentiodynamic polarization for corrosion of steel in sulfide polluted salt water at 25°C.

Conc., ppm	$-E_{\text{corr}}$ V	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_{\text{c}}$ mV dec^{-1}	β_{a} mV dec^{-1}	C.R., mmy^{-1}	θ	IE, %
blank	1.056	11470	265	209	133.19	-----	-----
50	1.176	6882	260	196	79.85	0.400	40.0
100	1.162	4817	252	189	55.93	0.580	58.0
150	1.186	2789	239	175	32.38	0.756	75.6
200	1.175	2133	221	156	24.76	0.814	81.4
250	1.162	1434	220	138	16.65	0.875	87.5

3.2. Adsorption isotherms

The extent of corrosion inhibition depends on the surface conditions and the mode of adsorption of the inhibitors [15]. One may made the assumption that the corrosion of the covered parts of the surface is equal to zero and that corrosion takes place only on the uncovered parts of the surface.

Lorenz and Mansfeld [16] classified the modes of inhibition effect of corrosion inhibitors into three categories: (i) the geometric blocking effect of adsorbed inhibitive species on the metal surface, (ii) the effect of blocking the active sites on the metal surface by adsorbed inhibitive species, and (iii) the electrocatalytic effect of either the inhibitor or its reaction products. Adsorption iso-

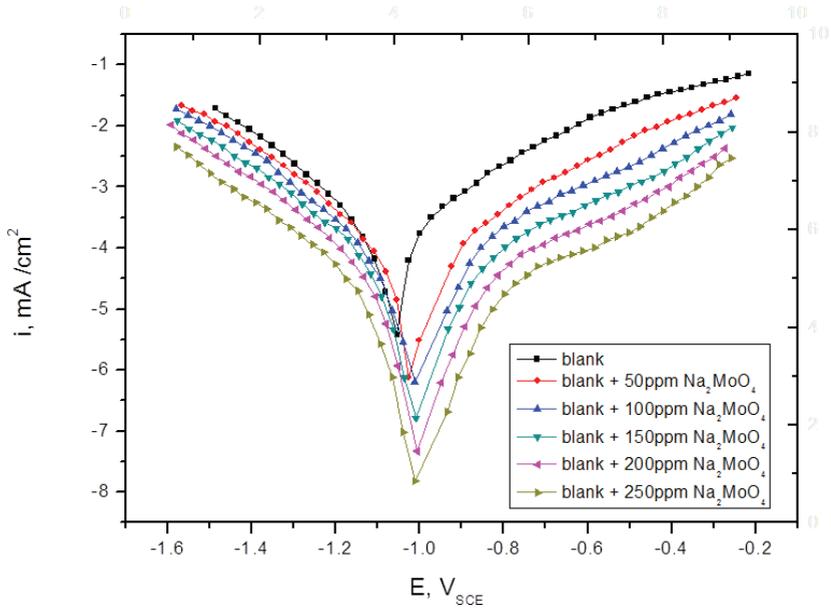


Fig. 1: Potentiodynamic polarization curves for the corrosion of steel in sulfide polluted salt water in the absence and presence of different concentrations of Na₂MoO₄ at 25°C

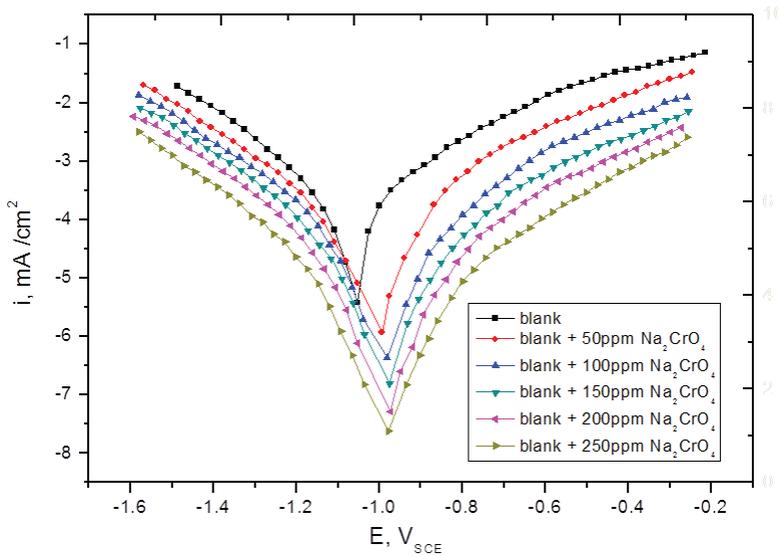


Fig. 2: Potentiodynamic polarization curves for the corrosion of steel in sulfide polluted salt water in the absence and presence of different concentrations of Na₂CrO₄ at 25°C

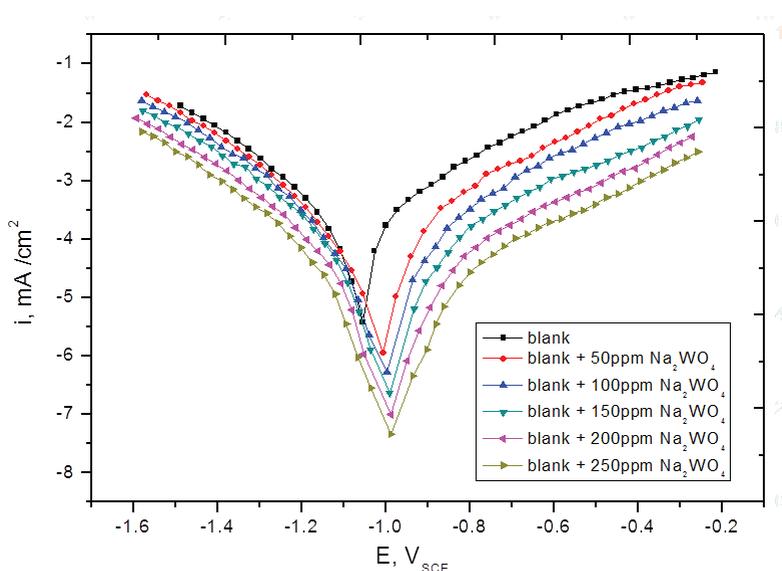


Fig. 3: Potentiodynamic polarization curves for the corrosion of steel in sulfide polluted salt water in the absence and presence of different concentrations of Na_2WO_4 at 25°C

therms give information about the interaction of inhibitor anions with steel. In this part of the study, the obtained values of surface coverage θ (see Tables 1-3) were fitted to different adsorption isotherms including Langmuir, Temkin, Frumkin, Flory-Huggins, Freundlich and Henry isotherm. The best fit was obtained by Langmuir isotherm.

The plotting of C/θ against C is given in Figure 4, where straight-line relationships with regression coefficient higher than 0.99 suggest that the adsorption on steel of these studied anions follows perfectly the Langmuir adsorption isotherm:

$$C/\theta = 1/K_{\text{ads}} + C \quad (2)$$

C is the concentration of inhibitor and K_{ads} is the adsorption equilibrium constant related to the

standard free energy of adsorption, $\Delta G_{\text{ads}}^\circ$, as following [17]:

$$K_{\text{ads}} = 1/55.5 \exp(-\Delta G_{\text{ads}}^\circ / RT) \quad (3)$$

The Langmuir isotherm postulates a monolayer adsorption, hence no interaction between the adsorbate species and the metal surface, and in such circumstances the slope of straight lines should be unity. The deviation of the slope from unity as observed in this study could be interpreted as existence of the interactions between adsorbate species and the metal surface, as well as changes in adsorption heat with increasing surface coverage [18], factors that were ignored in the derivation of Langmuir isotherm.

Values of the equilibrium constant (K_{ads}) were obtained for the studied anions, Table 4. The results confirm that the adsorption capability of

the investigated anions depends on the formation of insoluble complex of these anions precipitated on the metal surface in forms of FeMoO_4 , FeCrO_4 or FeWO_4 . The increasing in K_{ads} value reflects the increasing adsorption ability.

The standard free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ for each inhibitor was calculated and values were also listed in Table 4. The relatively high negative free energy values may indicate a relatively strong and spontaneous adsorption on the metal surface of the investigated compounds, which explains their high corrosion inhibition efficiency. A value of -40 kJ mol^{-1} is usually adopted as a threshold value between chemical and physical adsorption [19]. The calculated values of $\Delta G^{\circ}_{\text{ads}}$ for the investigated compounds are between -27.9 and $-29.5 \text{ kJ mol}^{-1}$, which means that the adsorption of these inhibi-

tors is physically, through electrostatic interaction between these anions and the metal surface. It is also observed that the calculated values of K_{ads} and $\Delta G^{\circ}_{\text{ads}}$ may be arranged in the following order: $\text{Na}_2\text{MoO}_4 > \text{Na}_2\text{CrO}_4 > \text{Na}_2\text{WO}_4$. This is in good agreement with the order of %IE of these anions.

Tab. 4: Values of inhibitor adsorption constant (K_{ads}), intercept of straightline, regression constant and standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) for the inorganic inhibitors of steel corrosion in 3.5% NaCl + 16 ppm Na_2S aqueous solution

Inhibitor	Parameters from Langmuir isotherm			
	$K_{\text{ads}} \times 10^{-2}$ M^{-1}	The intercept $\times 10^4, \text{M}$	R^2	$-\Delta G^{\circ}_{\text{ads}}$, kJ mol^{-1}
Na_2MoO_4	32.67	3.06	0.998	29.5
Na_2CrO_4	20.92	4.78	0.996	28.4
Na_2WO_4	16.77	5.96	0.993	27.9

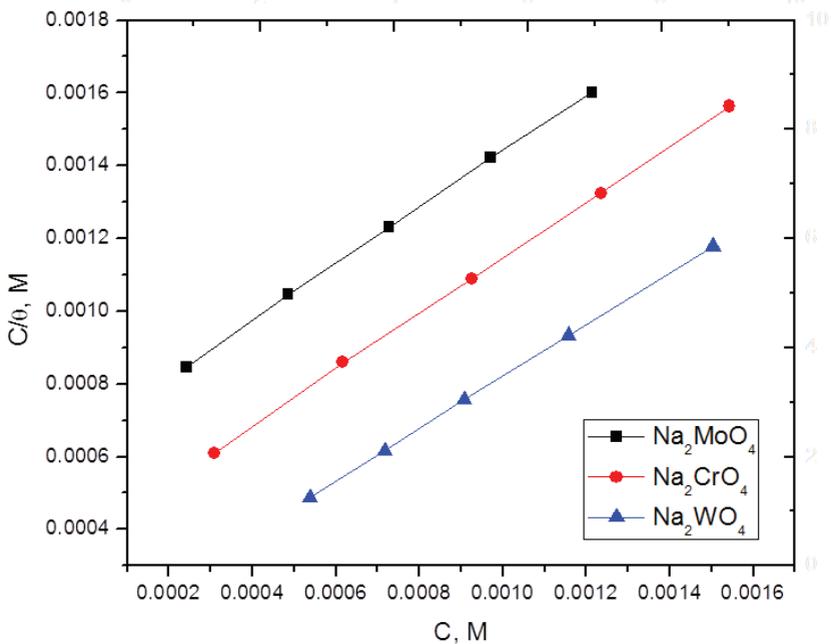


Fig. 4: Langmuir adsorption isotherm, plotted as C/θ vs. C , of Na_2MoO_4 , Na_2CrO_4 and Na_2WO_4 for the corrosion of steel in sulfide polluted salt water

3.3. Electrochemical Impedance Spectroscopy (EIS)

The corrosion inhibition processes were also investigated by EIS method at 25°C. Figures 5-7 show the Nyquist plots for corrosion of steel in solution with 3.5% NaCl and 16 ppm Na₂S in the absence and presence of different concentrations of investigated compounds. All the impedance spectra were measured at the corresponding open-circuit potentials. It is apparent that Nyquist plots show a single capacitive loop, in both uninhibiting and inhibiting solutions. The data with inhibitor describe a semicircle suggesting that the corrosion process is under charge-transfer control. The depressed semicircle is associated with the roughness of electrode surface and indicates a better quality of the inhibitor anion-containing film. It is obvious that causal relationship exists between adsorption and inhibition. According to Ramachandran [20], the film formed in the presence of inorganic inhibitors acts as a protective barrier against aggressive ions from the bulk solution. Thus, the corrosion processes in the presence of investigated inhibitors may be also considered under diffusion and charge transfer mixed mechanism.

The EIS data were simulated using equivalent electric circuits as shown in Figure 8, where R_s represents the solution (electrolyte) ohmic resistance, C_{dl} - the double layer capacitance and R_{ct} - the charge transfer resistance (polarization resistance).

The capacity of double layer C_{dl} can be calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (4)$$

where f_{max} is the frequency at which the imaginary component of the impedance is maximal.

The parameters obtained from impedance measurements with each inhibitor are given in Tables 5-7. It can be seen from these Tables that the values of charge transfer resistance increase with inhibitor concentration [21]. In the case of impedance studies, IE (calculated using R_{ct} values) increases with inhibitor concentration, too. Thus, the impedance study confirms the inhibiting character of inorganic anions illustrated above using potentiodynamic polarization method. It is also noted that the C_{dl} values tend to decrease when the concentration of these anions increases. This decrease in C_{dl} , which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the molecules of inhibitor have an inhibiting function by adsorption at the metal/solution interface [22].

The increase of R_{ct} values and the decrease of C_{dl} values with inhibitor concentrations may be due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, thus decreasing the extent of corrosion process. It can be seen that the inhibition efficiency obtained by EIS method for the investigated anions is in the order:



Tab. 5: Electrochemical kinetic parameters obtained by EIS technique for the corrosion of steel using Na₂MoO₄ as inhibitor in sulfide polluted salt water at 25°C

Conc., ppm	R_s Ω cm ²	C_{dl} μFcm ⁻²	n	R_{ct} Ω cm ²	θ	IE, %
blank	1.3	606	0.89	150	----	----
50	1.2	486	0.85	310	0.531	53.1
100	1.2	410	0.87	480	0.693	69.3
150	1.1	338	0.87	785	0.801	80.1
200	1.1	333	0.84	1546	0.898	89.8
250	1.1	319	0.86	3571	0.948	94.8

3.4. Electrochemical Frequency Modulation (EFM)

EFM is a non-destructive corrosion measurement technique that can directly give values of corrosion current without prior knowledge of Tafel constants [23]. The intermodulation spectra obtained from EFM measurements are presented in Figures 9-11 as confirmation of steel corrosion in 3.5% NaCl + 16 ppm Na₂S solution containing different concentrations of Na₂MoO₄,

Na₂CrO₄, and Na₂WO₄ at 25 °C. Each spectrum is a current response as a function of frequency. The two large peaks are the response to the 2 Hz and 5 Hz excitation frequencies. The calculated corrosion kinetic parameters (i_{corr} , β_a , β_c , CF-2 and CF-3) for 3.5% NaCl + 16 ppm Na₂S blank solution and with different concentrations of the investigated inhibitors at 25°C are given in Tables 8-10. From these Tables it is obvious that the corrosion current densities decrease by increasing the con-

Tab. 6: Electrochemical kinetic parameters obtained by EIS technique for the corrosion of steel using Na₂CrO₄ as inhibitor in sulfide polluted salt water at 25°C

Conc., ppm	R _s Ω cm ²	C _{dl} μFcm ⁻²	n	R _{ct} Ω cm ²	θ	IE, %
blank	1.3	605.5	0.89	150	----	----
50	1.1	445.2	0.88	269	0.443	44.3
100	1.2	443.7	0.85	426	0.648	64.8
150	1.1	338.6	0.86	714	0.790	79.0
200	1.2	331.5	0.85	1181	0.873	87.3
250	1.1	321.7	0.84	1898	0.921	92.1

Tab. 7: Electrochemical kinetic parameters obtained by EIS technique for the corrosion of steel using Na₂WO₄ as inhibitor in sulfide polluted salt water at 25°C

Conc., ppm	R _s Ω cm ²	C _{dl} μFcm ⁻²	n	R _{ct} Ω cm ²	θ	IE, %
blank	1.3	605.5	0.89	150	----	----
50	1.1	447.6	0.85	255	0.411	41.1
100	1.1	442.2	0.86	370	0.593	59.3
150	1.1	335.6	0.8	630	0.762	76.2
200	1.2	331.8	0.85	862	0.826	82.6
250	1.1	328.7	0.82	1282	0.883	88.3

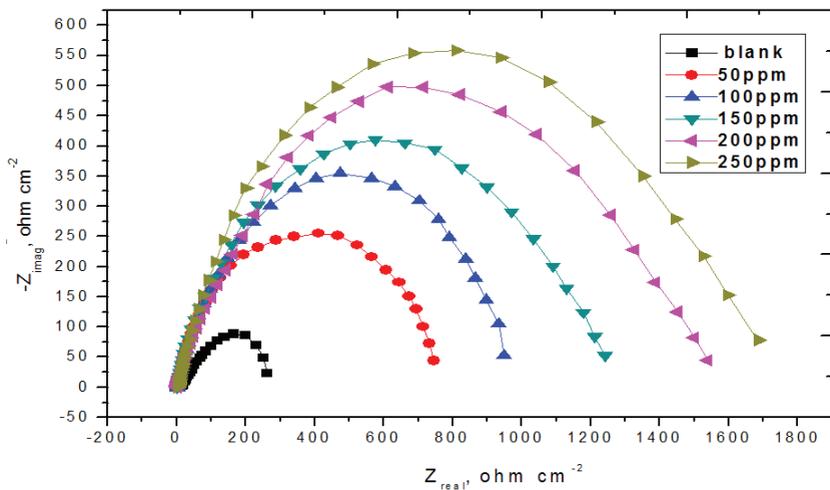


Fig. 5: Nyquist plots recorded for steel in 3.5% NaCl + 16 ppm Na₂S (blank) with and without various concentrations of Na₂MoO₄ at 25°C

centration of the anions and hence the inhibition efficiency increases. Also it is clear that the causality factors are very close to theoretical values (2 or 3, respectively), which according to EFM

theory should guarantee the validity of Tafel slope and corrosion current densities. In addition, the values of causality factors indicate that the measured data are of good quality [23]. The obtained

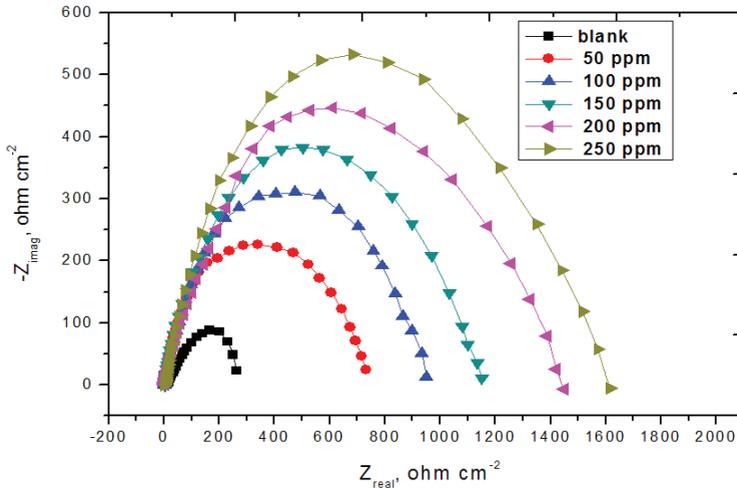


Fig. 6: Nyquist plots recorded for steel in 3.5% NaCl + 16 ppm Na_2S (blank) with and without various concentrations of Na_2CrO_4 at 25°C

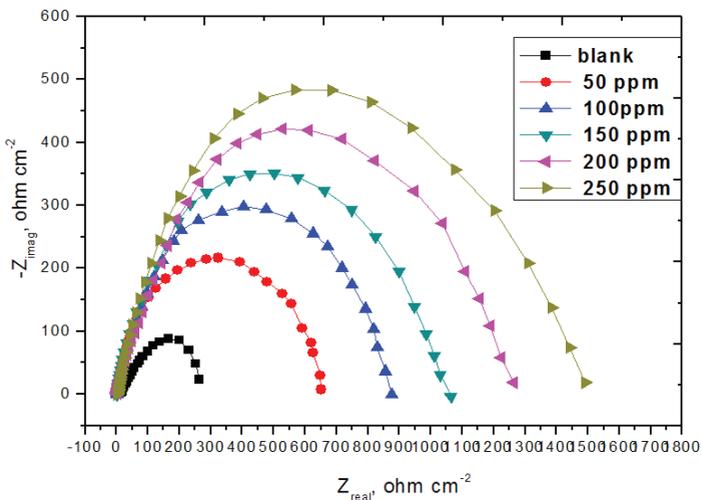


Fig. 7: Nyquist plots recorded for steel in 3.5% NaCl + 16 ppm Na_2S (blank) with and without various concentrations of Na_2WO_4 at 25°C

results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and EFM methods. The inhibition efficiency obtained by inorganic compounds may be certainly arranged in the order:

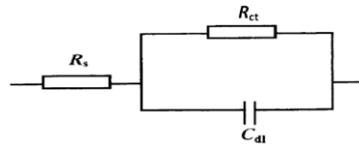
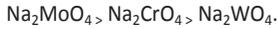


Fig. 8: Electrical equivalent circuit used to fit the impedance spectra

Tab. 8: Electrochemical kinetic parameters obtained by EFM technique for steel corrosion in 3.5% NaCl+16 ppm Na_2S blank solution and with different concentrations of Na_2MoO_4 at 25° C

Conc., ppm	i_{corr} $\mu\text{A cm}^{-2}$	β_{a} mV dec^{-1}	β_{c} mV dec^{-1}	CF-2	CF-3	C.R, mm y^{-1}	θ	IE, %
blank	13540	278	241	1.85	2.85	140.31	-----	-----
50	6486	261	233	1.79	2.98	67.21	0.521	52.1
100	4062	254	228	1.92	3.10	42.10	0.700	70.0
150	2437	250	223	1.82	2.90	25.25	0.820	82.0
200	1286	244	220	1.91	2.91	13.33	0.905	90.5
250	433	384	215	1.95	2.95	4.50	0.968	96.8

Tab. 9: Electrochemical kinetic parameters obtained by EFM technique for steel corrosion in 3.5% NaCl+16 ppm Na_2S blank solution and with different concentrations of Na_2CrO_4 at 25° C

Conc., ppm	i_{corr} $\mu\text{A cm}^{-2}$	β_{a} mV dec^{-1}	β_{c} mV dec^{-1}	CF-2	CF-3	C.R, mm y^{-1}	θ	IE, %
blank	13540	278	241	1.85	2.85	140.31	-----	-----
50	6880	268	238	1.67	2.95	71.29	0.492	49.2
100	4834	258	231	1.90	2.99	50.10	0.643	64.3
150	2667	250	229	1.79	2.87	27.63	0.803	80.3
200	1611	249	221	1.88	2.89	16.70	0.881	88.1
250	975	240	219	1.93	2.94	10.10	0.928	92.8

Tab. 10: Electrochemical kinetic parameters obtained by EFM technique for steel corrosion in 3.5%NaCl+16ppm Na_2S blank solution and with different concentrations of Na_2WO_4 at 25° C

Conc ppm	i_{corr} $\mu\text{A cm}^{-2}$	β_{a} mV dec^{-1}	β_{c} mV dec^{-1}	CF-2	CF-3	C.R, mm y^{-1}	θ	IE, %
blank	13540	278	241	1.85	2.85	140.31	0.420	-----
50	268.31	239	239	1.63	2.90	81.37	0.600	42.0
100	265.42	235	235	1.87	2.93	56.12	0.780	60.0
150	260.32	228	228	1.76	2.81	30.87	0.850	78.0
200	258.51	220	220	1.84	2.83	21.0	0.890	85.0
250	251.72	220	220	1.89	2.90	15.43	0.420	89.0

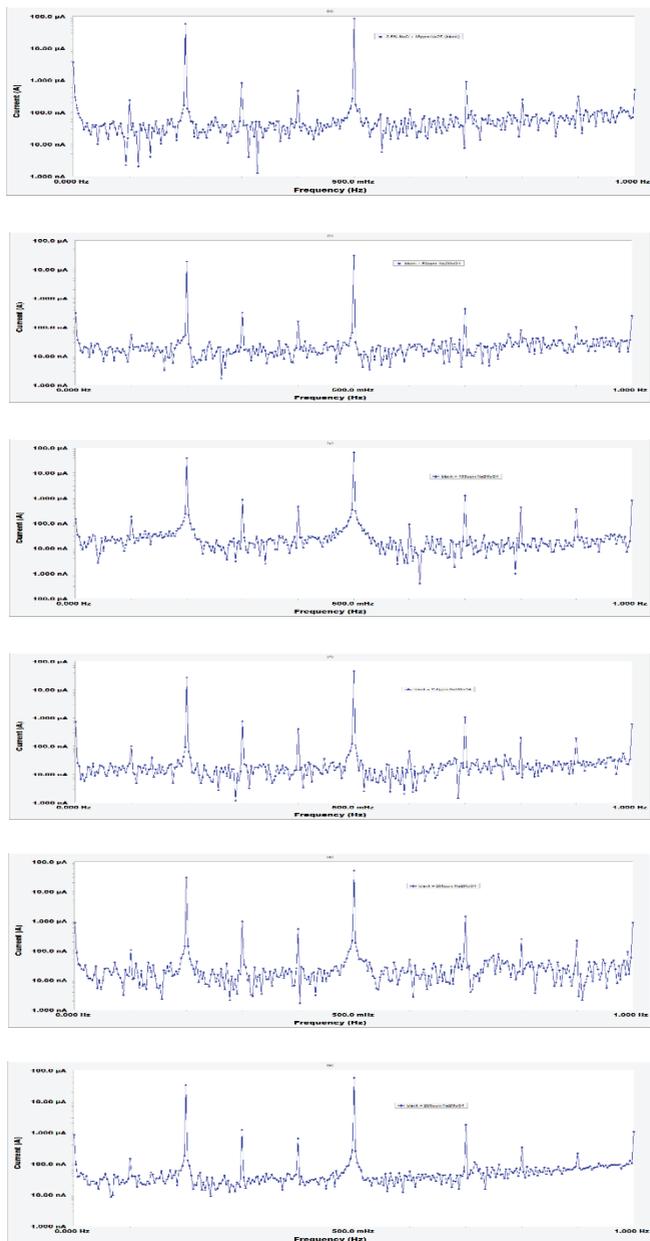


Fig. 9(a-f): Intermodulation spectra for steel corrosion in 3.5 %NaCl + 16 ppm Na_2S without and with various concentrations of Na_2MoO_4 at 25°C

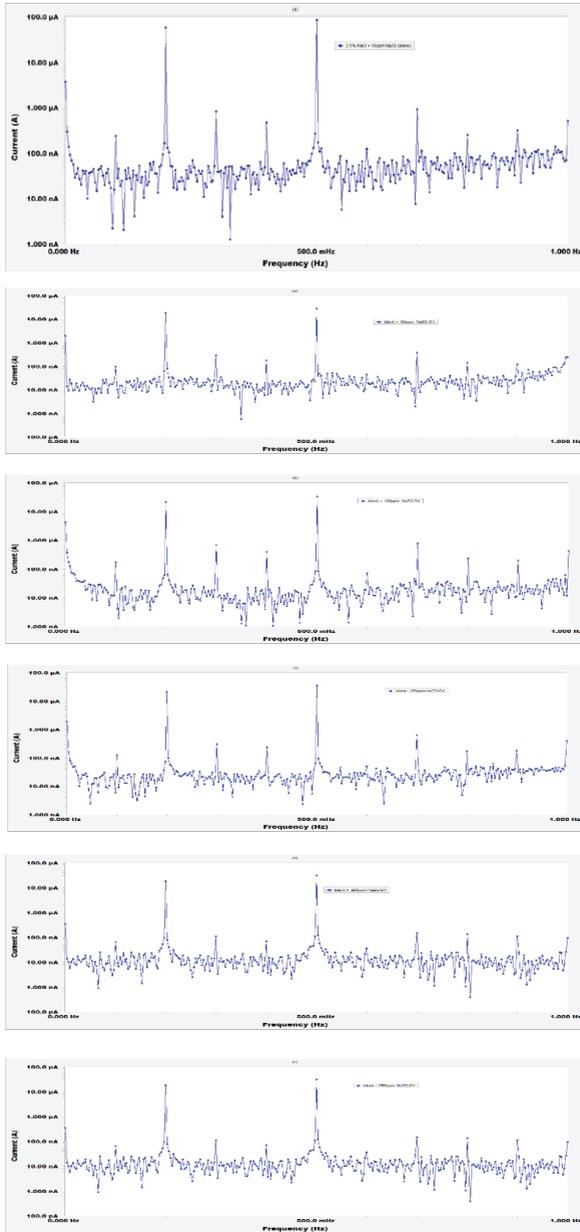


Fig. 10(a-f): Intermodulation spectra for steel corrosion in 3.5 % NaCl + 16 ppm Na_2S without and with various concentrations of Na_2CrO_4 at 25°C

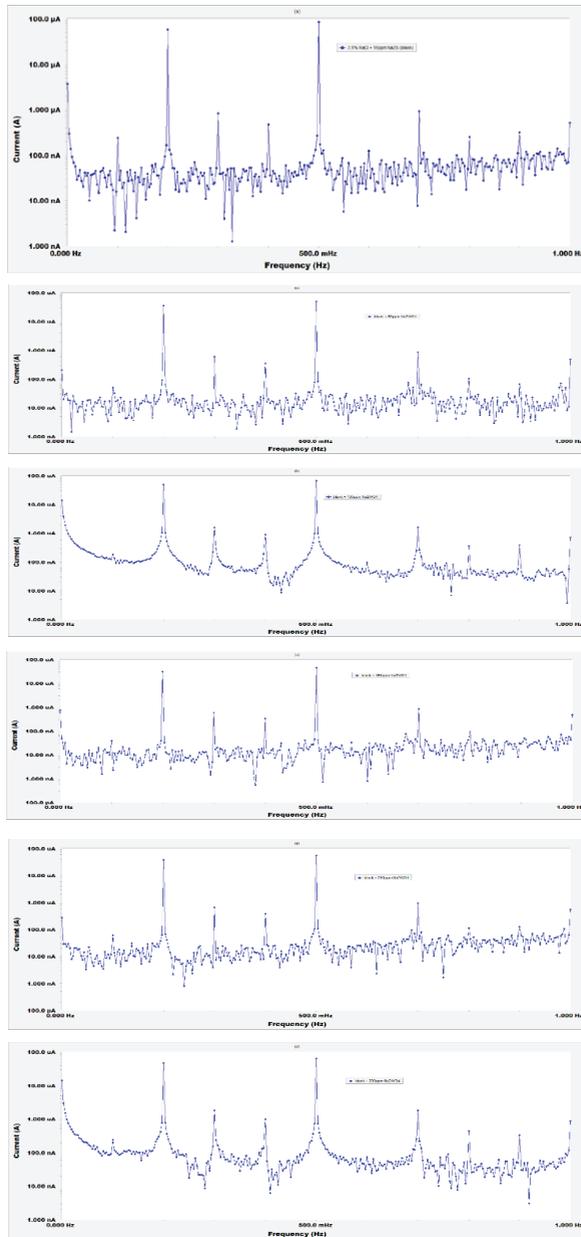


Fig. 11(a-f): Intermodulation spectra for steel corrosion in 3.5 % NaCl + 16 ppm Na_2S without and with various concentrations of Na_2WO_4 at 25°C

4. Conclusions

Sodium molybdate, chromate, and tungstate are good inorganic inhibitors to prevent steel corrosion in sulfide polluted salt water and may be used in sanitation plants.

Within 50-250 ppm concentration range of inhibitor the inhibition efficiency increases with anion concentration reaching maximal values of 95, 91.6 and 87.5 % for MoO_4^{2-} , CrO_4^{2-} , and WO_4^{2-} , respectively, determined from potentiodynamic polarization curves. The inhibition is due to the adsorption of the inhibitor species and possible

formation of complex molecules between Fe^{2+} and these anions. The adsorption on the metal surface obeys Langmuir adsorption isotherm.

Nyquist plots recorded as impedance spectra at open-circuit potential showed a single capacitive loop, in both uninhibiting and inhibiting solutions. The charge-transfer resistance increases and double layer capacitance decreases with respect to the blank solution when each inhibitor is added. Inhibition efficiencies obtained with EIS and EFM techniques are in good agreement with values obtained from polarization curves measurements.

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