

Kalanchoe Blossfeldina Extract as a Green Corrosion Inhibitor for Carbon Steel in Na₂S-polluted NaCl Solutions

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The potential of Kalanchoe blossfeldina extract (KBE) as a corrosion inhibitor of carbon steel (CS) in polluted NaCl solution (3.5% NaCl + 16 ppm Na₂S) was determined utilizing AC impedance (EIS), potentiodynamic polarization (PP) and mass loss (ML) methods. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX), and atomic force microscope (AFM) analyses were used to examine the CS surface. The adsorption of this extract follows Temkin isotherm. Maximum protection was achieved 92.6% at 300 ppm concentration. PP studies discovered that KBE behaved as a mixed-kind inhibitor in polluted NaCl solution. The inhibition efficiency (IE) of KBE obtained from the ML and electrochemical tests were in excellent agreement.

Keywords: Corrosion inhibition, Kalanchoe blossfeldina extract, HCl, PP, EIS

1. INTRODUCTION

Corrosion is a natural process commonly defined as the dissolution of a metal with its environment. Corrosion can affect dangerous and costly damage to petrochemical industries and public buildings etc. The cost of corrosion is very costly with 4 % of the Gross Domestic Product of industrial nations [1-2]. Corrosion can cause loss of steel equipment dominant in industrial applications; much of this loss is due to the contact with acid solutions. The corrosion inhibitor is one of the methods used to delay dissolution effects on the metallic surface. However, it is gradually keen to use the substances that may damage the environment. Most of the ecological inhibitors are biodegradable, non-toxic, readily available, and considerably in sufficiently developed over the past two decades [3-4]. Those advantages have encouraged many scientists to examine natural substances as corrosion inhibitors such as Aquilaria Crassna Leaves Extracts [5], Chenopodium Ambrosioides Extracts [6], Zingiber Officinal Roscoe Extract [7], Psidium Guajava Leaf Extract [8], oils [8-10], pure plant compounds [11,12], Chenopodium

Extract [13], Methanol Extract of Nerium Oleander [14], Ambrosia Maritima Extract [15] and Aqueous Valerian Extract [16]. The use of inhibitors with aims to protect steel from corrosion in acid solutions is required. It has been reported in many previous studies that that inhibitors containing organic compounds bearing heteroatom with high electron density like O, N and S atoms and these donate greatly to the protection of corrosion via altered mechanisms [17]. ML and electrochemical tests such as PP and EIS have studied the inhibitory action of KBE as eco-friendly and naturally happening substance on dissolution behavior of CS.

2. EXPERIMENTAL

2.1 Materials and solutions

Chemical conformation of the CS in weight % is as follows: C 0.15-0.20, Mn 0.35-0.60, P 0.016-0.024, Si 0.003-0.098, Cr 0.018-0.026, Co 0.145-0.245 and Fe balance. The aggressive solution of polluted NaCl was prepared by dissolution of appropriate weights of NaCl and Na₂S (3.5% NaCl & 16 ppm Na₂S) by bi-distilled water. The experimental measurements had achieved in the presence and absence of various concentrations of KBE.

2.2 Preparation of the extract (inhibitor)

The present investigation was carried out using the plant, namely Kalanchoe blossfeldina. The samples were picked from the Kalanchoe blossfeldina plant and ground into a fine powder to give 500 g of powdered materials, a known quantity of the materials was soxhlted using a bidistilled water. Finally the extract was dried out, weighed and preserved at 4°C and kept for the use when required.

2.3 Methods utilized for corrosion tests

2.3.1 Mass loss (ML) tests

Square coins of size 2 cm x 2cm x 0.2cm were used for ML measurements which were firstly polished to a mirror finish utilizing different grades (320–1200 grade) of emery papers, washed with bi-distilled water and dried by soft paper and weighed, then dipped in to the NaCl (3.5% NaCl + 16 ppm Na₂S) solution. The ML have obtained in polluted NaCl. IE and the (θ) of the KBE on corrosion of CS measured from Eq. (1) [18]:

$$\%IE = \theta \times 100 = [1 - (W/W^0)] \times 100 \quad (1)$$

2.3.2 PP measurements

Polarization measurements were achieved utilizing electrochemical cell with three electrodes (working, CS 1cm², counter, Pt foil, and reference, saturated calomel electrode) linked to Gamry

Instrument Potentiostat /Galvanostat with system based on ESA300. The scanned potential from -0.2 to -1.2 V with scan rate 1 mV/s. i_{corr} was utilized for the computation of IE and (θ) as next:

$$\%IE = \theta \times 100 = [1 - (i_{\text{corr}}/i_{\text{corr}}^0)] \quad (2)$$

2.3.3 EIS measurements

EIS measurements were done in The frequency range is between 100 kHz and 0.1 Hz and AC signal is 10 mV peak to peak. All impedance data fitted to appropriate circuit equivalent utilizing the Echem Analyst software.

2.3.4 SEM analysis

In order to perform surface investigations, the CS were exposed to the polluted NaCl solutions for 48 h at 25°C. The investigation of surface structure of the pure CS and exposed to polluted solution without and with the without of 600 ppm of the KBE were done utilizing SEM (Scanning Electron Microscope: JOEL 840, Japan) and using (Atomic Force Microscope: AFM device model is a Pico SPM2100) [19, 20].

3. RESULTS AND DISCUSSION

3.1 ML tests

Mass loss of CS was determined at different time intervals, with and without various concentrations of the extract (KBE) (Fig.1). Mass loss and corrosion rate (k_{corr}) lowered as the concentrations of the KBE rise and hence the %IE increases (Table 1)

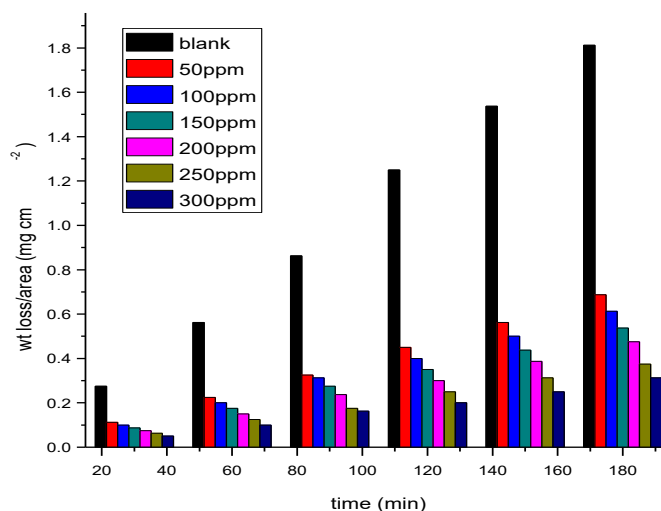


Figure 1. ML-time diagram for CS in polluted NaCl with and without various concentrations of KBE at 30°C

Table 1. % IE and θ of KBE for the corrosion of CS in polluted NaCl at different concentrations of KBE at 30°C

[inh] ppm	k_{corr} ($\text{mg cm}^{-2} \text{min}^{-1}$) $\times 10^3$	Θ	% IE
Blank	10.4	----	----
50	3.78	0.640	64.0
100	3.34	0.680	68.0
150	2.93	0.720	72.0
200	2.51	0.760	76.0
250	2.09	0.800	80.0
300	1.68	0.840	84.0

3.2 Effect of Temperature

Table 2 shows variation of IE and rate of corrosion (k_{corr}) of KBE with different temperatures (303-323K) with various concentrations of KBE for CS corrosion in polluted NaCl. By raising the temperature, k_{corr} improved and the % IE of the KBE lowered. This confirms that the extract is adsorbed physically on CS surface. Also, it confirmed that this extract acts as inhibitor at lower temperatures.

Table 2: %IE and k_{corr} of KBE for the corrosion of CS in polluted NaCl at different concentrations and at temperature range of 303-323 K

[Inh],ppm	303		308K		313K		318K		323K	
	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE
50	3.75	64.0	4.58	60.3	5.83	55.2	7.08	52.1	8.33	51.5
100	3.33	68.0	4.16	63.9	5.41	58.4	6.7	54.9	7.92	53.9
150	2.92	72.0	3.75	67.5	5.0	61.6	6.2	57.7	7.6	56.3
200	2.50	76.0	3.33	71.1	4.58	64.8	5.83	60.5	7.1	58.7
250	2.08	80.0	2.91	74.7	4.3	67.2	5.42	63.3	6.8	61.2
300	1.66	84.0	2.6	78.3	3.6	71.2	5.12	66.1	6.3	63.6

3.3 Adsorption Isotherms

Figure 2 represents the Temkin isotherm, which used to calculate Θ values for KBE. The Temkin equation represented as next [21].

$$\Theta_{\text{coverage}} = (2.303/a) \text{Log } K_{\text{ads}} + (2.303/a) \text{Log } C \quad (3)$$

Where K_{ads} is the adsorption constant, C is the KBE content (M) and “a” (Heterogeneous factor of surface of the metal).

The ΔG°_{ads} and K_{ads} data are recorded in Table 3. The ΔG°_{ads} founded by:

$$\Delta G^{\circ}_{ads} = - RT \ln (55.5 K_{ads}) \tag{4}$$

The KBE adsorption is spontaneous and this is proven by the ΔG°_{ads} negative sign. Generally, physical adsorption leads to ΔG°_{ads} is around -20 kJ mol^{-1} or lesser; those around -40 kJ mol^{-1} or upper includes chemisorption [22]. From the obtained data of ΔG°_{ads} in Table 3, it was found that KBE is adsorbed physically and chemically on CS surface.

Vant't Hoff equation can be used to measure ΔH°_{ads} and ΔS°_{ads} expressed by:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T \Delta S^{\circ}_{ads} \tag{5}$$

Figure 4 shows the relation between ΔG°_{ads} and T . A negative sign of ΔS°_{ads} proved that the disorder of corrosion process is decreases by using KBE and the ΔH°_{ads} is in 36.3 kJ mol^{-1} which designates that the KBE adsorption in polluted NaCl might be due to physical (Table 4) [23].

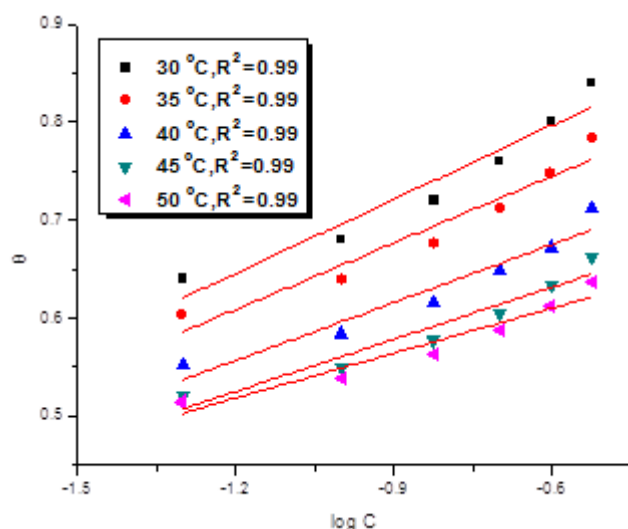


Figure 2. Temkin isotherm for the KBE of CS in polluted NaCl from ML test

Table 3. Thermodynamic parameters for the KBE adsorbed of on CS surface

Temperature, K	$K_{ads} \times 10^{-3}, M^{-1}$	$\Delta G^{\circ}_{ads}, \text{ kJ mol}^{-1}$
308	58.1	31.4
313	76.3	32.1
318	105.7	32.9
323	146.6	33.7
328	393.8	36.2

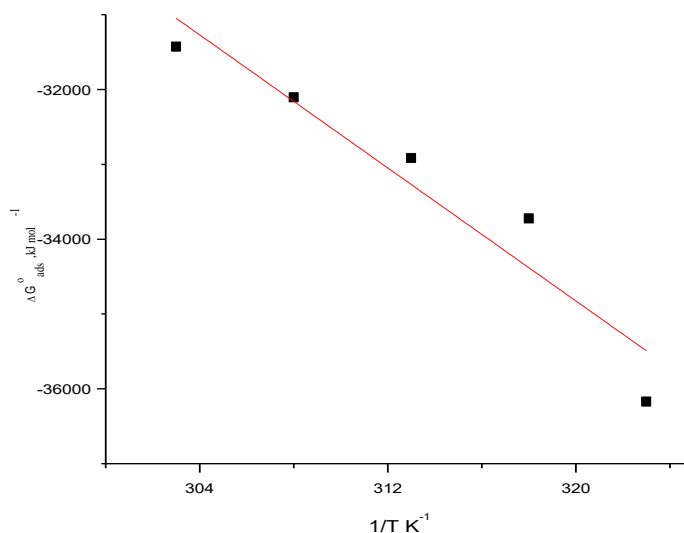


Figure 3. ΔG°_{ads} was plotted against $1/T$ (K^{-1}) for KBE

Table 4. Temkin data for CS without and using changed KBE contents at 303-323 K

Temperature, K	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹	ΔH°_{ads} , kJ mol ⁻¹	ΔS°_{ads} , J mol ⁻¹ K ⁻¹
303	31.42	36.3	69.8
308	32.11		71.3
313	32.91		73.1
318	33.72		74.9
323	36.17		80.3

3.4 Kinetic –Thermodynamic Corrosion Parameters

The equation of Arrhenius (6) can be used to measure the activation energy (E^*_a) of the activated complex [24]:

$$k_{corr} = A \exp (-E^*_a / RT) \tag{6}$$

where E^*_a is activation energy and T is the absolute temperature. Using Figure 4, E^*_a can be measured (Table 5). Inspection of the data show that the E^*_a is lower in the presence of the KBE than in its absence. The moderate rate of KBE adsorption with a resultant is closer approach to equilibrium during the experiments at higher temperatures [25].

$(\Delta H^*, \Delta S^*)$ are measured by eq. (7) [26-28]:

$$k_{corr} = RT/Nh \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \tag{7}$$

Figure 5 shows the relation between $\log (k_{corr} / T)$ and $(1/T)$ which used to measure the values of ΔH^* and ΔS^* (Table 5). In the chemisorption process, enthalpy must be or more than 100 kJ mol⁻¹[29].

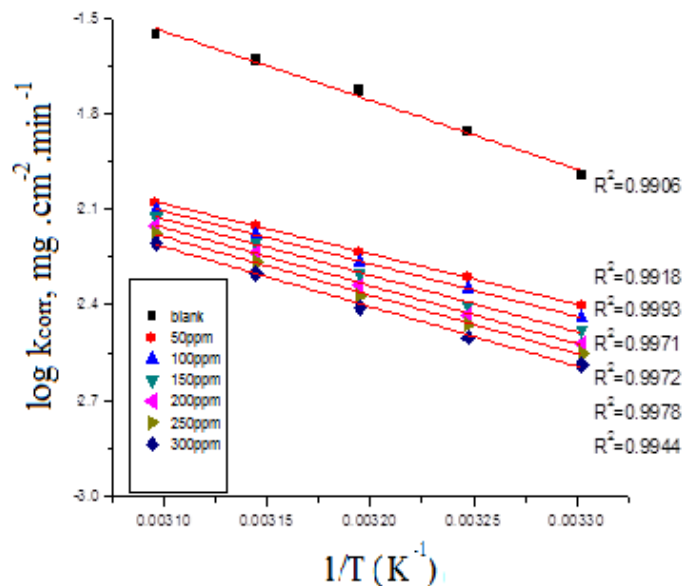


Figure 4. Log k_{corr} vs reciprocal of temperature plot for CS at various concentration of KBE

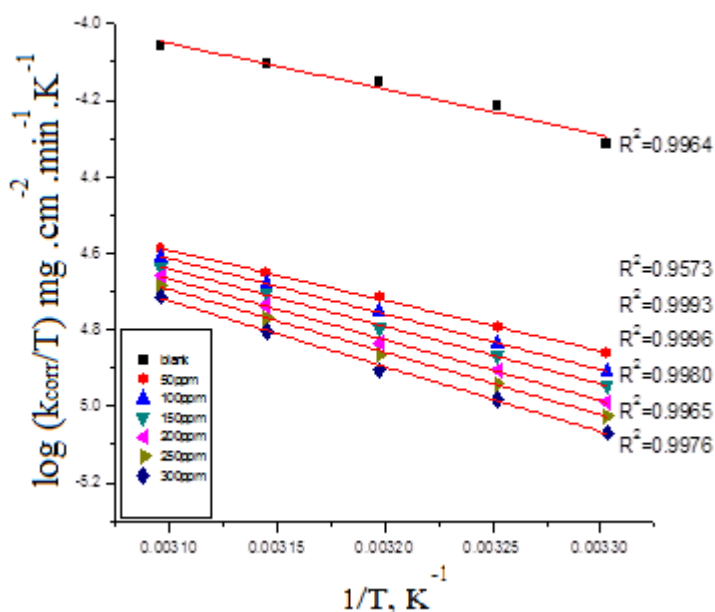


Figure 5. The relation between $\log (k_{corr} / T)$ and $1/ T$ diagrams for the CS without and with several KBE concentrations

Table 5. Data of activation for CS without and with range of KBE concentrations

[inh] ppm	E_a^* , kJ mol^{-1}	ΔH^* , kJ mol^{-1}	$-\Delta S^*$, $\text{J mol}^{-1}\text{K}^{-1}$
Blank	54.4	108.8	197.14
50	48.0	148.9	197.14
100	43.0	158.3	197.04
150	39.1	169.5	196.99
200	35.8	183.0	196.92
250	33.1	200.0	197.13
300	22.9	221.5	170.34

The rise in the (ΔH^*) with the occurrence of the KBE reflects the rise in the energy barrier of the corrosion process. The negative values of ΔS^* show that during the rate-determining step in the formation of activated complex is highly associated than the dissociated [30].

3.5 Potentiodynamic Polarization (PP) Measurements

Figure 6 displays the PP performance of CS in polluted NaCl with and without different concentrations of KBE. The outcome parameters such as (i_{corr}), (E_{corr}), (β_c), (β_a), (θ) and (% IE) were measure from the bends of (Figure 6) and are record in (Table 6).

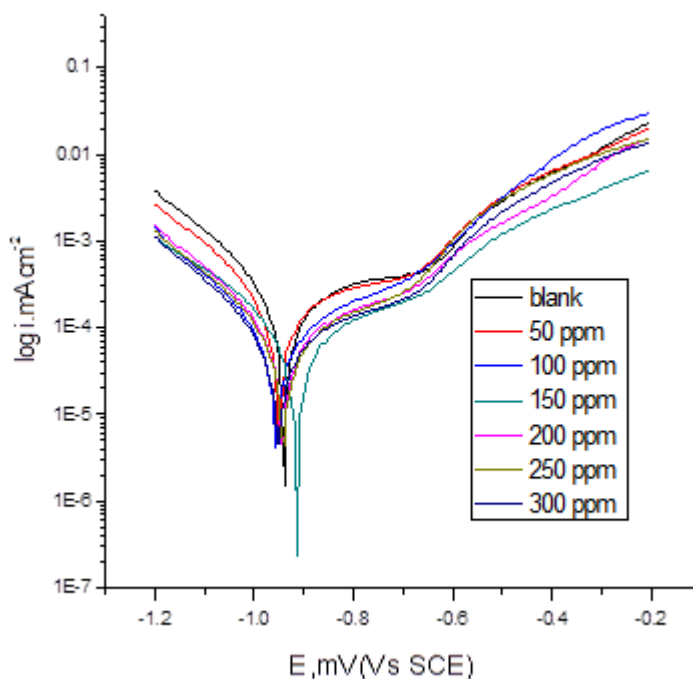


Figure 6. PP curves for the dissolution of CS in polluted NaCl without and with different concentrations of KBE at 30°C

Table 7. PP data of CS in polluted NaCl at 30°C for KBE

Conc., ppm	- E_{corr} , mV vs SCE	i_{corr} $\mu A cm^{-2}$	β_a mVdec ⁻¹	β_c mVdec ⁻¹	k_{corr} mpy	θ	% IE
Blank	867	256.9	127	188	121.5	--	--
50	643	87.92	129	139	40.18	0.657	65.7
100	835	70.36	97	181	32.15	0.726	72.60
150	882	65.75	97	196	30.04	0.744	74.4
200	880	57.44	96	153	26.25	0.774	77.4
250	875	43.47	71	74	19.86	0.830	83.0
300	849	33.88	76	107	15.48	0.868	86.8

Table 6 displayed that both the anodic and cathodic responses are influenced by the KBE inhibitor presence and the rise in the protection efficiency as the KBE dose improve. The slight change in the values of E_{corr} and the slight changes in Tafel slopes with addition of the extract show that KBE act as mixed-kind inhibitors. i_{corr} decreases clearly after the addition of KBE in polluted NaCl and % IE improve with increase the KBE dose. The parallel Tafel lines indicate that there is no change in the mechanism of the process with and without adding extract.

3.6 Electrochemical Impedance Spectroscopy (EIS) Measurements

EIS is settled and it is vital strategy for concentrate the corrosion [31,32]. Fig.7 demonstrates the Nyquist (a) and Bode (b) plots obtained at open-circuit potential both in the absence and presence of improving concentrations of KBE at 30°C.

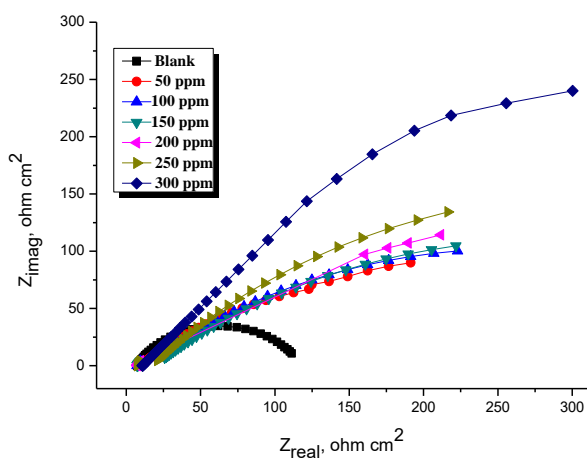


Figure 7a Nyquist plots recorded for liquefactions of CS in polluted NaCl with and without different concentrations of KBE at 30°C

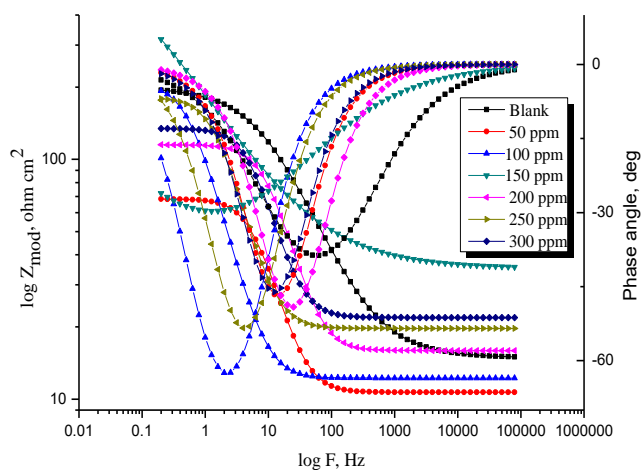


Figure 8b Bode plots recorded for liquefactions of CS in polluted NaCl with and without various concentrations of KBE at 30°C

Table 7. EIS parameters for liquefactions of CS in polluted NaCl with and without various concentrations of KBE at 30°C

Conc., ppm,	R_{ct} , $\Omega \text{ cm}^2$	C_{dl} , $\mu\text{F cm}^{-2}$	θ	%IE
blank	110.5	37.1	---	---
50	339.7	8.03	0.674	67.4
100	498.5	3.91	0.778	77.8
150	544.5	3.62	0.797	79.7
200	638.2	2.75	0.826	82.6
250	823.0	1.54	0.866	86.6
300	1456	1.05	0.924	92.4

3.7 SEM examination

Figure 9, establish the micrograph given for CS sheets in presence and absence of 300 ppm of KBE after dipping for one day. Surface examination can be detected when dipping CS in polluted NaCl solution, as exposed in Figs. 9 (a -c) correspondingly. This deterioration is largely lowered in the attendance of the KBE (Fig. 1c), demonstrating the inhibition ability of the KBE on the CS corrosion in polluted NaCl.

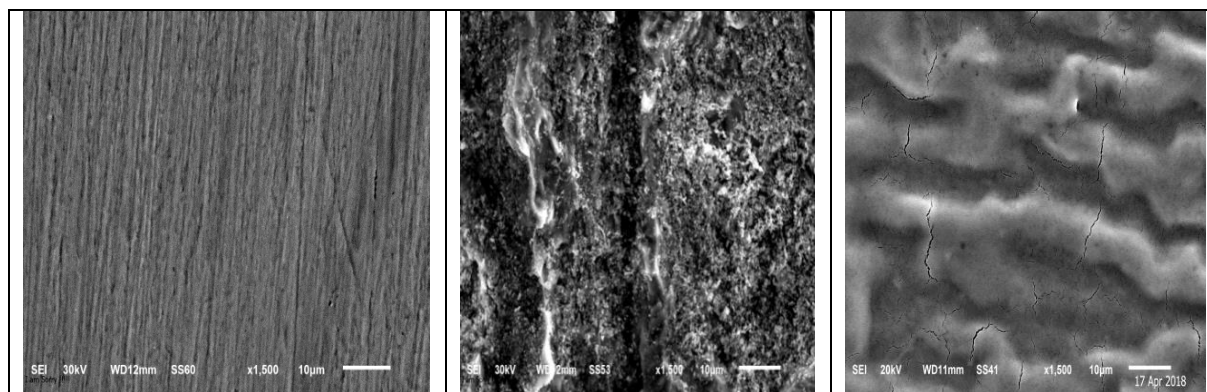


Figure 9(a) SEM of CS free **Figure 9(b)** SEM of CS + polluted NaCl metal, **Figure 9(c)** SEM of CS + polluted NaCl + 300 ppm of KBE

3.8 Atomic Force Microscopy (AFM) Analysis

AFM is a remarkable technique used for measuring the surface roughness with high resolution [33]. Many details about alpha brass surface morphology can be obtained from AFM measurements that help to explain the corrosion process. The three dimensional AFM images represented in Fig (10).

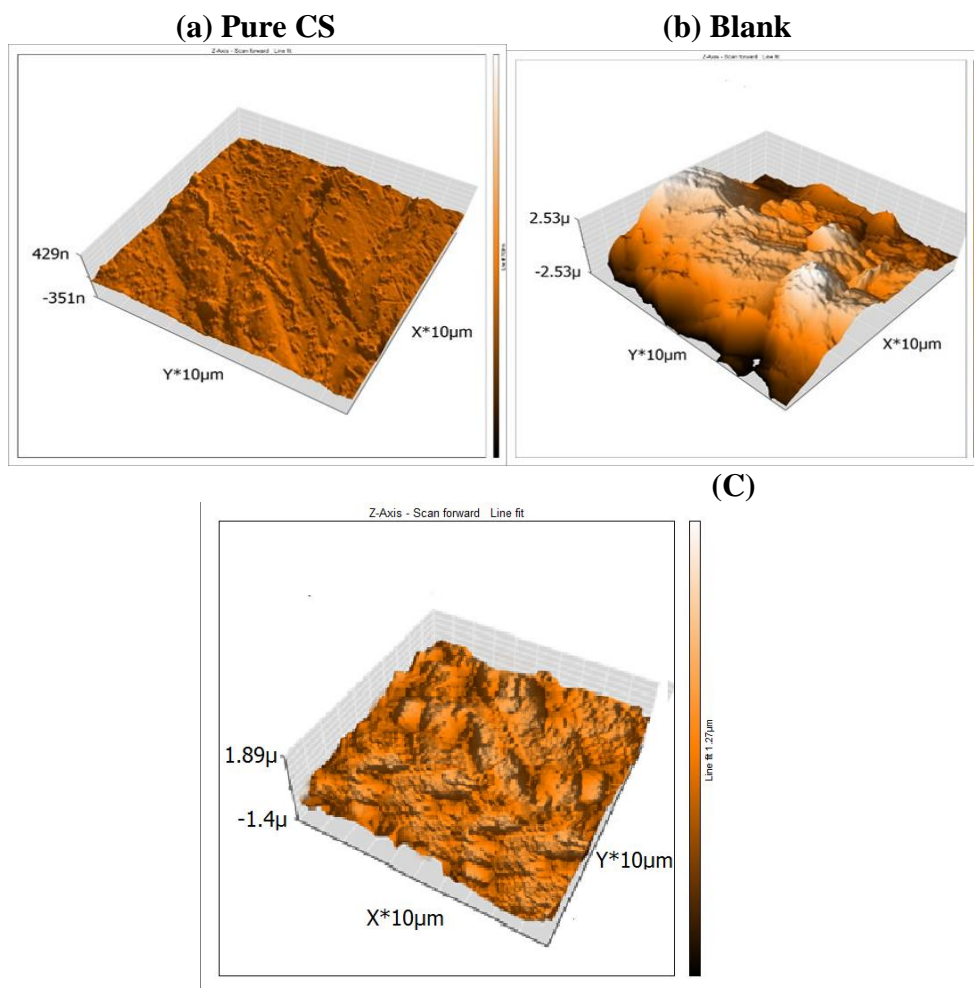


Figure 10. AFM 3D images CS, free specimen, with polluted NaCl for 24 hrs and KBE with polluted NaCl containing KBE for 24 hrs

Table 9. AFM data of KBE for 24 hrs at 25°C

Parameters	a	b	c
The roughness average (Sa)	17.46	993.76	201.58
The mean value (Sm)	-9.4478	11.064	-20.018
The root mean square (Sq)	22.976	1234.9	293.35
The valley depth (Sv)	-108.22	-5.068	-829.62
The peak height (Sp)	151.72	2710.1	885.85
The peak-valley height (Sy)	259.93	7.7781	1715.5

The roughness calculated from AFM image has summarized in Table (9). The values showed that the roughness rise with adding polluted NaCl due to the corrosion happens on the CS surface but decreased with adding the prepared.

3.9 Mechanism of Corrosion Inhibition

The protection mechanism involves the adsorption of KBE on the CS in polluted NaCl solution. Four types of adsorption [34] may take place connecting organic molecules at the metal–solution interface: 1) Electrostatic fascination among the charged atoms and the charged metal; 2) Interaction of unshared electron matches in the particle with the metal; 3) Interaction of π -electrons with the metal; 4) Summation of all the above mentioned. From the observations drawn from the various tests, corrosion protection of CS in polluted NaCl solutions by KBE as designated from ML, PP and EIS techniques were found to be dependent on the concentration and the nature of components of the KBE. Chloride ions, of smaller size and having no primary hydration coverings, are more strongly adsorbed on the positively charged metal surface making the surface negatively charged. Then the protonated molecules in the KBE can be adsorbed on the Cl^- ions that adsorbed on the metal surface by electrostatic interaction (physical adsorption).

4. CONCLUSIONS

The KBE shows the corrosion inhibition for CS in polluted NaCl solution, where IE ratio improved by rise of extract concentration. The IE is decreasing with rise of temperature resulting from the destruction of the adsorbed KBE molecules present on the CS surface. The presence of KBE on the surface follows Temkin equation. Tafel curves showed that KBE is mixed-kind inhibitor. (C_{dl}) reduced by the rise of the KBE concentration, while (R_{ct}) rise. The adsorbed layer on the CS surface was proved by SEM, AFM and FTIR analysis

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