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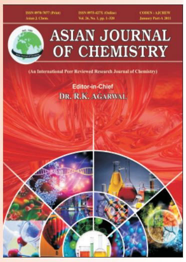

Inhibition of Steel Corrosion in Natural Seawater Using Natural Inhibitor (Algae)

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Chemical (weight loss) and electrochemical (potential dynamic polarization and electrochemical impedance spectroscopy) measurement were applied to evaluate the potential of algae for inhibiting the corrosion of steel in sea water (0.5 M NaCl). It was found that the inhibition efficiency increases with the increase of algae concentration. Adsorption of inhibitor species was found to follow Langmuir and Dubinin-Radushkevich isotherm models and the ability of algae species to be adsorbed physically on the steel surface was illustrated by Dubinin-Radushkevich isotherm parameters. The data obtained from chemical and electrochemical measurements are in reasonably good agreement. Physical adsorption mechanism of algae species on steel surface in sea water becomes clear cut by following the trend of inhibitor adsorption with solution temperature. Inhibition was found to increase with increasing concentration of the extract but decreases with increasing temperature. The associated activation parameters were determined and discussed.

Keywords: Corrosion inhibition, Steel, NaCl (sea water), Algea, Langmuir, Dubinin-Radushkevich, Physical adsorption.

INTRODUCTION

Corrosion of metals is a common problem that has economic implications costing billions of dollars each year. Corrosion environment can be broadly classified as atmospheric, underground/soil waste, acidic, alkaline and combinations of these. A wide variety of acid or alkaline conditions are encountered in common environments.

Many of the several corrosion problems encountered in the industries involves acids and in certain cases due to alkalis and solvents. Hence corrosion inhibition programs are now required in many industries such as oil and gas exploration and production, petroleum refining, chemical manufacturing and the product additive industries. The corrosion inhibition is achieved by the addition of inhibitors to the system that prevent corrosion from taking place on metal surface.

Inhibitors are chemicals that often work by adsorbing themselves on the metallic surface, protecting the metal surface by forming a film[1].

Fungi have been implicated in the corrosion of carbon steel[2,3], aluminium[4,5] and zinc coatings[4,6], with corrosion in all cases being associated with the generation of organic acids[3]. Fungal corrosion of aluminium has received considerable attention due to its impact on the integrity of aircraft[2] with significant damage being recorded on a number of occasions[2]. Fungal corrosion *via* acid generation is associated with the degradation of organic materials such as lubricants[7], cladding[2] and jet fuel[8,9] where there is a relatively high level of organic material and some water. In case of the fuel tanks, fungal growth is closely related to condensation forming immediately above the fuel surface due to the presence of water in the fuel[8,9]. It should be noted that fungi are able to generate a wide range of organic acids under aerobic conditions[10], which is different to bacteria (which generally generate organic acids under anaerobic conditions). Many of these acids are generated to allow the sequestration of metals from the environment[10,11]. The impact of organic acids on the corrosion of radioactive waste containers was reviewed by Smart *et al.*[12]. They indicated that formic acid and acetic acid were able to promote steel corrosion particularly if present as a vapour. However, the concentrations of organic acid quoted by Smart *et al.*[12] appear to be significantly greater than would be expected through the growth of fungi.

The association between fungal corrosion and aluminium appears to be due to the close association between aluminium and organic materials such as polyurethane and fuel rather than a specific susceptibility of aluminium to fungal attack. This is a situation very different to that expected in ILW stores or the pre-closure period of the GDF where the organic loading is significantly lower. Atmospheric corrosion of aluminium *via* fungi has been identified in electrical distribution pylons[13], but has not been reported for stainless steel.

A role for algae in microbiologically influenced corrosion (MIC) was proposed by Javaherdashti *et al.*[14] where oxygen generated by algae contributes to the generation of a differential aeration cell which facilitates the corrosion of steel reinforcements in concrete. A more likely role for algae in MIC is the generation of biofilms that allow anaerobic microbiology *e.g.*, SRBs, to become established at the interface between the biofilm and the metal. This type of algal biofilm is most likely to occur on horizontal surfaces where atmospheric deposits have allowed algae to become established. Although the accumulation of particulate material on horizontal surfaces has been described for ILW stores[15] it is not clear whether these deposition rates would be sufficient to allow an algal biofilm to form within a GDF.

Chloride is not the only main cause of corrosion of reinforced concrete structures in seawater environment. Microorganisms, such as bacteria and microalgae, in the seawater can induce microbiologically influenced corrosion that leads to degradation of the concrete structures by formation of biofilm on the metallic surface. In this preliminary study, the impact of microalgae on the corrosion of steel reinforced bars in fly ash geopolymer concrete was studied.

Corrosion potential, algae cells number and pH measurement were carried out for fly ash geopolymer concrete and a control mix ordinary portland cement samples. The results indicate that the corrosion potential of fly ash geopolymer concrete was influenced by the cathodic reaction during photosynthesis activities. The geopolymer concrete in algae-inoculated medium was found to be more tolerant to algal growth than the control mix (ordinary portland cement concrete). There was a positive correlation between algae cell densities and the potential reading of the geopolymer[16].

Algae, like fungi, are relatively large organisms. Algae commonly cause slimy deposits in cooling towers where sunlight and water are present. Deposits of dead algae provide food for bacteria and fungi. Algae are not known to cause corrosion directly, except for occasional occurrence under their deposits. Control can be effected by covering cooling tower decks to prevent sunlight from reaching the tower water, or with chemicals such as chlorine, quaternary ammonium compounds and copper salts[17-19].

The objective of this study is to evaluate the potential of aqueous extract of algae (Fig. 1) for inhibiting the corrosion of steel in seawater solutions by chemical [hydrogen evolution (HE) and weight loss] and electrochemical (electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, measurements. The effect of temperature on the corrosion rate of steel with and without a certain concentration of inhibitor was also investigated and some thermodynamic parameters for activation process were computed and discussed.

EXPERIMENTAL

The composition of the steel specimens used is C, 0.21; Mn, 2.5; Si, 0.35; P, 0.04 and S, 0.04 wt % having dimensions 0.5 cm × 2 cm × 5 cm with exposed area of 18 cm^2. Before each experiment, steel panels were polished with a series of emery papers with different grades (320-600-1200), starting with a coarse one and proceeding in steps to fine grades. Steel panels were degreased with acetone and dried with a stream of air and washed with de-ionized water. All chemicals were of analytical grade.

Extract of algae: Algae were collected from red sea beach in Jeddah region of Saudi Arabia (Fig. 1).

Fig. 1

Corrosive media: Sea water from red sea. The required weight (2, 4, 6, 8,10 and12 g) of algae were prepared by weight with 250 mL sea water. In all experiments, the temperature of solutions was controlled at 30 °C using a water thermostat.

Chemical measurements: The weight loss measurement of steel samples in the investigated solutions were determined over different immersion period as follows.

250 mL of tested solution (sea water) with and without certain weight of algae were placed in bucker and a degreased, weighed steel sample was introduced into the solution. After complete of each test steel sample is separated from the test solution, washed with bi-disilled water and with acetone, dried with stream of air and then re-weighting.

The percentage of inhibition efficiency (IE %) obtained from ML measurement can be calculated as:

$$\text{Inhibition efficiency (IE \%)} = (1\text{-CR/CR}^\circ) \times 100 \quad (1)$$

$$\text{Corrosion rate (CR)} = (\text{g day}^{-1}\text{ cm}^{-2}) = \text{W/t} \quad (2)$$

where CR and CR° are the corrosion rates obtained either from ML measurements with and without of certain weight of algae, respectively. Where W_1 and W_2 are the weight losses (g/dm^3) for steel in the absence and presence of the inhibitor in sea water solution, respectively.

Electrochemical measurements: Electrochemical experiments were conducted through an ACM Gill AC instrument model 655 by using a conventional electrochemical cell of three electrodes with Al as working electrode, Ag/AgCl(s)/KCl saturated (aq) as the reference electrode and platinum wire as the auxiliary electrode.

The EIS measurements were performed at open circuit potential after 15 min of immersion in the tested solution with amplitude of 10 mV. The covered frequency range was 30 KHz to 0.1 Hz. The charge transfer resistance (R_{ct}) values were calculated from the difference in the impedance at low and high frequencies. The capacitance of the double layer (C_{dl}) values is estimated from the frequency (f) at which the imaginary component of the impedance (-Z$''$) is maximum and obtained from the equation:

$$f(-Z''_{max}) = \left(\frac{1}{2\pi c_{dl} R_{ct}}\right) \qquad (3)$$

The potentiodynamic polarization measurements were carried out after the impedance test was completed at a sweep rate of 1 mV/s and with in the potential range from -850 to -350 mV. Tafel lines extrapolation method was used for detecting the electrochemical parameters for the studied systems such as corrosion current density (i_{corr}) and corrosion potential (E_{corr}). The percentage inhibition efficiency can be obtained from electrochemical measurements as follows:

$$\text{PDF: } IE_i\% = \left(1 - \frac{i_{corr}}{i_{corr}{}^{0}}\right) \times 100 \qquad (4)$$

where i_{corr} and i^{o}_{corr} are the corrosion current densities with and without of certain concentration of algae, respectively.

$$\text{EIS: } IE_R = \left(1 - \frac{R_{ct}{}^{0}}{R_{ct}}\right) \times 100 \qquad (5)$$

where R_{ct} and R^{o}_{ct} are the charge transfer resistance with and without of certain concentration of algae, respectively.

It must be mentioned that all chemical and electrochemical measurements were conducted in open air and we used unstirred solutions at 30 °C unless otherwise stated.

RESULTS AND DISCUSSION

Chemical measurements (weight-loss method): The corrosion of metals is fundamental academic and industrial concern that has received a considerable amount of attention. Inhibitors are generally used in these processes to control metal dissolution.

The main aim of this work is testing and developing the anticorrosive property of green algae as a natural low toxic paint additive and evaluate its efficiency for steel protection immersed in red sea marine environments.

Effect of algae on the corrosion behaviour of steel in aqueous solution: The first part of this work was aimed to study the effect of algae on the corrosion behavior of bare steel in sea water.

Weight-loss of steel was determined, at various time intervals, in the absence and in the presence of the filtrate of solutions containing different concentrations of algae that have been soaked for different time (3-12 days) in sea water. The obtained weight-loss-time curves are represented in Fig. 2 for algae. The inhibition efficiency of corrosion was found to be dependent on the inhibitor concentration, the curves obtained that in the presence these of inhibitors fall significantly below that of free sea water. In all cases,the increase in the inhibitor concentration was accompanied by a decrease in weight-loss and an increase in the percentage inhibition.

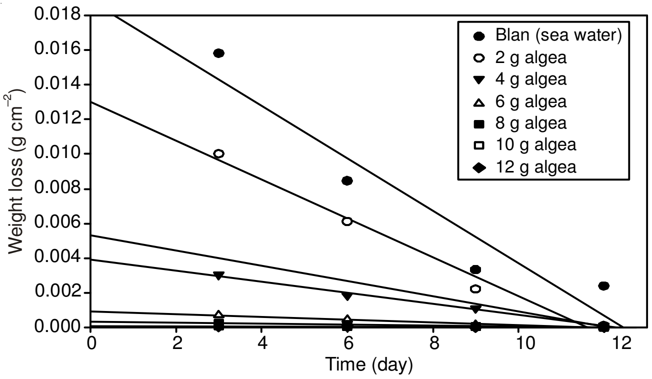

Fig. 2. Weight loss curves for steel in sea water in the absence and presence of different concentration of algae at 30 °C

These results lead to the conclusion that the algae under investigation are fairly efficient as inhibitors for steel dissolution in sea water. The values obtained are summarized in Table-1. The degree of surface coverage (θ) by inhibitors, was calculated from eqn. (6)

$$\theta = 1-(\Delta W_{inh}/\Delta W_{free}) \qquad (6)$$

TABLE-1
VALUES OF % INHIBITION EFFICIENCIES OF INHIBITOR FOR THE CORROSION OF STEEL IN SEA WATER FROM WEIGHT-LOSS MEASUREMENTS AT DIFFERENT CONCENTRATIONS, DIFFERENT TIME AT 30 °C

Weight (g)	Inhibition efficiency (Inh. %)			
	3	6	9	12
2	18.63	27.61	33.33	56.41
4	78.08	80.76	88.49	91.36
6	87.22	94.74	95.54	95.55
8	89.35	97.800	98.22	98.37
10	96.17	99.33	99.47	99.70
12	98.65	99.67	99.74	100

where ($\Delta W_{inh}/\Delta W_{free}$) are the weight losses per unit area in the presence and absence of algae, the variation of the percentage inhibition (Inh %) of algae of inhibitor with their weight was calculated according to eqn. (1)

Electrochemical measurements

Electrochemical impedance spectroscopy measurements: The EIS of steel in sea water (0.5 M NaCl) with and without various concentrations of algae are summarized as Nyquist plots in Fig. 3.

The effect of algae concentration as inhibitor is studied in sea water (0.5 M NaCl) shown in Fig. 3 as Nyquist plots. The diameter of the depressed uncompleted circles increases with increasing algae concentration which suggests that the formed surface film increased in its stability with increasing inhibitor concentration. It is well known that chloride ions have a smaller degree of hydration and they can bring excess negative charges in the vicinity of the interface due to specific adsorption, then, positively charged ions may adsorb onto the surface. In the present study, algae may be protonated in the sea water. Since steel surface contains positive charges in the sea water, results can be explained on the assumption that in the presence of Cl^-, the negatively charged Cl^- would attach to positively charged surface. Then, near the interface, the concentrations of Cl^- and protonated algae are much higher than those in bulk solution, the protonated algae do not attach directly to the positively charged steel surface because of repulsive interaction between the protonated algae and the positively charged steel surface. The protonated algae, however, can attach to the steel surface by means of electrostatic interaction between Cl^- and protonated algae[20] (Table-2).

Potentiodynamic polarization measurements: Fig. 4 shows the effect of algae on the anodic and cathodic polarization

TABLE-2
CORROSION PARAMETERS OBTAINED FROM EIS MEASUREMENTS FOR STEEL IN SEA WATER WITH AND WITHOUT DIFFERENT CONCENTRATIONS OF ALGAE

C_{inh}	CPE	R_p	W_d	IE_R (%)
0.00	5.49×10^{-3}	142.9	5.49×10^{-3}	0.00
2.00	657×10^{-6}	3.024	3.48×10^{-3}	97.88
4.00	736×10^{-6}	1.238	657×10^{-6}	99.13
6.00	12.8×10^{-3}	777×10^{-3}	736×10^{-6}	99.45
8.00	3.48×10^{-3}	298×10^{-9}	12.85×10^{-3}	99.99
10.0	6.24×10^{-3}	296×10^{-9}	6.24×10^{-3}	99.99
12.0	280×10^{-6}	390×10^{-9}	280×10^{-6}	99.99

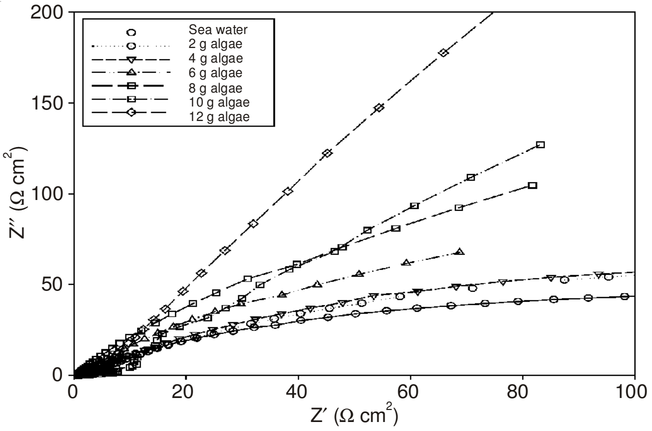

Fig. 3. Nyquist plots for steel in sea water in absence and presence of different concentration of algae at 30 °C

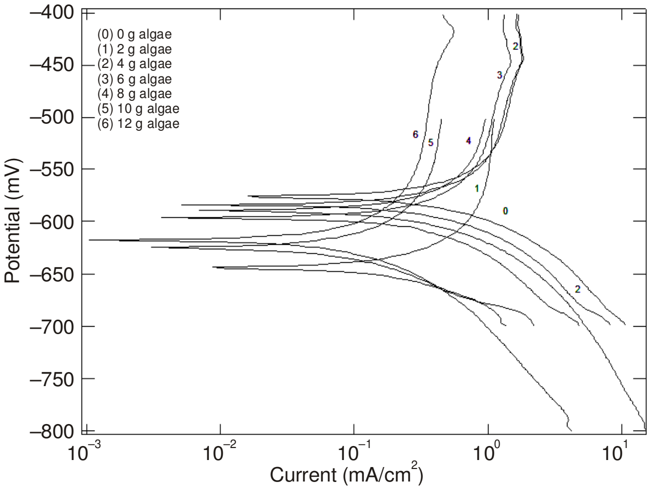

Fig. 4. Potentiodynamic polarization curves for mild steel in sea water in absence and presence of different concentration of algae at 30 °C

curves for steel in sea water (0.5 M of NaCl). It was observed that, in sea water extracts increase also both of the anodic and cathodic overpotentials but its influence on the cathodic side is much less obvious (*i.e.*, act predominately as anodic inhibitors). All polarization parameters, that is, corrosion potential ($E_{corr.}$), Tafel slopes (b_c and b_a), corrosion current density ($i_{corr.}$) and the corresponding, inhibition efficiency $i_{corr.}$ (%) values for steel corrosion in both acids in absence and presence of different concentrations of algae were estimated and listed in Table-3. The following observation could be drawn:

- The anodic (b_a) and cathodic (b_c) Tafel slopes do not change significantly in inhibited solution as compared to uninhibited solution. These observations suggest that both algae adsorb on the metal surface by blocking the active sites of steel surface without affecting the mechanism of corrosion.
- The values of $E_{corr.}$ change somewhat to more negative. Values with increasing extracts concentration in sea water.
- The IE $i_{corr.}$ values are in good agreement with that obtained from EIS measurements.

TABLE-3
CORROSION PARAMETERS OBTAINED FROM POTENTIODYNAMIC POLARIZATION MEASUREMENTS FOR STEEL IN SEA WATER WITH AND WITHOUT DIFFERENT CONCENTRATIONS OF ALGAE

C_{inh} (g L^{-1})	$-E_{corr}$(mV)	i_{corr} (mA cm^{-2})	b_a (mV)	b_c (mV)	IE_i (%)
0.00	577	0.55	59	39	0.00
2.00	583	0.32	67	51	41.33
4.00	589	0.31	72	43	44.57
6.00	593	0.20	72	52	63.22
8.00	617	0.17	66	56	68.71
10.0	618	0.125	77	50	77.27
12.0	643	0.07	48	37	86.80

Adsorption behaviour: The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor. The decrease in the corrosion rate by the addition of algae is attributed to either adsorption of the algae components on the metal surface or, the formation of a barrier film separating the metal surface from the corrosive medium[21,22].

Fig. 5 shows the relation between Inh % and log C_{inh} for the invegeated from weight loss (gravimetric method). As can be readily seen, almost the plots have the from of S-shaped adsorption. This indicates that the algae inhibit the dissolution of steel by adsorption the molecules of the algae at steel in sea water interface, also the obtained figure indicated one step of adsorption.

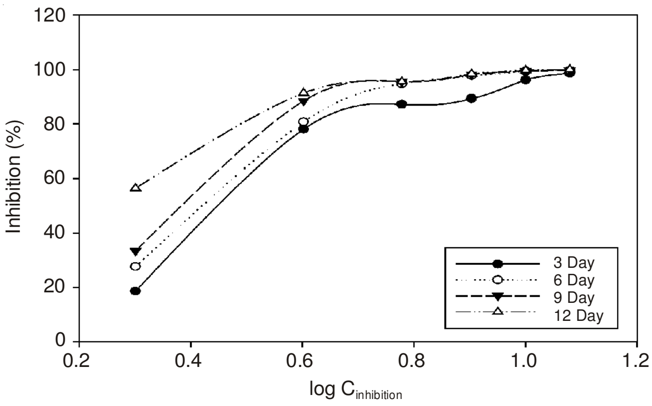

Fig. 5. Variation of inhibition efficiency (Inh. %) againts log C for steel in sea water

Basic information on the interaction between the inhibitor and the steel surface can be provided by the adsorption isotherm for this purpose. The values of surface coverage (θ) at diffrernt concentrations of algae in sea water have been evaluated from weight loss measurement using the eqns. 1 and 6 to explain the best isotherm to determine the adsorption process from the experimental data obtained.

Attempts were made to fit these θ values to various isotherms including Frumkin, Langmuir, Temkin and Freundlich.

Fig. 6 illustrates the variations of surface coverage θ = IE/100 obtained from weight loss *vs*. algae concentration. All plots have an S-shaped adsorption isotherm which characterized with the initial increase in the surface coverage with increasing algae concentration up to certain concentration after which the increase in the surface coverage with algae concentration becomes limited, indicating that at a higher level of algae concentration, the metal surface reaches saturation conditions with the adsorbed species.

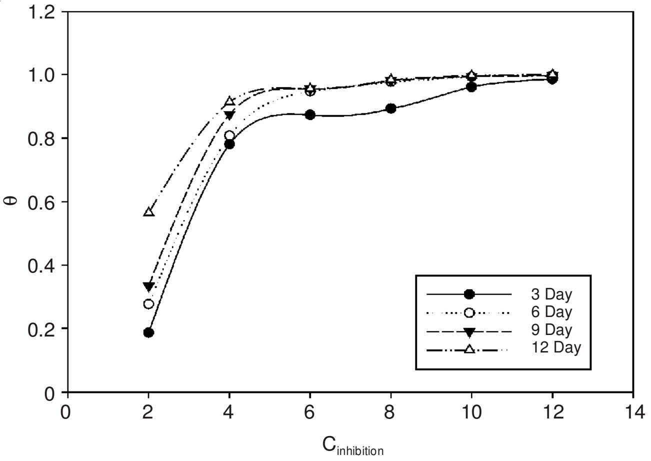

Fig. 6. Relation between steel surface coverage and concentration of algae

To optimize the design of the above adsorption systems, various isotherm models have been tested to describe the equilibrium characteristics of these systems.

Langmuir isotherm model[23]**:** The basic assumption in Langmuir theory is that the adsorption takes place at specific homogeneous sites within the adsorbent. The Langmuir model is given by the following equation:

$$C_{inh}\theta^{-1} = 1/K_{ads} + C_{inh.} \qquad (7)$$

where K_{ads}(L × g^{-1}) is the Langmuir constant, which is defined as the equilibrium adsorption constant. Fig. 7 shows the relationship between $C_{inh}\theta^{-1}$ and C_{inh} for the obtained data from weight loss technique. The regression between $C_{inh}\theta^{-1}$ and C_{inh} has been done using the computer software Sigma Plot 10 and the corresponding parameters are listed in Table-4. It was found that all the linear correlation coefficients (r^2) and slopes are close to unity, meaning that the amount of adsorbed species on steel surface increases with the increase of algae concentration up to saturation conditions at which monolayer of adsorbate may be formed.

Value can be related to the free energy of adsorption ($\Delta G_{ads.}$) by the following equation:

$$\log K_{ads} = \log C_{H_2O} - \Delta G_{ads}/2.303RT \qquad (8)$$

where C_{H_2O} is the concentration of water in solution expressed in g L^{-1}, R (kJ mol^{-1} K^{-1}) is the universal gas constant and T (K) is the absolute temperature. In the present work, this mistake was avoided and the calculated values are listed in Table-4. The negative values of ΔG_{ads} suggests that the adsorption of algae onto the steel surface is a spontaneous process.

TABLE-4
LANGMUIR AND DUBININ–RADUSHKEVICH ISOTHERM PARAMETERS OBTAINED FROM WEIGHT LOSS FOR ALGAE ADSORPTION ON STEEL SURFACE IN SEA WATER AT DIFFERENT TIME

LIM	3	6	9	12
r^2	99.7	99.7	99.7	99. 8
Slope	1.12	1.13	1.11	1.08
K(L g^{-1})	151.485	178.813	214.193	305.434
$-\Delta G_{ads}$(kJ mol^{-1})	22.769	23.187	23.642	24.536
Dubinin–Radushkevich isotherm				
r^2	0.98	0.99	0.98	0.98
θ_{max} (L g^{-1})	1.09	1.11	1.10	1.04
α(mol^2 kJ^{-2})	0.09	0.10	0.09	0.04
E(kJ mol^{-1})	2.29	2.18	2.27	3.54

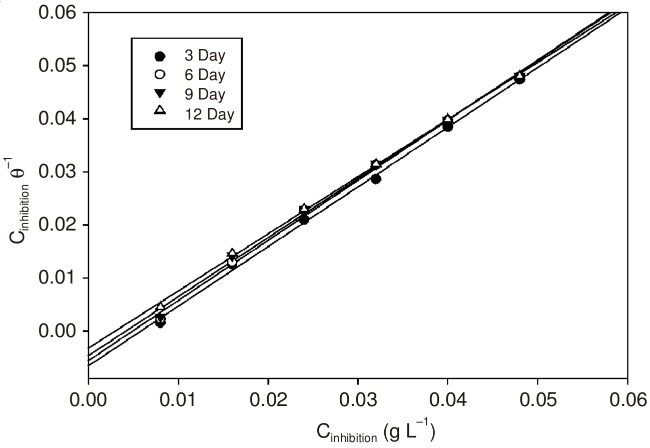

Fig. 7. Fitting for the results obtained by weight loss measurement to Langmuir isotherm mode

Dubinin-Radushkevich isotherm model[24]**:** Dubinin-Radushkevich isotherm model was used to distinguish between physical and chemical adsorption for the removal of some pollutants from aqueous solutions by adsorption on various adsorbents[25-28]. It can be expressed as:

$$\theta = \theta_{max} - \alpha\sigma^2 \qquad (9)$$

where θ_{max} is the maximum surface coverage and σ (polany potential) can be correlated as:

$$\sigma = RT \ln (1 + 1/C_{inh.}) \qquad (10)$$

The constant α gives the mean adsorption energy (E), which is the transfer energy of 1 mole of adsorbate from infinity (bulk solution) to the surface of the adsorbent:

$$E = \frac{1}{\sqrt{2\alpha}} \qquad (11)$$

The magnitude of E gives information about the type of adsorption, if this value is less than 8 kJ mol^{-1}, adsorption type can be explained by physical adsorption[29]. Fig. 8 shows the relationship between ln θ and σ^2 for the obtained data from weight loss technique. The regression between ln θ and σ^2 has been done and the corresponding parameters are listed in Table-4.

E values were estimated from weight loss technique and are given in Table-4. As can be seen, the numerical values of E reflect the physical adsorption mechanism.

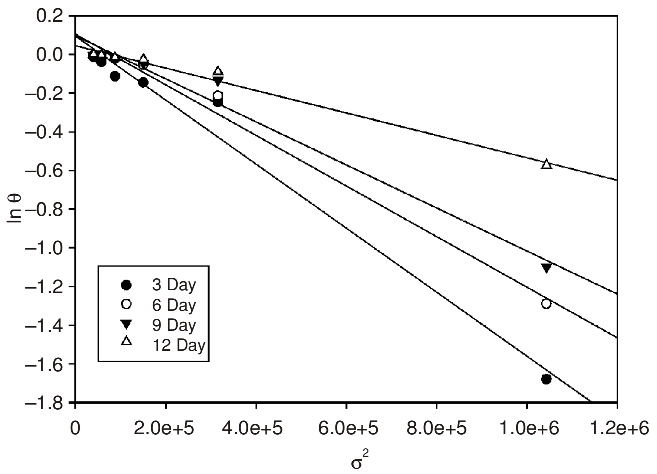

Fig. 8. Fitting for the results obtained by weight loss measurement to Dubinin-Radushkevich isotherm model

Determination of the activation parameters: To gain insight into the nature of inhibitor adsorption, the effect of temperature (303, 323, 343 and 363 °C) on the corrosion behavior of steel in absence and presence of algae was studied by weight loss measurement. The results revealed that steel corrosion rate in sea water with and without algae increases with temperature increase obeying Arrhenius-type reactions (Fig. 9a) while the corresponding IE % value decreases somewhat with the increase of solution temperature (Fig. 9b).

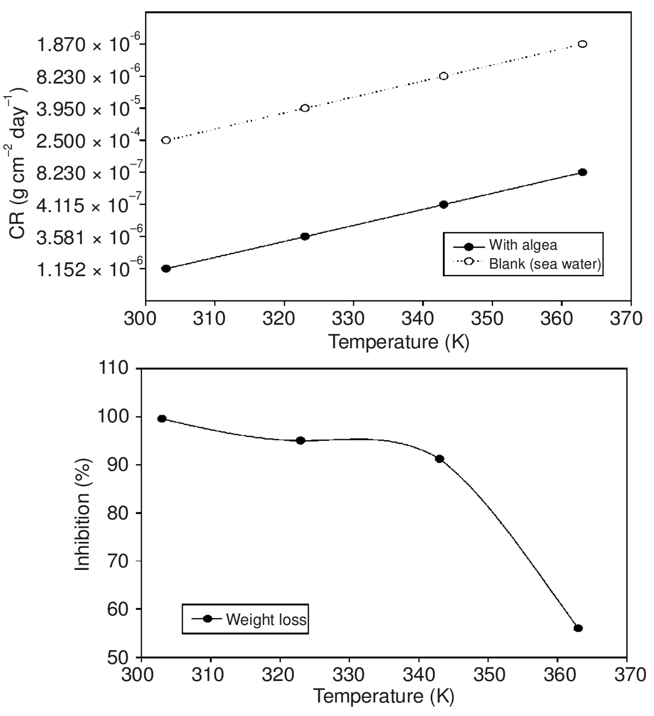

Fig. 9. Variation of (a) CR and (b) Inh. % with temperature

The apparent activation energy, E_{app}, for the corrosion reaction of steel in sea water with and without 12 g/250 mL of algae can be obtained with the help of Arrhenius equation:

$$\log CR = \log A - E_{app}/2.303RT \quad (12)$$

where A is the frequency factor. A plot of log CR *vs*. 1/T gives straight lines (Fig. 10) with slope E_{app}/2.303RT. It was found that the values of E_{app} for the steel corrosion in 0.5 M NaCl without and with 12 g/250 mL algae are 30.66 kJ mol^{-1} and 74 kJ mol^{-1}, respectively. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies with and without inhibitor gives some insight into the possible mechanism of inhibitor adsorption. Popova *et al.*[29] reported that a decrease in the inhibition efficiency with a rise in temperature with a corresponding increase in corrosion activation energy in the presence of an inhibitor compared to its absence is frequently interpreted as being suggestive of physical adsorption. For more confirmation, an estimate of the heat of adsorption (Q_{ads}) can be obtained from the trend of surface coverage with temperature as follows[30]:

$$Q_{ads} = 2.303R \log [\theta_2/(1-\theta_2) - \log \theta_1/(1-\theta_1)]T_1T_2/(T_2-T_1) \quad (10)$$

where θ_1 and θ_2 are the surface coverage at temperature T_1 (30 + 273) K and T_2 (70 °C + 237) K. It was found that the adsorption of algae species on the steel surface is an exothermic process associated with a low negative value of adsorption heat (Q_{ads} = -52.53 kJ mol^{-1}), so the earlier proposed physical adsorption mechanism is clear cut.

It has been pointed out by several of authors[31-33] that the logarithm of the corrosion rate (k) is a linear function with the reciprocal of the absolute temperature 1/T (Arrhenius equation):

$$\ln k = -E_a/RT + A \quad (13)$$

where E_a is the apparent effective activation energy, T the absolute temperature, R the universal gas constant and A is Arrhenius pre-exponential factor.

An alternative formulation of the Arrhenius equation is the transition state equation:

$$k = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad (14)$$

where N is the Avogadro's number, h the Plank's constant, $-\Delta H^*$ the enthalpy of activation and S^* is the entropy of activation.

The corrosion rates were taken as the slope of the linear part of the gasometry plot, considering pseudo zero-order condition.

Figs. 10 and 11 show the plot of ln CR and ln CR/T *versus* 1/T for steel in sea water in presence and absence of 12 g/250 mL algae. As seen, the plots give straight lines from which the activation parameters were determined from their slopes and intercepts. The values of E^*_a, ΔS^* and ΔH for steel dissolution in sea water free from and containing sea water in presence and absence of 12 g/250 mL algae are given in Table-5. Inspection of the results reveals that E_α and ΔH^* values increase in presence of the algae, meaning a higher protection efficiency is attained due to raising the energy barrier for the reaction. In addition, the entropy of the activation in the presence and absence of the inhibitor is small and negative. This implies that the adsorption process is rather slow and activated complex in the rate determining step represents association rather than dissociation step, meaning that a decrease in disordering take place on going from reactants to activated complex.

Conclusions

The following results can be drawn from this study:

- Algae could acts as effective corrosion inhibitor for the sea water corrosion of steel.

TABLE-5
ACTIVATION PARAMETERS E_a,ΔH^* AND ΔS^* FOR STEEL IN SEA WATER FREE FROM AND CONTAINING SEA WATER IN THE ABSENCE AND THE PRESENCE OF ALGAE

$C_{inh.}$	E_a(kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1} k^{-1})
0.0	30.66	33.47	-259.2
12 g	74.00	76.84	-140.3

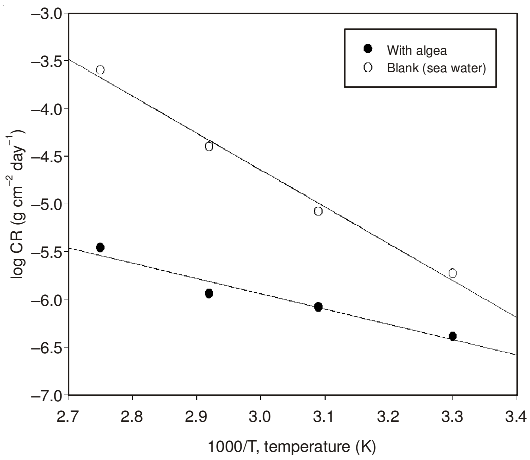

Fig. 10. Arrhenius plot for steel corrosion in 0.5 M NaCl with and without algae

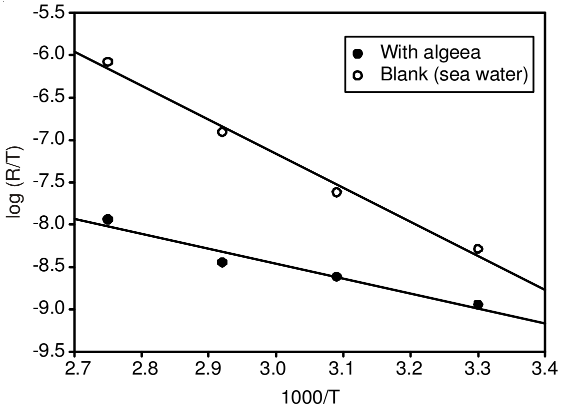

Fig. 11. Variation of log (R/T) *vs.* 1/T for steel in 0.5 M NaCl in presence and absence of 12 g/250 mL algae

- The inhibition mechanism is independent on the storage time.
- The inhibition efficiency of the studied inhibitor increases with decreasing in temperature and increasing of inhibitor concentration.
- Electrochemical measurements revealed that algae acts as mixed-type inhibitor with inhibition category belonging to geometric blocking.
- Adsorption of inhibitor species was found to follow Langmuir and Dubinin-Radushkevich isotherm models and the ability of algae species to adsorbed physically on steel surface was illustrated by Dubinin-Radushkevich isotherm parameters.
- $E^*_{app.}$ value for all inhibited systems is higher than that of the uninhibited system and it is concentration-dependent.
- Thermodynamic adsorption parameters ($\Delta H_{ads.}$, $\Delta S_{ads.}$ and $\Delta G_{ads.}$) show that the studied inhibitor are adsorbed on steel surface by an exothermic, spontaneous process.
- Physical adsorption mechanism of algae species on steel surface in sea water becomes clear cut by following the trend of inhibitor adsorption with solution temperature.

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