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# The inhibition of carbon-steel corrosion in seawater by streptomycin and tetracycline antibiotics: An experimental and theoretical study

Maryam Dehdab [a], Zahra Yavari [a], Mahdieh Darijani [a], Afshar Bargahi [b,*]

[a] Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran
[b] The Persian Gulf Marine Biotechnology Research Center, Bushehr University of Medical Sciences, Bushehr, Iran

## HIGHLIGHTS

- The inhibition of Tetracycline and Streptomycin on carbon-steel corrosion in seawater was evaluated.
- This corrosion inhibition act as spontaneous mixed-type and obey the Langmuir adsorption isotherm.
- For inhibition efficiencies (IE %), the quantum chemical data were confirmed by experimental data.
- As indicated by molecular dynamics simulations, adsorption and configuration energies for Streptomycin are higher.
- The SEM morphometric showed reasonable protection of carbon-steel in seawater by Tetracycline and Streptomycin.

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## ABSTRACT

The corrosion inhibition of Tetracycline and Streptomycin on the carbon-steel, Fe (110), in seawater was evaluated using weight loss, Tafel polarization, electrochemical impedance spectroscopy and SEM morphometric methods.

The surface adsorption of inhibitors follows the Langmuir adsorption isotherm and acts as spontaneous mixed-type corrosion inhibitors on the carbon-steel surface. The related thermodynamic parameters ($E_a$, $K_{ads}$, $\Delta G_{ads}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) were evaluated and the interaction energy for Streptomycin was more than the Tetracycline. The SEM morphometric showed a good protection effect of inhibitors on carbon-steel in the presence of seawater and this was more efficient for Streptomycin. To emphasize the further insight into the efficiency of inhibitors, the Quantum chemical analysis and molecular dynamics simulations were used to find the most stable configuration and adsorption energies for inhibitors on the carbon-steel surface. The theoretical quantum chemical data such as $E_{HOMO}$, $\eta$, $\chi$, molecular surface area, MV, $\mu$, $\alpha$ and $\Delta N$ were in agreement with inhibition efficiencies (IE %) that were obtained experimentally. Also, the molecular dynamics simulation showed the most stable configuration and adsorption energies of Streptomycin and Tetracycline on the carbon-steel and this follows the order of Streptomycin > Tetracycline, as verified by the experimental data.



## 1. Introduction

Carbon–steel, Fe (110), has been one of the most important metals in various industrials such as power plants, petrochemical plants, oil and gas refineries, boilers and ships, in which piping must transport fluids and gasses at high pressures and temperatures. In industries, to restrain the corrosion after several working cycles, the acid treatment is used which results in severe corrosion during exposure to the aggressive media [1–3]. Chloride containing solutions, like seawater are in most cases corrosive due to the depolarization effects of chloride ion. The main problem concerning carbon-steel applications is its relatively low resistance to the corrosion in acidic media. For decreasing or stopping the corrosion process, using the corrosion inhibitor is a choice. The theoretical and experimental evaluation of corrosion inhibitors on carbon-steel in the acidic medium have been shown as a valuable research field in industries [4,5]. In the recent years, many studies were made to find the non-toxic corrosion inhibitors [6–8].

In the current study, the mechanisms of Tetracycline and Streptomycin (Fig. 1) inhibition on the corrosion of carbon-steel in seawater were investigated using weight loss, Tafel polarization, electrochemical impedance spectroscopy, Scanning Electron Microscopy (SEM), isotherm calculation, Molecular Dynamic (MD) simulation, and quantum chemical calculations.

* Corresponding author.
*E-mail address:* abargahi@yahoo.com (A. Bargahi).

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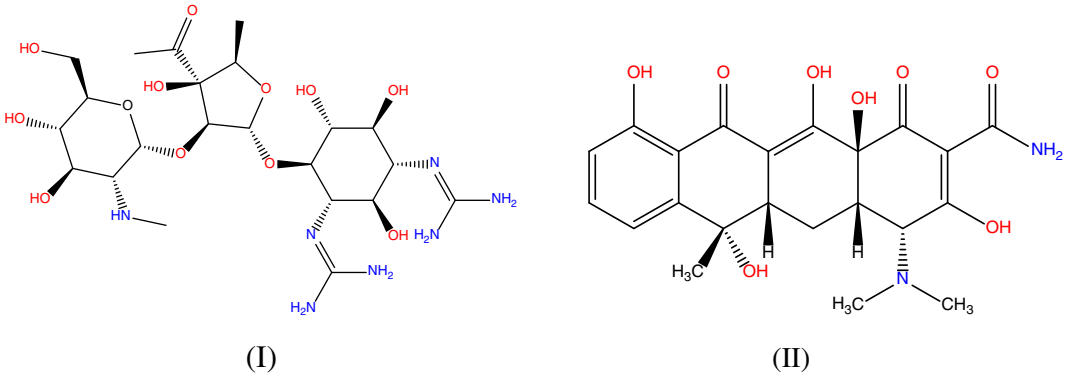


**Fig. 1.** Molecular structure of Streptomycin (I) and Tetracycline (II).

## 2. Experimental

### 2.1. Materials

Tetracycline and Streptomycin were obtained from Sigma-Aldrich (St Louis, MO, USA) and used without any further purification. Fresh seawater without any treatments was prepared from coastal waters of Bushehr province, Iran. The physicochemical parameters of fresh seawater were obtained using CTD instrument (OCEAN SEVEN 316, IDRONAUT; Italy) as follow: pH (7.8), T (32 °C), Salinity (39.78 psu), Chloride concentration (3000 mg/L), Fluoride concentration (2.64 mg/L).

### 2.2. Sample preparations

The metal specimens with 20 × 20 × 1 mm dimensions were polished using different grades of emery paper, washed in double distilled-water (dd-water), degreased, and treated with ultrasound in an acetone bath for 5 min and dried at room temperature.

### 2.3. Instrumentation

The surface morphology of corroded carbon-steel in the presence and absence of inhibitors were imaged using SEM electron microscope (S4160 FE, Hitachi) with 20 kV acceleration.

The analysis of electrochemical impedance spectroscopy and Tafel linear polarization were carried out by Metrohm Autolab potentiostat-galvanostate PGSTAT 302 equipped with a conventional cell with triple-electrode. The obtained data and equivalent circuits were fitted simulated by Nova 1.11 software.

### 2.4. Weight loss measurements

The gravimetric weight loss is the most useful method for the measuring of inhibition efficiency [9]. The ease and reliability of the results which offers by the gravimetric are such that has made this as a basic method for corrosion measurements and monitoring studies [10].

For weight loss measurements, the cleaned carbon-steel sheets with 20 × 20 × 1 mm dimension were weighted before and after immersion in an open beaker containing the test solution for 3 h. Before experiments, all specimens were abraded with sandpapers (from 500 to 1000 grit), rinsed with dd-water and absolute acetone in ultrasound bath until the corrosions remaining on the surface of specimens were removed. The sample were dried at 70 °C for 30 min, desiccated under nitrogen gas and weighted. The weight loss assays were performed at 296, 305 and 315 K temperatures in the presence of inhibitors in seawater solution and the average weight loss for identical experiments were calculated in $mg \cdot cm^{-2}$. The corrosion rate (CR) in $g \cdot cm^{-2} \cdot h^{-1}$ was obtained by Eq. (1) [11]:

$$A = \frac{W}{(Area \times Time)} \tag{1}$$

The inhibition efficiency (%IE) was calculated using the following equation [12]:

$$IE\ (\%) = \left[\frac{(W_0 - W)}{W_0}\right] \times 100 \tag{2}$$

where, W and $W_0$ are the weight loss of carbon-steel sheet in the presence and absence of inhibitors, respectively. The surface coverage (θ) of the inhibitor on the carbon-steel surface was expressed by the following equation [13]:

$$\boldsymbol{\theta} = \frac{\boldsymbol{IE}\ (\%)}{100} \tag{3}$$

### 2.5. Electrochemical measurements

A cut of carbon-steel sheet (20 × 20 × 1 mm) was set as working electrode. A platinum electrode and a saturated calomel electrode (SCE) were used as control and reference electrodes respectively. The working electrode (Fe specimens) was polished mechanically, washed in acetone, dd-water and dried. All measurements were carried out with freshly polished electrodes and de-aerated in the test solution. The cathode and anode polarization curves were recorded at a sweep rate of 10 $mV \cdot s^{-1}$. To obtain the corrosion current densities, the linear Tafel segment of the cathode and anode curves was extrapolated to the potential of corrosion.

The corrosion rate in different test solutions was determined using the Stern–Geary equation from the polarization measurements [14]:

$$J_{cor} = \frac{\beta_a \times \beta_c}{2.303 \times R_p \times (\beta_a + \beta_c)} \tag{4}$$

whereas $J_{cor}$ is the current density of corrosion, $R_p$ is the polarization resistance and $\beta_c$ and $\beta_a$ are the respective cathode and anode Tafel slopes at 0.1 $V \cdot dec^{-1}$ in our measurements.

So, the polarization resistance can be measured on the basis of following Eq. (5) [15]:

$$R_p = \frac{\Delta E}{\Delta J} = \frac{\partial E}{\partial J} \tag{5}$$