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Research Article

The inhibitory effect of Saffron extract (Crocus sativus., L) on copper corrosion in seawater

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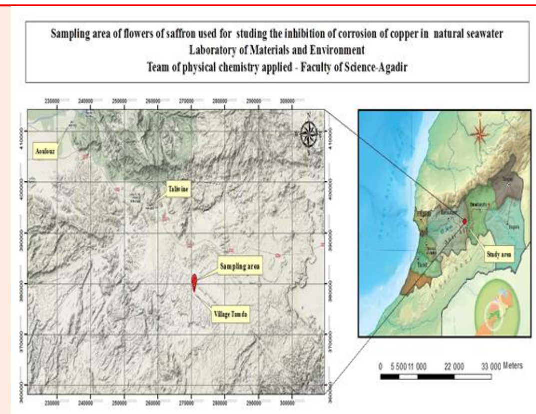
Abstract

Saffron extract (Crocus sativus., L) flower (Petals and Stamens) (SE) was tested as inhibitor for copper corrosion in natural sea water. The techniques used in this work were gravimetric and potentiodynamic polarisation measurements. Chemical analysis showed that Picrocrocine, Safranal and Crocine are major component of SE. The inhibition efficiency was found to increase with inhibitor content to attain 84% for SE at 2000ppm. Inhibition efficiency E (%) obtained from gravimetric and electrochemical methods are in reasonably good agreement. The plant extract behaves as Cathodic–type inhibitor. Results confirm the performance of copper in natural seawater containing Saffron extract.



Keywords: Corrosion; Copper; Inhibition; Saffron extract; Natural sea water

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Introduction

Copper is used at various fields in industry and technological applications, especially in the manufacture of some high-end devices: in shipbuilding industry, aerospace and household industries because it is a great conductor for electricity, and is one of the most widely used metals for musical instruments. It is also used in construction materials and even the jewelry industry and precious sculptures, copper been through different uses over the years, and it remains one of the most used commodities today, due to some characteristics such as excellent electrical and thermal conductivity, corrosion resistant, particularly malleable, perfect for alloys, bactericidal and fungicidal natural.

There are many researches on the corrosion of copper and copper alloys in different medium which reveals the presence of aggressive elements such as chloride and sulfide responsible of there accelerate corrosion[1-3]. The aim of this study is the investigation of the corrosion inhibition of copper in natural sea water by SE [4]. The goal of this study is to find alternative green inhibitors to some toxic inhibitors such heterocyclic organic compounds [5-9] or inorganic inhibitors [10] which are very expensive. Many experiments were conducted to use the eco-friendly substances which were characterized by their abundance as corrosion inhibitors, instead of the harmful synthetic chemicals [11-16].

Experimental Section

Materials and Reagents

Botanic and chemical composition of saffron

Since 3500 years ago, Saffron or Crocus sativus has been cultivated as a source of spice saffron [17,18]. It is classified in the division of Magnoliophyta, class Liliopsida, order Asparagales, it belongs to the family Iridaceae

Crocus genus (Table 1). Iridaceae family comprises about 60 kinds and 1500 species. The Crocus kind comprises about 80 species [19], who is the best known is the saffron with its high economic value [20].

Table 1 Scientific classification of Crocus sativus L. [21, 22]

Kingdom	Plantae
Division	Magnoliophyta
Class	Liliopsida
Subclass	Monocots
Order	Asparagales
Family	Iridaceae
Genus	Crocus
Species	Crocus sativus L.

The table 2 gives us an idea of the most important components of Saffron:

Table 2 Proximate analysis of Saffron [4]

Components	Mass %
Water-soluble components	53.0
(i) Gums	10.0
(ii) Pentosans	8.0
(iii) Pectins	6.0
(iv) Starch	6.0
(v) α–Crocin	2.0
Other carotenoids	1.0
Lipids	12.0
(i) Non-volatile oils	6.0
(ii) Volatile oils	1.0
Inorganic matter ("ash")	6.0
(i) HCl-soluble ash	0.5
Protein	12.0
Water	10.0
Fiber(crude)	5.0

Description and geographic localization Crocus sativus., L area sample

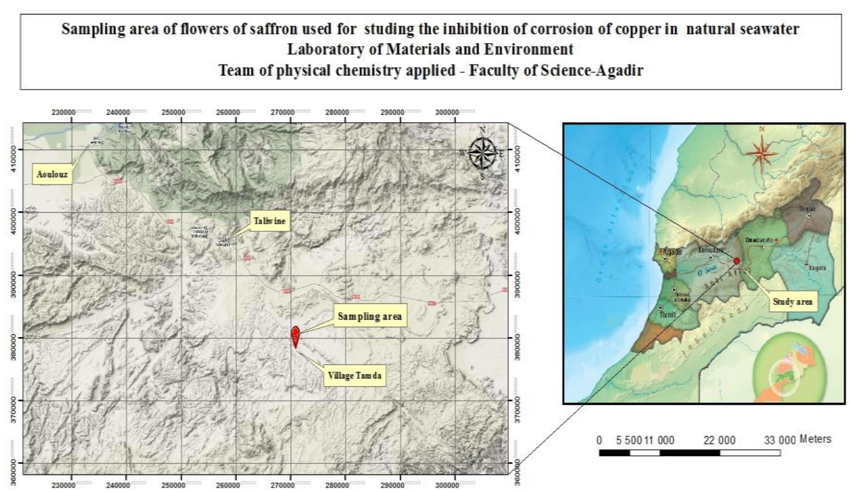

Figure 1 Sampling site of saffron flowers (Taliuoine)

The Lambert indinates of the plot are: X=270794, 45 and Y=380059, 87

The geographic indinates of the site are: 32° 27′ 04″ North and 5° 38′ 00″ West

Seawater samples

Area of the sample

The sampling area as represented in the figure 2 is located in Agadir beach about 2 km south of the port: Between P1(X= 96218.632; Y=385938.244) and P2 (X=96313.633; Y=385381.447).

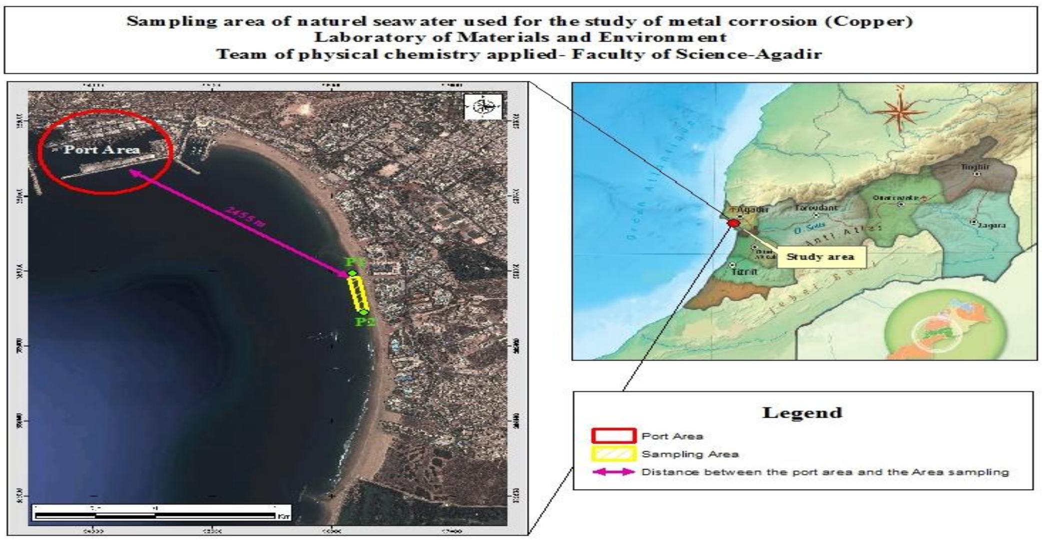

Figure 2 Sampling site of seawater

The physicochemical parameters

We provide large quantities of sea water from the specified area periodically, every time we measure the following factors (The physicochemical parameters): Dissolved oxygen, pH, Salinity, Conductivity and Temperature T. The summary table 3 shows the average values of the physicochemical parameters that are found:

Table 3 Physicochemical parameters of sample seawater

Physicochemical Parameters	Average value
Dissolved oxygen (mg/l)	6.8
pH	8.21
Salinity (mg/l)	36500
Conductivity (µs/cm)	54800
T (°C)	19

Weight loss measurements

The weight loss experiments were carried out using copper (99% purity) with a total area of 4 cm^2. The pieces of copper were polished with different emery paper up to 1200, degreased with ethanol, washed thoroughly with distilled water, and drying at room temperature. The immersions time for the weight loss varied from 8 hrs to 360 hrs. After the corrosion test, the specimens of copper were carefully washed with distilled water, dried and then weighed.

Electrochemical measurements

The polarization curves of copper in sea water are recorded with a potentiostat PGP 201, controlled by a computer. The scan rate is 30 mV/min and the potential is ranged from catholic to anodic potentials. Before recording each curve, the working electrode is maintained with its free potential of corrosion Ecorr for 30 min. We used for all electrochemical tests a cell with three electrodes and double wall thermostats (Tacussel Standard CEC/TH). Saturated calomel (SCE) and platinum electrodes are used as reference and auxiliary electrodes, respectively. The working electrode is in the form of a disc from pure copper of the surface 1 cm^2.

Results and Discussion

Preparation of plant and their extracts (Solutions preparation):

After harvesting of saffron in the second half of November 2013, we collected a sample of (Crocus sativus., L) (petals and stamens) from the village "Tamda" on the outskirts of Taliouine. The samples were then transferred to the chemical laboratory where they were dried at the room temperature in a dark condition.
After drying the sample of saffron flower (Petals + Stamens), the powder plant was air-dried in the laboratory at room temperature. A sample of 2g was subjected to sea water collected, and the solution is mixed for 24 h at room temperature. By diluting another media were prepared, example: (2000ppm; 500ppm; 200ppm; 100ppm; 50ppm)

Analysis of plant extract

After drying and crushing plant, we analyzed the sample by UV 2300 spectrophotometer; figure 3 and figure 4 show abundant molecules in our samples:

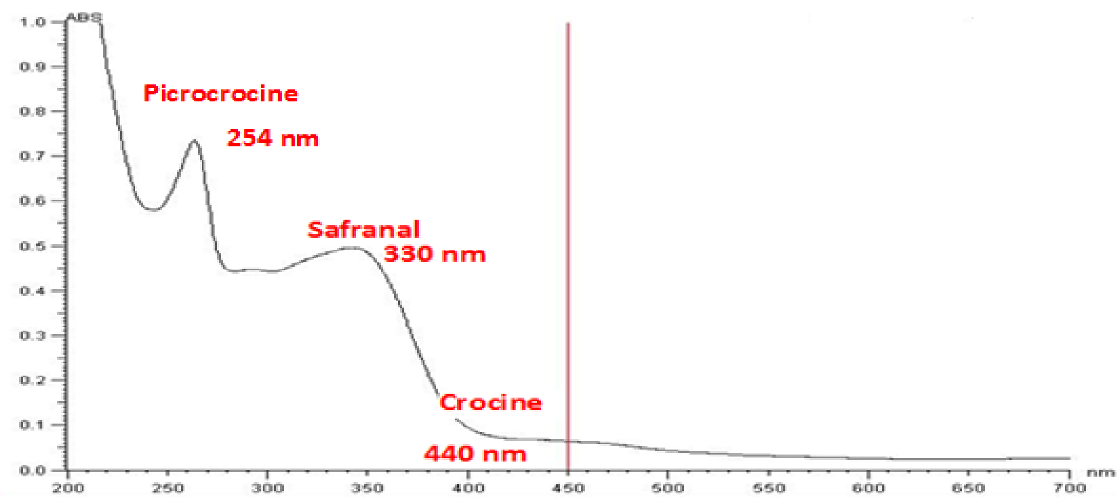

Figure 3 UV spectrum of the (Crocus sativus., L) (petals and stamens)

We compared the UV spectrum of (Crocus sativus., L) (petals and stamens) with another UV spectrum of stigma extracts to know exactly the abundant molecules:

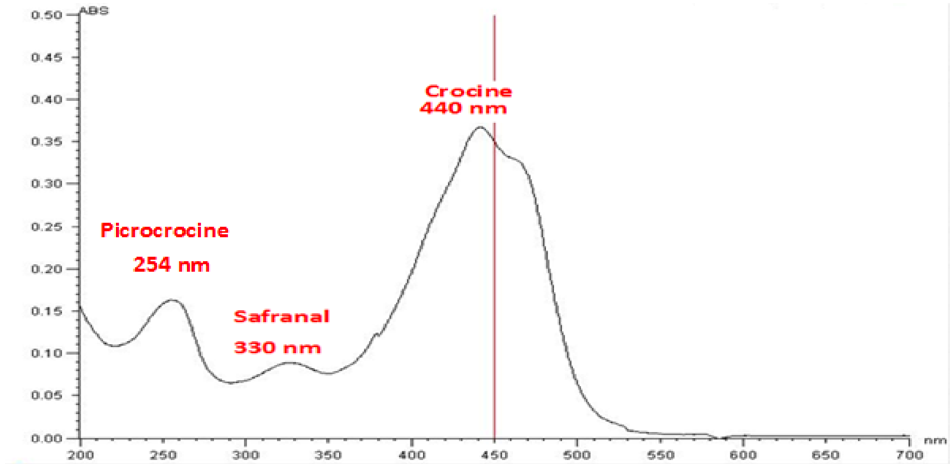

Figure 4 UV spectrum of stigma extracts (50 mg in 100 ml bi-distilled water undiluted)

The comparison of these two specters shows that (Crocus sativus., L) (petals and stamens) and stigma contain almost the same molecules, but with different concentration we observe in these two specters tree characteristics pics, the first in 254 nm indicates the presence amply of Picrocrocine [23] in both samples, and the second in 330 nm indicates the presence of Safranal [24] by a considerable quantity, there are also in 440 nm indicates the presence of Crocine [25] with less concentration in our samples. Figure 5 shows the structures of abundant molecules in the samples:

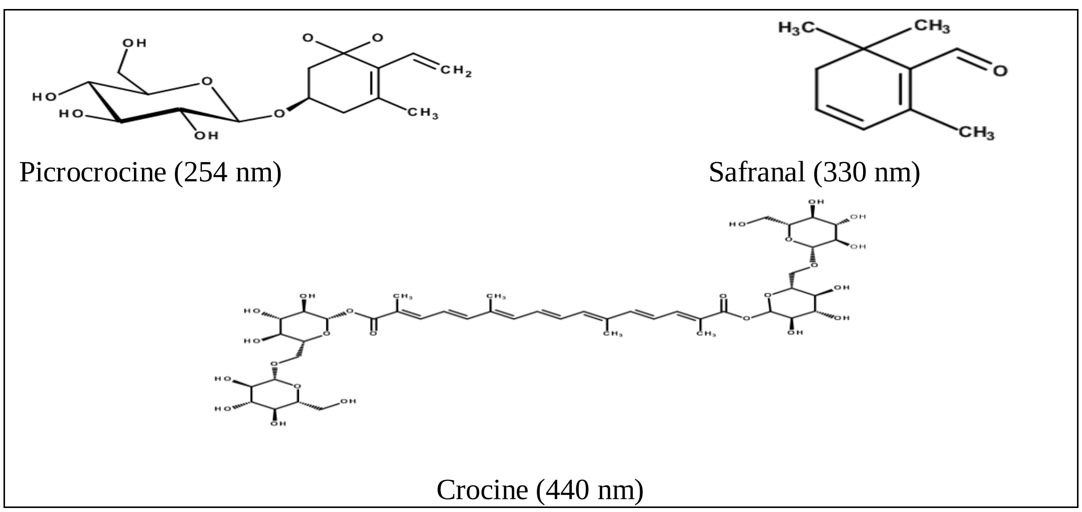

Figure 5 Majority molecules in the Crocus sativus composition [26, 27]

Weight loss measurements

The gravimetric method (weight loss) is probably the most widely used method of inhibition assessment. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring.

The corrosion rate Wcorr is calculated as follow:

$$W corr = \frac{m - m'}{t.S} \qquad (1)$$

Where: m-m'=Weight-loss in milligrams
t = time of exposure of the metal sample in hours and S = area of sample in cm^2
The inhibition efficiency (E_w%) were calculated as follows:

$$Ew\% = 1 - \frac{Wcorr(inh)}{Wcorr} X\,100 \qquad (2)$$

Where, W_{corr} is the weight loss of the sample in the blank solution and $W_{corr(inh)}$ the weight loss of the sample in presence of the inhibitor. The evolution of corrosion rate of copper with SE concentration is represented in the figure 6 and table 5. According to this data, it's clear that the corrosion rate of copper in the blank is higher in comparison with the inhibitor. W_{corr} decreases with increasing concentration of ES and the time of immersion. The addition of SE at different concentration into the aggressive medium reduces the corrosion rate and ameliorate the performance of copper in sea water (figure 7 and table 6):The inhibition efficiency of ES increases as function of its concentration and the time of immersion.

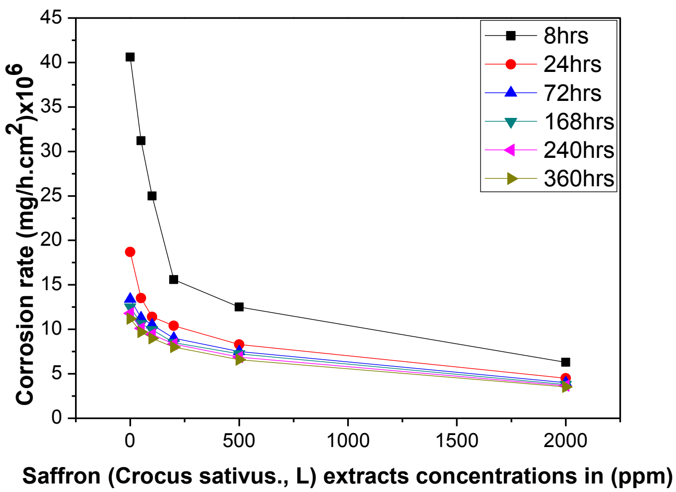

Figure 6 Variation of corrosion rate of copper in natural seawater depending on the concentration of the inhibitor and the immersion time

Table 5 Corrosion rate of copper in natural seawater with addition of extract of Saffron at various immersion time (T= 298 K)

Corrosion rate (W_{Corr} (mg/h.cm^2)x10^6 depending on the immersion time in (hours)							
		8 hrs	**24 hrs**	**72 hrs**	**168 hrs**	**240 hrs**	**360 hrs**
concentration of the inhibitor in (ppm)	**0**	40.6	18.7	13.4	12.5	11.8	11.2
	50	31.2	13.5	11.3	10.64	10.1	9.7
	100	25	11.4	10.5	9.95	9. 42	8.97
	200	15.6	10.4	9	8.5	8.36	8
	500	12.5	8.3	7.5	7.25	6.86	6.57
	2000	6.3	4.5	4	3.8	3.65	3.52

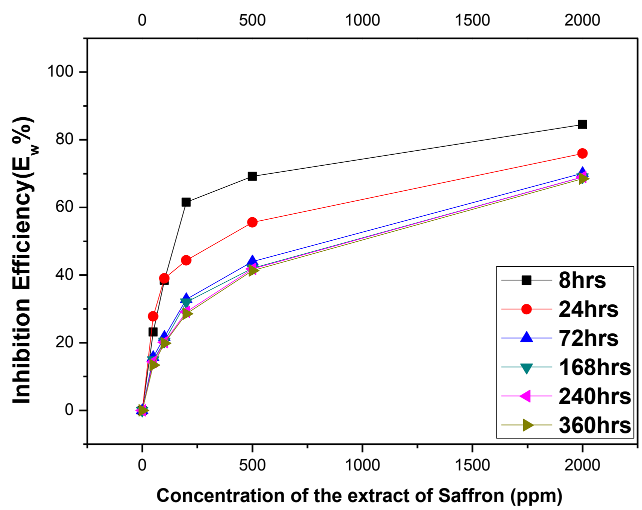

Figure 7 Variation of inhibition efficiency of copper in natural seawater depending on the concentration of the inhibitor and the immersion times

Table 6 Inhibition efficiency E_w (%) of copper in natural seawater with addition of extract of Saffron at various immersion times (T= 298 K)

Inhibition efficiency E_w (%) depending on the immersion time							
		8 hrs	**24 hrs**	**72 hrs**	**168 hrs**	**240 hrs**	**360 hrs**
concentration of the inhibitor in (ppm)	**0**	0	0	0	0	0	0
	50	23	28	16	15	14	13
	100	38	39	22	20	20	20
	200	62	44	33	32	29	29
	500	69	56	44	42	42	41
	2000	**84**	76	70	69	69	69

Electrochemical measurements

Figure 8 represents the potentiodynamic polarization curves of copper in natural sea water in the absence and presence of various concentrations of SE. Table 7 gives the electrochemical parameters, corrosion potential (Ecorr), anodic Tafel slopes (bc), corrosion current density (Icorr), percentage inhibition efficiency (IE %) and corrosion rate. The inhibition efficiency, IE%, was calculated from polarization measurements according to following equation:

$$E_i(\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \quad (3)$$

Where, Icorr and I'corr are the uninhibited and inhibited current density, respectively.

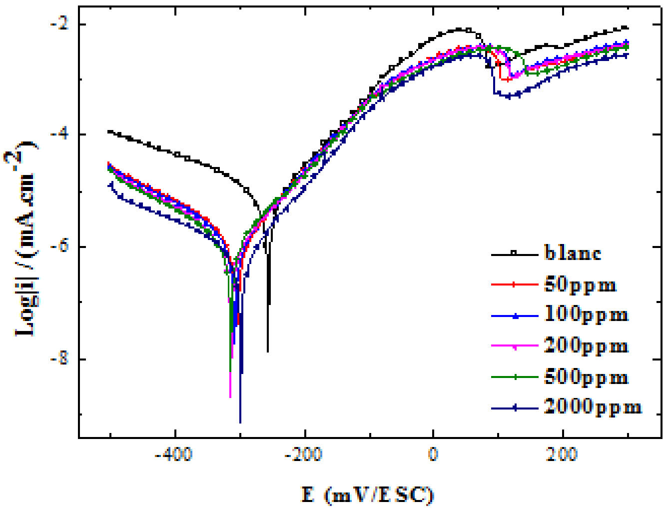

Figure 8 Cathodic and anodic plots of copper in natural seawater at various concentrations of extract saffron (Crocus sativus., L).

Table 7 Electrochemical parameters of copper at various concentrations of extract saffron (Crocus sativus., L) in naturel sea water and corresponding inhibition efficiency

Concentration of Saffron extract in (ppm)	$-E_{corr}$ (mV/SCE)	I_{corr} ($\mu A/cm^2$)	β_a (mV/dec)	E_I (%)
Blanc	291	6.06	76	--------
50	302	2.1	76	65
100	306	2.01	73	67
200	312	1.47	77	75
500	314	1.37	79	77
2000	301	1.09	74	82

As it can be noticed, both cathodic reaction of the copper corrosion electrode were inhibited with the increase of SE concentration. This result suggests that the presence of SE inhibitor blocks the site cathodics of copper and acts as cathodic inhibitor. It could be noted that E% increased with increasing inhibitor concentration, reaches 82 % 2000 ppm ; SE is a good inhibitor for copper in natural sea water.

Effect of temperature

The effect of temperature on the corrosion behavior of Copper in sea water containing the inhibitor at a concentration 2000 ppm is studied in the temperature range 293-323K by using electrochemical measurements. The anodic and cathodic polarization curves obtained are shown in figure 10 and figure 11. The corresponding electrochemical parameters deduced from these curves are listing in Table 8.

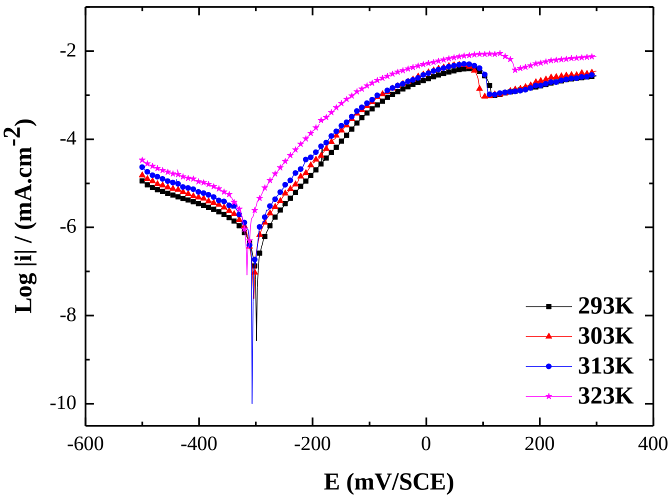

Figure 9 Cathodic and anodic plots of copper in natural seawater with the presence of 2000ppm of SE at various temperature.

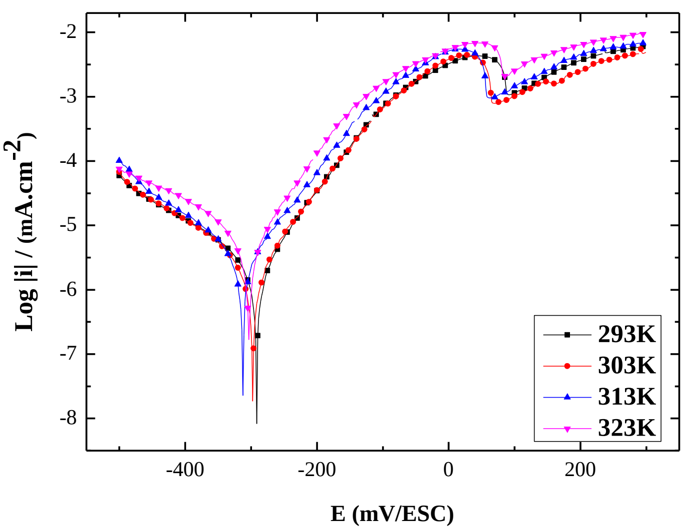

Figure 10 Cathodic and anodic plots of copper in natural seawater without inhibitor at various temperature.

Table 8 Effect of temperature on the copper corrosion parameters in the absence and presence of 2000ppm of SE in natural sea water

Concentration (ppm)	Temperature (K)	$-E_{corr}$ (mV/SCE)	I_{corr} (µA /cm^2)	β_a (mV/dec)	E_I (%)
Blanc	293	291	6.04	76	----
	303	297	6.5	74	----
	313	310	6.8	73	----
	323	305	7.4	72	----

2000	293	301	1.09	74	82
	303	304	2	69	69
	313	306	2.5	69	63
	323	313	3.7	70	50

We note that inhibition efficiency of SE (2000 ppm) decrease slightly with the rise of temperature in the seawater.

Conclusion

From all of these experimental results carried out, we can deduce the following overall conclusions:

- Chemical analysis showed that Picrocrocine, Safranal and Crocine are the major component of SE.
- SE acts as good inhibitor for the corrosion of copper in naturel seawater.
- The inhibition efficiency of SE increases with concentration to attain 84% for 2000ppm.
- SE acts as cathodic corrosion inhibitor, by blocking the cathodic sites of the corrosion process.
- The results obtained from weight loss and Electrochemical measurements are in reasonably good agreement.
- Inhibition efficiency of the natural substance (Saffron extract) decreases slightly with the increase of temperature.

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