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Inhibition of copper corrosion in sodium chloride solution by *Padina pavonica* (*Linnaeus*) Thivy algal extracts

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Abstract

This study examined the inhibition efficiency of the phenolics from brown algae *Padina pavonica* (Linnaeus) Thivy ethanolic extract against the corrosion of copper in the 0.5 mol/l sodium chloride (NaCl) solution. The phenolics of *P. pavonica* were extracted by ultrasound-assisted extraction using different solvent systems (25, and 75% (v/v) of ethanol in water). The total phenolic content (TPC) of the extracts was determined spectrophotometrically. The 75% ethanolic extract exhibited the highest TPC and it was selected for studying its inhibition properties on copper corrosion in NaCl solution by electrochemical methods at various concentrations of the algal extract and temperatures. The results show that the algal extract performed very well as a mixed-type copper corrosion inhibitor in the test solution, with inhibition efficiency increasing with concentration and temperature. The maximum inhibition efficiency was 93.11% for an algal extract of 1.4% v/v at 303 K. The evaluation of the adsorption and activation parameters indicated a spontaneous mixed physical and chemical adsorption of this inhibitor on the copper surface which obeyed Langmuir adsorption isotherm. Furthermore, studies using a scanning electron microscope/energy-dispersive X-ray spectroscope (SEM/EDS) confirmed the calcification of *P. pavonica*. They showed that, under particular circumstances, a protective layer formed on the surface of the copper specimen. The findings advance the understanding of marine algae as a natural source of corrosion inhibitors and highlight the potential benefits of *P. pavonica* phenolics in preventing copper corrosion.

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Introduction

Due to its exceptional physical, mechanical, and chemical properties, including electrical and thermal conductivity, high strength, ductility and malleability, and corrosion resistance, copper is one of the most versatile and widely used materials [1]. However, the widespread usage of copper has exposed it to corrosive conditions. Particularly, exposure of copper to specific atmospheric conditions, such as high temperature, high humidity, or certain environments, such as in the presence of oxygen and certain anions, such as chloride, carbonate, bicarbonate, sulphate, nitrate, and others, can result in corrosion [2–5].

One of the key strategies for preventing copper corrosion in many copper applications is the use of inhibitors. The literature has emphasised the importance of organic compounds such as azoles, amines, and amino acids as effective copper corrosion inhibitors [6–11]. Several studies have reported that organic compounds have high copper corrosion prevention capabilities, particularly products extracted from natural plant-based sources such as herbs, seeds, fruits, leaves, and flowers [12–21]. Furthermore, marine algae are considered a natural source of corrosion inhibitors for copper and its alloys [22–24] as well as for various metals and alloys [24–26].

The brown algae *Padina pavonica* (family *Dictyotaceae*, order *Dictyotales*, class *Phaeophyceae*) widely inhabits the Adriatic Sea [27, 28] and it is considered a rich source of bioactive compounds such as polysaccharides, polyunsaturated fatty acids, pigments, sterols, terpenes, minerals, phenolics, *etc*. [28–36]. Nevertheless, bioactive compounds found in algae, such as phenolic compounds, have been effective as sustainable corrosion inhibitors of different metals and alloys [12, 26, 37–39]. These compounds are plants' secondary metabolites made of an aromatic benzene ring with one or more hydroxyl groups bonded directly to the ring, and their structures diversify from simple to complex, higher molecular weight compounds [32]. It has been shown that their corrosion-inhibitive action is related to their chemical structure (presence and arrangement of functional groups) and physicochemical properties, electron density at the donor atom, *p*-orbital character, and the molecule's electronic structure [12, 18]. Additionally, a link between phenolics' antioxidant/free radical scavenging activities and their capacity to inhibit corrosion has been reported [26, 38]. Therefore, the goals of this study were to quantitatively analyse the total phenolic content of different *P. pavonica* (Linnaeus) Thivy ethanolic extracts and to establish a correlation between the total phenolic content and the algal extracts' effectiveness as a copper corrosion inhibitor in sodium chloride solution at different concentrations and temperatures, as such studies on *P. pavonica*, according to the authors' knowledge, have not been previously reported. Electrochemical methods are used in this study complemented by morphological and compositional studies of *P. pavonica* by a scanning electron microscope/energy-dispersive X-ray spectroscope (SEM/EDS) analysis and surface morphology analysis of the copper specimen by SEM.

Experimental

General

All chemicals, reagents, and solvents used were of adequate analytical grade and were obtained from Kemika (Zagreb, Croatia) and Sigma-Aldrich (St. Louis, MO, USA).

Sample collection, extraction, and determination of total phenolics

Brown algae, *Padina pavonica* (*Linnaeus*) Thivy samples were collected in the Adriatic Sea in front of Port Authority Split, Republic of Croatia in February 2018. The sea temperature was 284 K and the depth was 1 m. Harvested algal biomass was washed thoroughly with fresh water and air-dried in a shaded and aerated place at room temperature. The dried samples were pulverised (1 min in a high-speed grinder, Model 980, Moulinex, France) and the obtained powder was used for the preparation of extracts. The algal extracts were prepared by ultrasound-assisted extraction (Transsonic 310/H bath, Elma, Singen, Germany) using 1 g of the sample, at 313 K for 1 h with ethanol 25%, and 75% (v/v) being used as solvents. After the extractions, samples were centrifuged at 4000 rpm for 5 min and filtered.

The total phenolic content (TPC) in samples was determined by the Folin–Ciocalteu method [40]. Briefly, 25 μL of the extract was mixed with 1.975 mL of distilled water and 125 μL of Folin–Ciocalteu reagent. After stirring the mixture for a minute, 375 μL of a 20% sodium carbonate solution was added. Samples were left in the dark at room temperature for 2 h. The absorbance was measured using a spectrophotometer (SPECORD 200 Plus, Edition 2010, Analytik Jena AG, Jena, Germany) at 765 nm. The standard calibration (50–500 mg/l) curve was plotted using gallic acid (calibration curve equation $y = 0.0007x + 0.0973$, $R^2 = 0.988$). The TPC was expressed as mg of gallic acid equivalents per litre of extract (mg GAE/l).

Metal preparation and electrochemical measurement

For electrochemical research on the corrosion behaviour of copper, cylinder-shaped electrodes were cut from a 99.9% pure copper rod (Sigma-Aldrich). These electrodes were then soldered to isolated copper wires, and insulated with acrylate material (Polirepar S), so the working electrode area was 0.28 cm^2. Before measurements, the electrode was machine-grinded with successive wet SiC emery papers (from 400 to 1500) using a Metkon Forcipol 1V grinder/polisher, polished with Al_2O_3 suspension (particle size 0.05 μm), degreased with ethanol and rinsed with demineralised water.

The electrochemical measurements were carried out in a three-electrode water-jacketed glass electrochemical cell connected to a potentiostat (Princeton Applied Research; PAR; M273A). A platinum plate was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE) which was connected to the working electrode over the Luggin capillary. Electrochemical tests of copper were conducted in 0.5 mol/l NaCl solution with or without the addition of 75% ethanolic extract of *P. pavonica* at various concentrations

(0.2%, 0.8%, 1.4% and 2% v/v) at 303 K. The optimal concentration of algal extract was determined by electrochemical tests at 303 K and experiments at additional temperatures (283, 293 and 313 K) were conducted only using this concentration. The testing protocol consisted of a one-hour open-circuit potential (E_{oc}) measurement, followed by linear polarization measurements ($E_{\text{corr}} \pm 20$ mV with the scan rate of 0.2 $\text{mV}\cdot\text{s}^{-1}$), and the potentiodynamic polarization (−0.250 V to 0.400 V (*vs.* E_{oc}), at a scan rate of 0.5 mV s^{-1}). Each experiment was performed at least thrice, and the values given for the various determined parameters are the average of the multiple measurements.

Scanning electron microscopy/energy-dispersive X-ray spectroscopy analysis and imaging

The *P. pavonica* was characterized by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS). Also, SEM was used to characterize the surface morphology of copper after potentiodynamic polarization measurements. A Thermo Fisher Scientific Quattro S scanning electron microscope (SEM) with secondary and backscattered electron detectors were used for microscopic inspection. In both low vacuum mode (150 Pa) and environmental scanning electron microscopy (ESEM) mode (240 Pa), the SEM was operated at an acceleration voltage of 10 keV, with a beam spot size of 4.0 and a bias of 60.31%. An EDS Ultim® Max detector was used for the elemental analysis to identify and quantify the elements in the algae sample.

Results and Discussion

Total phenolic content

Phenolic compounds are important plant constituents that act as reducing agents, hydrogen donors, and free radical scavengers [12, 18]. The quality and quantity of brown algae phenolics are influenced by various biotic and abiotic factors, whereas factors impacting their analysis include the complexity of the matrix, the structure of the phenolics, chemical interactions, drying techniques, extraction methods, measuring techniques, *etc*. [32]. In this study, the total phenolic content (TPC) of two different extracts of *P. pavonica* prepared using solvents with different ethanol: water ratios were determined by Folin–Ciocalteu (F-C) method using gallic acid as the standard, and results are presented in Figure 1.

The 75% ethanolic extract of *P. pavonica* was found to contain 1.4 times more phenolics than the 25% ethanolic extract, namely 59.10 mg GAE/l and 43.38 mg GAE/l, respectively. These results are in agreement with those reported by Čagalj *et al.* [34] which showed that a better extraction yield of TPC from *P. pavonica* was obtained by using hydroalcoholic mixture solvents in contrast to water solvents. In summary, these results show that the potential of phenolic compounds extraction varied depending on the concentration of ethanol in the solvent system due to variations in phenolic profiles. The presence of different phenolic classes characterised by high structural variety results in their different polarity and solubility that affect their partitioning and extracting properties.

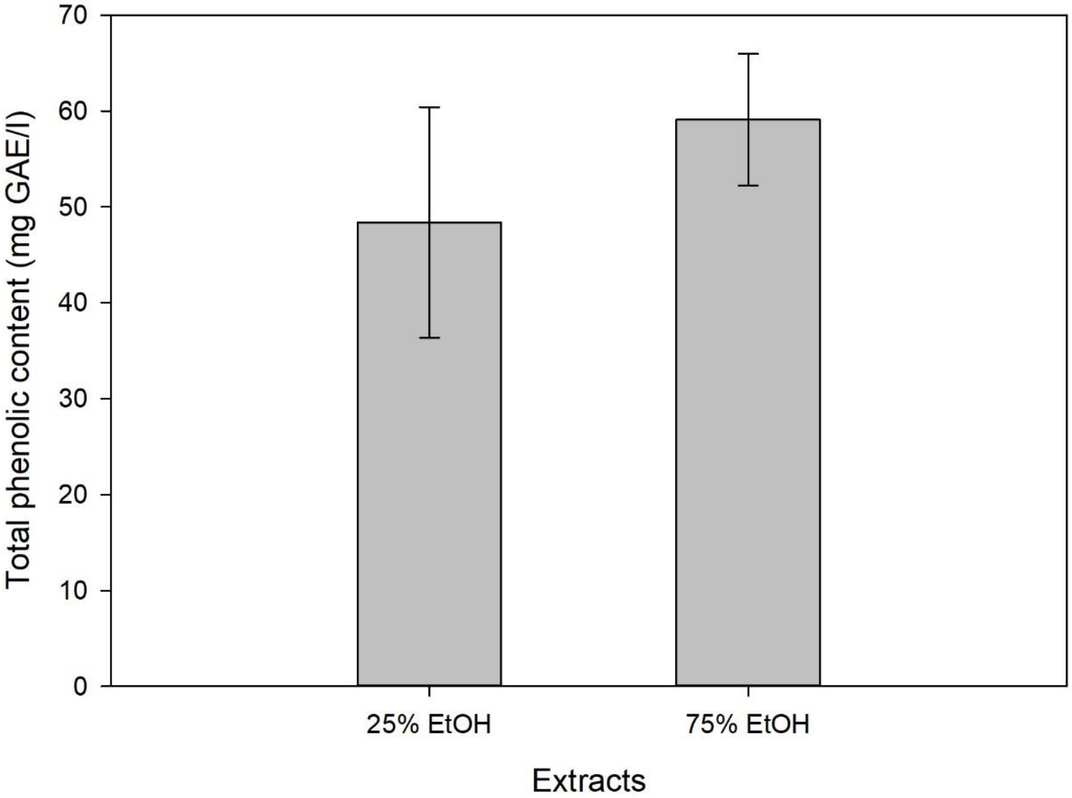

Figure 1. Total phenolic content of *P. pavonica* ethanolic extracts.

Bound forms and high molecular weight phenolics, like phlorotannins which are dominant phenolics in brown algae, may be highly intractable; the polarity of the compounds varies substantially with their structure, conjugation status, and connection with the sample matrix. Additionally, the distribution of phenolic compounds inside the plant is not uniform, and the stability of these compounds varies greatly; whereas certain phenolic compounds are relatively stable, others are volatile, thermolabile, and/or readily susceptible to oxidation [31–33].

Based on TPC results, the algal *P. pavonica* ethanolic extract with the highest TPC, *i.e.* the 75% ethanolic extract, was selected to be tested for its efficiency as a copper corrosion inhibitor in NaCl solution.

Optimum concentration determination

The optimum concentration of ethanol-extracted phenolics of *P. pavonica* at 303 K was determined by measuring open-circuit potential, and polarization resistance, and using the Tafel extrapolation method. The electrochemical parameter that is most readily quantifiable is the open circuit potential (E_{oc}). This straightforward method offers preliminary insights into the nature of ongoing processes at the metal/electrolyte interface. The E_{oc} recorded as a function of time for copper in 0.5 mol/l NaCl solution without and with different concentrations of 75% ethanolic extract of the brown algae *P. pavonica* (0.2%, 0.8%, 1.4% and 2% v/v) at 303 K are shown in Figure 2.

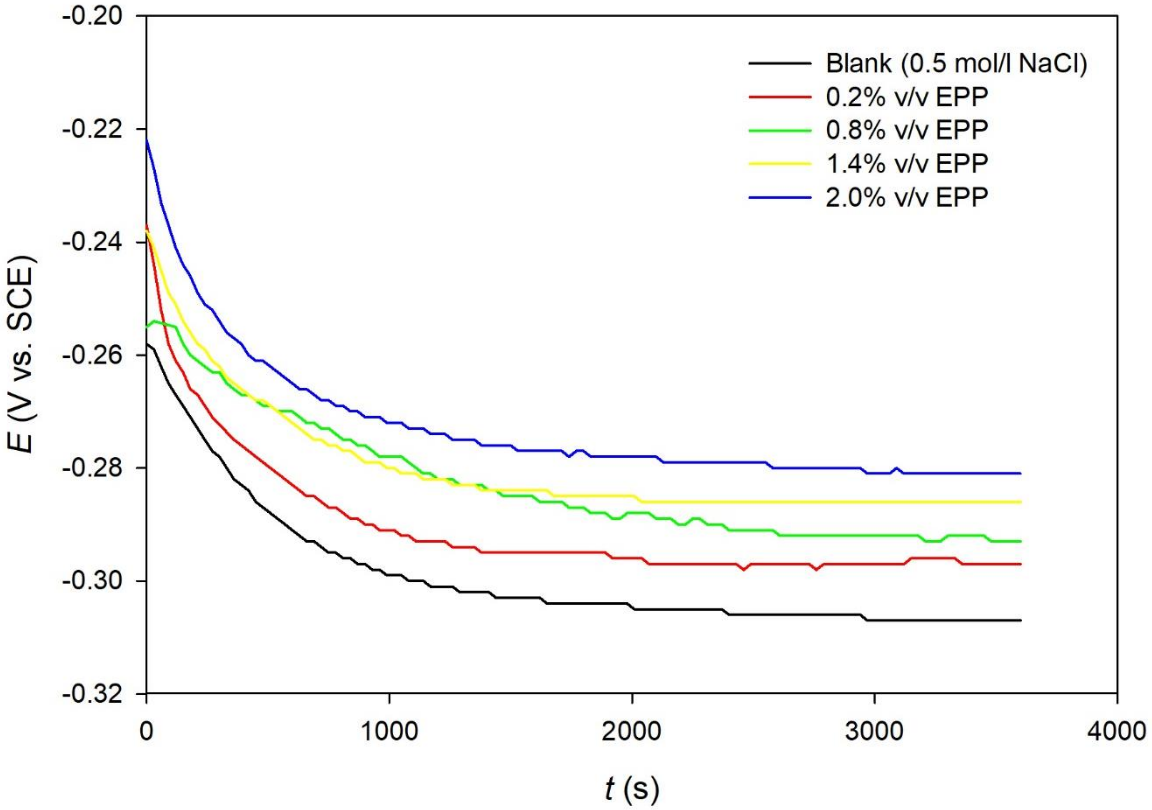

Figure 2. Dependence of open circuit potential for Cu in 0.5 mol/l NaCl solution without and with different concentrations of 75% ethanolic extract of the brown algae *P. pavonica* at 303 K.

According to Figure 2, in the chloride solution, a continuous negative shift in the copper's E_{oc} is seen before a stable value is obtained; the chloride solution led to negative potential values, possibly due to copper dissolution, as shown by the following equation [2, 41–44]:

$$Cu \rightarrow Cu^{+} + e^{-} \tag{1}$$

Cu^+ reacts with chloride ion from the solution to form CuCl [41–44]:

$$Cu^{+} + Cl^{-} \rightarrow CuCl \tag{2}$$

The copper surface is partially protected by CuCl, which then transforms to the cuprous chloride complex, $CuCl_2^-$, through which the dissolution of copper occurs and may eventually cause a negative shift in potential values [41–44],

$$CuCl + Cl^{-} \rightarrow CuCl_2^{-} \tag{3}$$

Under these conditions, copper corrosion is controlled by both copper dissolution and the diffusion of soluble $CuCl_2^-$ from the Helmholtz plane into the bulk solution [41–44].

$$CuCl^{-}_{2(surface)} \rightarrow Cu^{2+} + 2Cl^{-} + e^{-} \tag{4}$$

In the presence of algal extract, a somewhat analogous E_{oc} behaviour of copper was observed; E_{oc} decreased steadily before reaching a steady state value but the E_{oc} values were more positive during the entire testing period. Figure 2 shows that after 30 minutes of electrode immersion in the solution with algal extract, the steady state potential was reached. As algal extract concentrations increase, the steady state E_{oc} shifts to a more positive value in the following order: 0.2% v/v<0.8% v/v<1.4% v/v<2.0% v/v. According to the obtained data, *P. pavonica* 75% ethanolic extract inhibits copper corrosion in the presence of chloride ions.

The corrosion behaviour of copper in NaCl solution without and with different concentrations of 75% ethanolic extract of the brown algae *P. pavonica* was investigated by polarization measurements, *i.e.*, by the method of linear polarization to determine polarization resistance (R_p) and recording potentiodynamic polarization curves in a wide range of potential for determining corrosion parameters and predict anodic behaviour of copper in examined solutions.

The R_p values were determined from linear polarization measurements by calculating the slope of the $E-i$ plot at the free-corrosion potential. The calculated R_p values are shown in Table 1. From the table, R_p values are higher in the presence of algal extract compared to the blank indicating that algal extract inhibits copper corrosion in the presence of chloride ions. The inhibition polarization resistance increases in the following order, 0.2% < 2% < 0.8% < 1.4% v/v.

Figure 3 shows potentiodynamic polarization curves for copper in 0.5 mol/l NaCl solution at 303 K, without and with the addition of various concentrations of 75% ethanolic extract of the *P. pavonica*. Table 1 shows the corrosion parameters, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes (b_a and b_c), determined by intersecting the tangents drawn to the anodic and cathodic parts of the polarization curves in the Tafel region. The inhibition efficiency (η) of algal extracts was calculated at different concentrations using equation (5) presented below [45]:

$$\eta = (i^0_{corr} - i_{corr}) / i^0_{corr} \tag{5}$$

where i^0_{corr} and i_{corr} are the corrosion current densities for copper in sodium chloride solution without and with inhibitor, respectively.

Consistent with the literature for Cu in chloride media [41–48], this research found that the anodic polarization curve consists of three main regains of potential: the apparent Tafel region at lower overpotentials extended to a peak current density, followed by a region of decreasing current density values as potential increased until a minimum value of current density was reached, and finally, a region of a sudden increase in current density values as potential increased further. The nature of polarisation curves for copper in NaCl solution with the addition of ethanol-extracted phenolics of the brown algae *P. pavonica* at all concentrations is comparable to the curve without it, with a minor gradual shift to lower current densities observed in all areas.

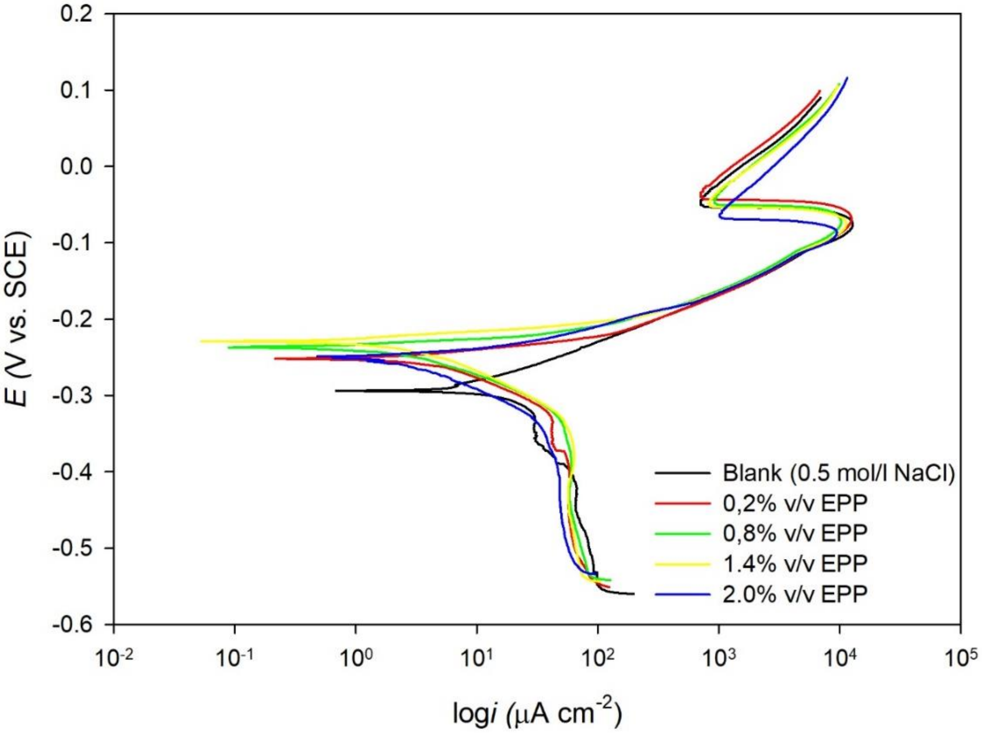

Figure 3. Potentiodynamic polarization plots for copper in 0.5 mol/l NaCl solution without and with different concentrations of 75% ethanolic extract of the brown algae *P. pavonica* (EPP) at 303 K.

Anodic Tafel slopes close to 60 mV/dec were obtained for Cu in solution without and with the addition of ethanolic extract. This implies that the anodic behavior of Cu in chloride solutions is dominated by the diffusion rate of soluble cuprous chloride ion complexes ($CuCl_2^-$), formed during the dissolution of copper [46, 47]. The polarization curve's cathodic branch obtained in a blank solution represented a reduction of CuCl followed by oxygen reduction [48]. The presence of inhibitors shifted the curves toward a lower current density. The decrease in current density observed in the presence of ethanol-extracted phenolics from algae should be attributed to the blanketing of the cathodic surface caused by inhibitor molecule adsorption. The current density remained lower than in the blank solution due to the decreased metal surface area accessible for O_2 reduction since part of it was covered by adsorption inhibitor molecules. As the inhibitor concentration increased, O_2 reduction began before CuCl reduction was complete, even though adsorbed molecules did not cover the entire surface.

Figure 3 shows that the addition of algal extract to the NaCl solution decreased the corrosion current with the corrosion potential values shifted in the less negative direction indicating the corrosion-inhibiting ability of the algal extract. The literature [45] states that an inhibitor can be identified as either anodic or cathodic if the displacement in the corrosion potential value of the inhibited solution to the uninhibited solution is more than ±85 mV. In this paper the maximum displacement in the corrosion potential value was less than 85 mV, indicating that the algal extract affects both the anodic and cathodic reactions by acting as a mixed-type inhibitor. According to Table 1, corrosion current density decreased while the inhibition efficiency increased with an increase in the concentration of the algal extract concentration up to 1.4% v/v 75% ethanolic extract of *P. pavonica* and reached the maximum inhibitory efficiency of 93.1%. Furthermore, at higher concentrations (above 1.4% v/v), corrosion current density increases while inhibition efficiency decreases, indicating that the algal extract accelerates corrosion [49]. This can be attributed to the fact that organic compounds that function as mixed-type inhibitors adsorbed on the metal surface provide a barrier to dissolution at the anode and a barrier to oxygen reduction at the cathodic sites. The persistence of inhibitor molecules on the surface and the stability and impermeability of inhibitor protective layers are important for corrosion inhibition. Due to the complexity of corrosion inhibition, good inhibitors should adsorb strongly enough to persist on the surface, but not too strongly, or else it can promote metal dissolution [50, 51].

Based on the results presented above, we conclude that 1.4% v/v 75% ethanolic extract of *P. pavonica* is the most effective corrosion inhibitor for copper in near-neutral chloride solutions.

These findings are consistent with those of Rahal *et al.* [52], Refait *et al.* [53], and Zdravković *et al.* [15], who found that extracted phenolics from natural plant sources are effective corrosion inhibitors for copper in 0.5 mol/l NaCl solution, with inhibition efficiency exceeding 90%.

Table 1. Potentiodynamic polarization and linear polarization resistance parameters for copper in 0.5 mol/l NaCl solution without and with different concentrations of 75% ethanolic extract of the brown algae *P. pavonica* at different temperatures. The accuracy of the determined parameters is about ±0.5 mV for E_{corr}, ±10% for i_{corr}, ±1 V dec^{-1} for anodic and cathodic Tafel slopes, and ±13% for Rp.

c (% v/v)	E_{corr} (V)	i_{corr} (μA·cm^{-2})	b_{a} (V·dec^{-1})	b_{c} (V·dec^{-1})	η (%)	R_{p} (kΩ·cm^2)
			T=283 K			
0	–0.246	6.31	0.050	–0.159	–	5.03
1.4	–0.244	2.47	0.044	–0.117	60.83	12.41
			T=293 K			
0	–0.264	14.68	0.064	–0.331	–	2.35
1.4	–0.240	1.87	0.048	–0.179	87.27	15.25
			T=303 K			
0	–0.292	18.61	0.074	–0.238	–	2.51
0.2	–0.254	4.46	0.050	–0.172	76.01	6.87
0.8	–0.241	1.57	0.048	–0.179	91.52	18.16
1.4	–0.233	1.28	0.053	–0.197	93.11	24.63
2.0	–0.251	2.23	0.041	–0.105	88.01	13.11

***c* (% v/v)**	***E*corr (V)**	***i*corr (μA·cm^{-2})**	***b*a (V·dec^{-1})**	***b*c (V·dec^{-1})**	**η (%)**	***R*p (kΩ·cm^2)**
			T=313 K			
0	–0.310	19.20	0.073	–0.167	–	2.94
1.4	–0.257	5.82	0.057	–0.259	69.79	5.46

Adsorption isotherm

It is commonly accepted that corrosion inhibition is due to the adsorption of the inhibitor molecule at the metal–solution interface [45, 49–51]. An organic inhibitor can adsorb on a metal surface in two ways: physical or electrostatic adsorption and chemisorption. In corrosion inhibition studies it is assumed that the inhibition efficiency of a given corrosion inhibitor is proportional to its surface coverage (θ), *i.e.*

$$\eta = \theta \cdot 100 \tag{6}$$

The values of inhibitor surface coverage as a function of the inhibitor concentrations can be represented with adsorption isotherm. To study the adsorption behaviour of *P. pavonica* extract, various adsorption models were used (Langmuir, Frumkin, Freundlich, and Temkin), and it was found that the Langmuir adsorption isotherm best fit the experimental data. The Langmuir adsorption isotherm is described by the following [54]:

$$c/\theta = 1/K + c \tag{7}$$

where c is inhibitor concentration and K is equilibrium adsorption constant. Figure 4 shows the dependence of c/θ as a function of the concentration c of *P. pavonica* extract. The obtained plot is linear with correlation coefficients (R^2) almost equal to 1 and the slope is close to 1 which implies that the actual equation is $c/\theta = 1/K + mc$, with m being the slope. Deviation from the slope of 1 implies adsorption due to inter-adsorbate interactions, multi-site adsorption, or surface heterogeneity [54, 59].

The relation between the equilibrium constant of adsorption and the standard adsorption Gibbs energy (G^0_{ads}) is Equation 8 [49]:

$$K = 1/c_{\text{H}_2\text{O}} \exp(-G^0_{\text{ads}}/RT) \tag{8}$$

where $c_{\text{H}_2\text{O}}$ is the molar concentration of water (55.55 mol/l), R is the universal gas constant, and T is the absolute temperature. The calculated ΔG^0_{ads} is −22.38 kJ/mol. The negative value of ΔG^0_{ads} indicates a spontaneous adsorption process of inhibitor on the copper. In the literature values of the ΔG^0_{ads} greater than −20 kJ/mol are attributed to physisorption and values smaller than −40 kJ/mol are attributed to chemisorption [50]. The value of ΔG^0_{ads} obtained in the present paper suggested that the adsorption mechanics of ethanol-extracted phenolics of the brown algae *P. pavonica* on the copper surface may involve both types of interactions, physical as well as chemical adsorption. Phenolic compounds' corrosion-inhibitive action is mainly attributed to the presence of aromatic hydroxyl groups.

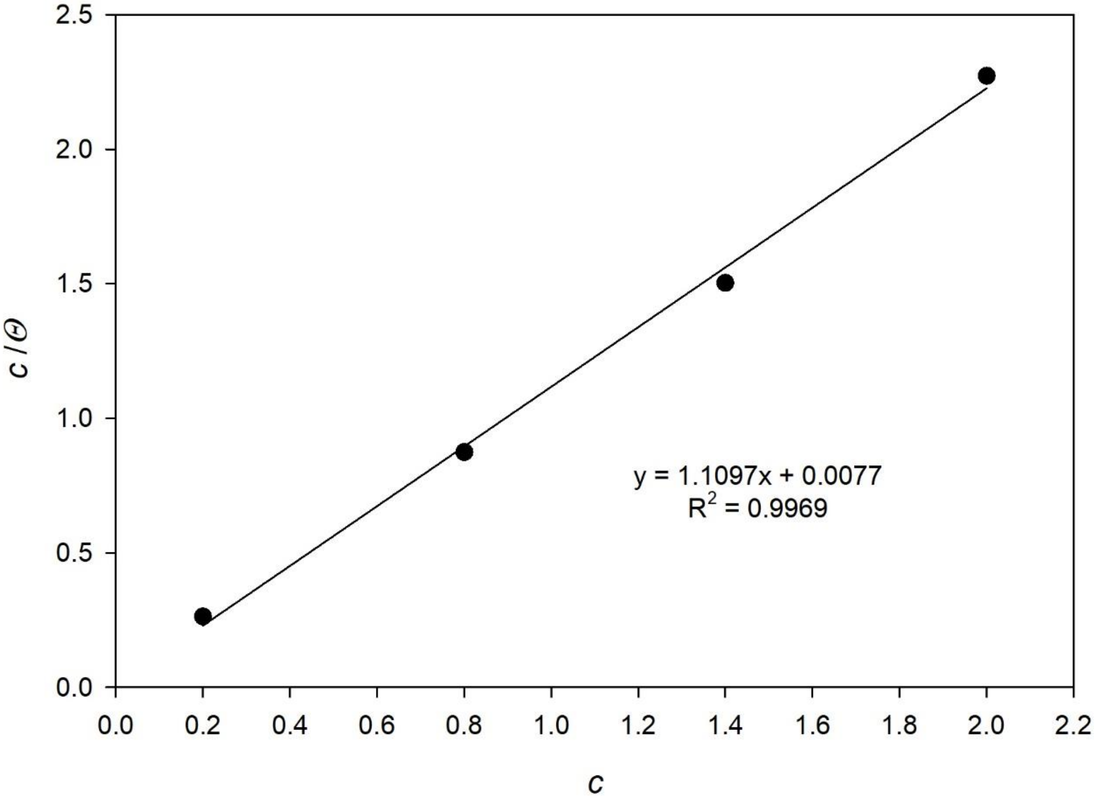

Figure 4. Langmuir adsorption isotherm for ethanol-extracted phenolics of the brown algae *P. pavonica* on copper in 0.5 mol/l NaCl solution at 303 K.

This can be explained by heteroatoms' ability to coordinate bonds with vacant d orbitals of the copper through electron donation. Furthermore, the interactions with rings containing conjugated bonds π electrons, enable the adsorption of molecules on the copper surface [12, 28].

Effect of the temperature

The effect of the temperature on the corrosion behaviour of copper in the 0.5 mol/l NaCl solution without and with the addition of 1.4% v/v of 75% ethanolic extract of *P. pavonica* at a temperature range from 283 K to 313 K was studied by potentiodynamic measurements (Figure 5).

Corrosion parameters obtained by Tafel polarization measurements at different temperatures are given in Table 1. It can be seen from the data in Table 1 that in the absence of algal extract corrosion current increased with an increase in temperature. On the other hand, in the presence of an algal extract corrosion current declined up to 303 K and thereafter increased as the temperature was raised to 313 K. Consequently, inhibition efficiency (calculated with Equation 5) increased up to 303 K, after which it decreases. An increase in inhibition efficiency with an increase in temperature is often ascribed to the chemisorption of the inhibitor molecules on the metal surface.

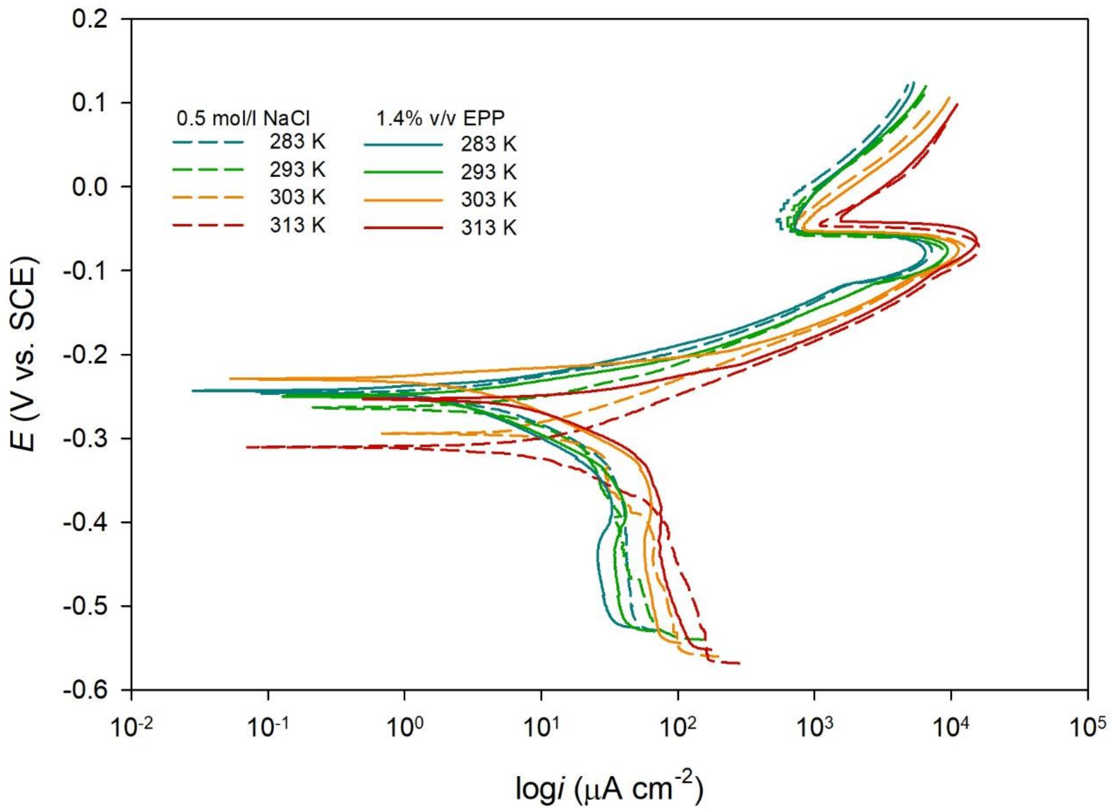

Figure 5. Potentiodynamic polarization plots for copper in 0.5 mol/l NaCl solution in the absence and presence of 1.4% v/v ethanolic extract of the brown algae *P. pavonica* (EPP) in a temperature range from 283 K to 313 K.

The apparent decrease in inhibition efficiency as the temperature was raised from 303 K to 313 K could be related to the change of adsorption mode from chemisorption to physisorption. The effect of temperature towards the corrosion rate can be expressed by Arrhenius Equation [49]:

$$\ln i_{\mathrm{corr}} = \ln A(-E_{\mathrm{a}} / RT) \tag{9}$$

where i_{corr} is current density, directly proportional to the corrosion rate, A is the Arrhenius pre-exponential factor, E_{a} is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. The Arrhenius plot of ln i_{corr} *vs.* 1/T is linear with a slope $-E_{\mathrm{a}}/R$ obtained (Figure 6). Hence the values of E_{a} were determined: 26.71 kJ/mol in the blank solution, and 15.18 kJ/mol in the presence of *P. pavonica* extract. The lower value of E_{a} in the presence of an inhibitor compared to the blank is ascribed to the chemical adsorption of the inhibitor [56–59]. Moreover, the relationship between corrosion current (or corrosion rate) and temperature may be expressed using the Eyring equation derived from the transition state (Equation 10) [52]:

$$\ln(i_{corr} / T) = \left[\ln(RT / N_{\mathrm{a}} h) + (\Delta S_{\mathrm{a}}^{0} / R)\right] - (\Delta H_{\mathrm{a}}^{0} / RT) \tag{10}$$

where N_a is Avogardo's number, h is Plank's constant, and ΔS^* and ΔH^* are entropy and enthalpy of activation, respectively. The values of the activation enthalpy and entropy are determined from the slope and intercept of a line fit to $\ln(i_{corr}/T)$ versus the reciprocal of temperature (Figure 7). The obtained values of the parameters are listed in Table 2. The data in Table 2 show that the activation entropy both in the solution with and without an inhibitor is negative. In the literature, the negative values of the entropy indicate a decrease in the degree of randomness which occurs when the reactants are transformed into activated complexes. The positive values of enthalpy as obtained in the present study indicate that the adsorption of inhibitors is in an endothermic process [59].

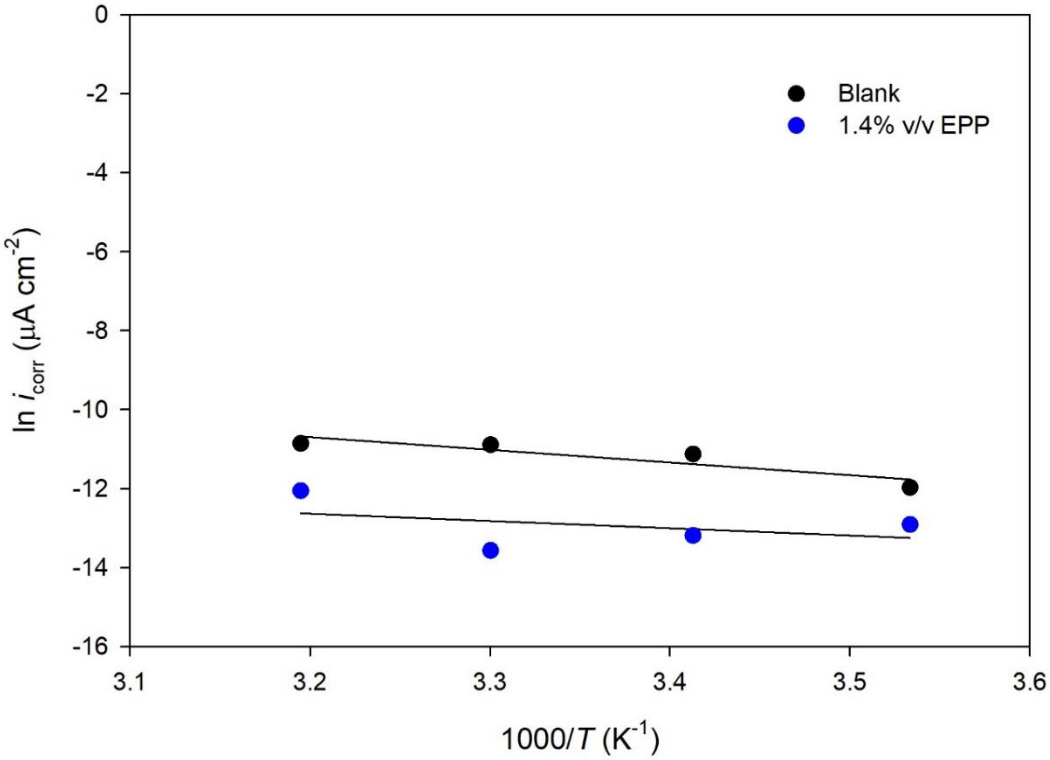

Figure 6. Arrhenius plot for copper in 0.5 mol/l NaCl solution in the absence and presence of 1.4% v/v ethanolic extract of the brown algae *P. pavonica* (EPP).

Table 2. Activation parameters for copper corrosion in 0.5 mol/l NaCl solution without and with 1.4% v/v ethanolic extract of the brown algae *P. pavonica.*

c (% v/v)	**E_a (kJ·mol^{-1})**	**ΔH^* (kJ·mol^{-1})**	**$-\Delta S^*$ (J·mol^{-1} K^{-1})**
0	26.71	24.24	256.71
1.4	15.18	12.71	309.76

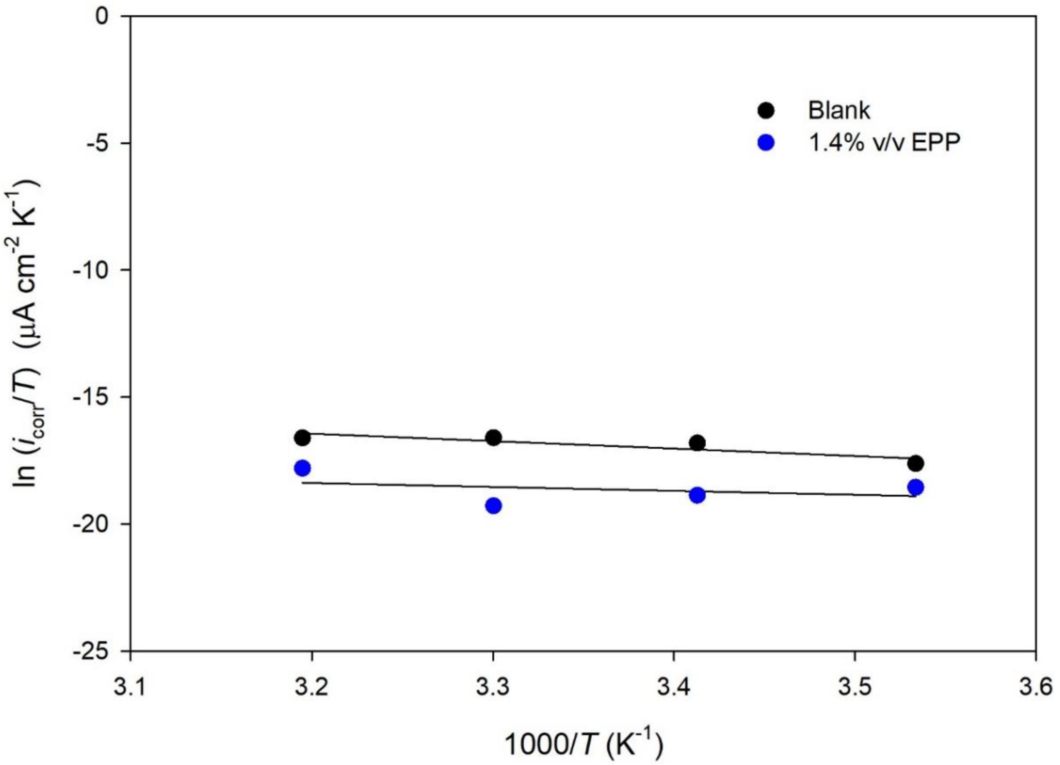

Figure 7. Transition state plot of ln (i_{corr}/T) *vs.* $1/T$ for copper corrosion in 0.5 mol/l NaCl solution in the absence and presence of 1.4% v/v ethanolic extract of the brown algae *P. pavonica* (EPP).

Surface analysis

Figure 8 shows low- (Figure 8a) and high- (Figure 8b) magnification SEM images of *P. pavonica*. The surface of the algae sample shows an irregular morphology and needle-like particles. According to published research, *P. pavonica* possesses a biologically induced extracellular calcification which results in whitish precipitations of calcium carbonate ($CaCO_3$) predominantly as needle-like aragonite particles [27, 60, 61].

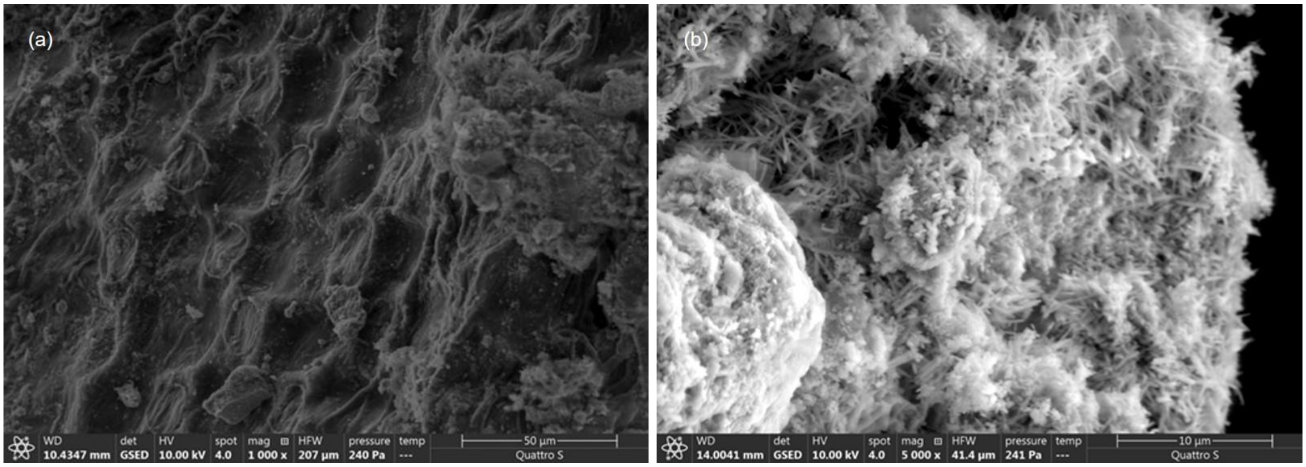

Figure 8. SEM images at magnification (a) ×1000 and (b) ×5000 of the brown algae *P. pavonica*.

EDS qualitative analysis and elemental mapping show high surface concentrations of carbon (18.29% w/w), calcium (21.91% w/w), and oxygen (51.15% w/w), indicating the presence of calcium carbonate. The macro- and micronutrient mineral elements have also been identified. The dominant element was silicon 6.08% w/w. Additionally, the algal sample contained important micronutrients such as sodium (0.46% w/w), magnesium (0.39% w/w), potassium (0.38% w/w), chlorine (0.31% w/w), and iron (0.14% w/w). Other results for elements such as sulphur (0.65% w/w), and aluminium (0.24% w/w) are consistent with the literature [62].

Figure 9 depicts the alteration observed in polished copper surface morphology after potentiodynamic polarization measurements in 0.5 mol/l NaCl solution in the presence of 0.2% and 1.4% v/v of 75% ethanolic extract of the brown algae *P. pavonica*. Surface micrographs of the copper specimens were obtained by SEM. As Figure 9a shows, the copper specimen in the presence of the smallest quantity of algal extracts was corroded; there were cracks along grain boundaries, branches, and corrosion pits visible on the rough surface. The here presented results appear to be consistent with the mechanism, in that the corrosion propagates gradually by anodic dissolution of copper in sodium chloride solution [3, 63].

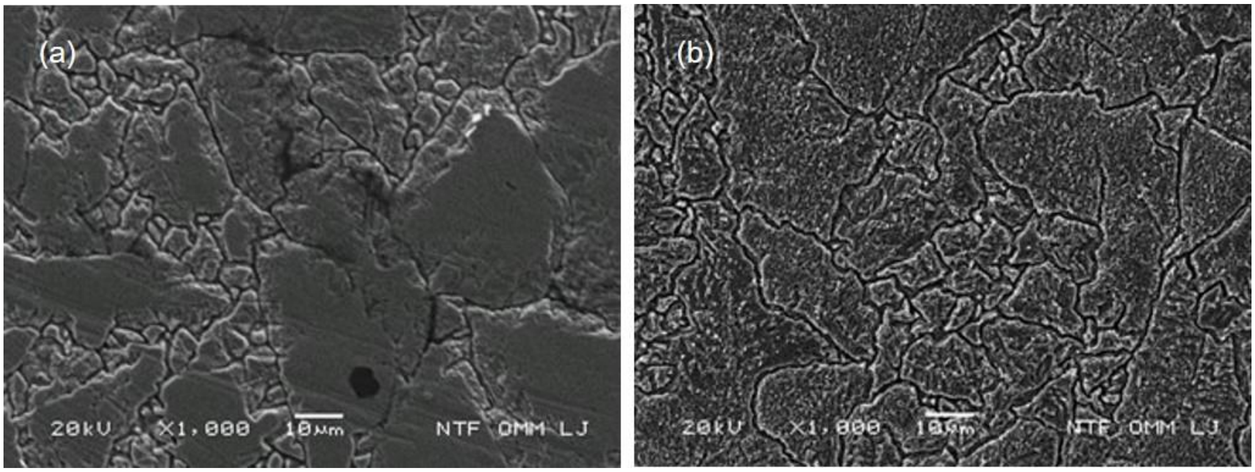

Figure 9. SEM images of copper after potentiodynamic polarization measurements in 0.5 mol/l NaCl solution containing (a) 0.2% and (b) 1.4% v/v of 75% ethanolic extract of the *P. pavonica* at 303 K.

In contrast, the copper surface was less damaged in the presence of optimum concentration of the inhibitor extract (1.4% v/v of 75% ethanolic extract of the brown algae *P. pavonica*) (Figure 9b). This indicates that the brown algae *P. pavonica* ethanol-extracted phenolics can prevent the copper from corroding in a near-neutral chloride solution by formation of a protective inhibitor film on the substrate surface; the exact structure will be the subject of further investigations. These findings further support the idea of algae phenolics as corrosion inhibitors.

Inhibition mechanism

The mechanisms of action of different organic inhibitors are influenced by various factors, such as the composition of the inhibitors, their chemical structure, the metal substrates used, their charge, their distribution, the presence of other interfering substances, etc., as well as the nature of the interaction between inhibitor and metal. Although several inhibition mechanisms have been proposed for organic corrosion inhibitors (*e.g.* adsorption, film formation, electrostatic repulsion, complex formation, pH of the medium, cathodic protection, and oxygen scavenging), it is generally recognised that active functional groups in the chemical structure of the inhibitors play a key role in their effectiveness [12, 18, 37–39, 45].

Phenolic compounds exhibit a wide variety of compounds, ranging from simple structures containing a single aromatic ring with a hydroxyl group attached to it to highly complex polymers, such as the phlorotannins, characteristic of algal samples. However, all phenolics have conjugated double bonds formed by aromatic rings and polar oxygen-containing functional groups, which are recognised to be responsible for their good antioxidant and corrosion inhibitive activity [12, 18, 26, 32]. In this study, the activity of extracts obtained with different solvents was investigated and the extracts obtained were chemically characterised (total phenolic content) using only a non-selective spectrophotometric method. However, the extracts tested are complex mixtures of different phenolic compounds that were not individually identified and quantified. The identification and quantification of individual phenolics in extracts are extremely difficult, especially for algal samples, which contain a special class of highly complex compounds (phlorotannin) compared to the extracts of terrestrial plants, most of which are still unknown or/and for which there are no commercially available standards. On the other hand, in case of single phenolics, it's structural and electronic properties and its interaction with the metal surface greatly facilitate the explanation of the inhibitor's mechanism of action. The obtained results show that ethanol-extracted phenolics of the brown algae *P. pavonica* act as a mixed-type corrosion inhibitor for copper in NaCl solution with efficiency above 93%. Corrosion inhibition occurs by spontaneous mixed physical and chemical adsorption; heteroatom can coordinate bonds with vacant d orbitals of the copper through electron donation, furthermore, the interactions with rings containing conjugated bonds π electrons, enable the adsorption of molecules on the copper surface [12, 28, 45].

Conclusions

Experimental and theoretical methods were applied to research the inhibition ability and inhibition mechanism. The following conclusions are obtained:

1. The electrochemical tests and SEM measurements demonstrate that the ethanol-extracted phenolics of the brown algae *P. pavonica* as a mixed-type inhibitor can prevent copper corrosion in sodium chloride solution effectively.

2. Corrosion inhibition performance is found to depend on the concentration of the inhibitors and temperature.
3. Adsorption isotherm studies demonstrated that adsorption for this work was a spontaneous mixed physical and chemical adsorption which obeyed Langmuir adsorption isotherm.
4. Morphological observations with SEM and elemental analysis with EDS of *P. pavonica* confirmed aragonite.
5. The current research contributed to the knowledge of marine algae as a natural source of corrosion inhibitors since the obtained ethanol-extracted phenolics of the brown algae *P. pavonica* have been effective corrosion inhibitors of copper in sodium chloride solution. Furthermore, these findings highlight the potential usefulness of *P. pavonica* phenolics as an effective, biodegradable, non-toxic, and environmentally friendly corrosion inhibitor for preventing copper corrosion in chloride-containing environments. Further analysis should be performed to separate, identify, and quantify individual phenolics from the *P. pavonica* extract and, to investigate the single contributions of the different constituents to the mechanism of copper corrosion inhibition.

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