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Inhibition of corrosion of mild steel by an alcoholic extract of a seaweed *Sargassum muticum*

ABSTRACT

An alcoholic extract of a sea weed *Sargassum muticum* has been used to control corrosion of mild steel in 0.5 N HCl. Weight loss method and Electrochemical studies have been used in this study. Weight loss study reveals that 500 ppm of the inhibitor offers 99.25 % inhibition efficiency. Polarization study reveals that the inhibitor functions as an anodic inhibitor at higher concentration. The AC impedance spectra confirm the formation of a protective film on the metal surface. Adsorption of inhibitor molecules on the metal surface follows Langmuir adsorption isotherm.

Keywords: corrosion inhibition, mild steel, sea weed, *Sargassum muticum*, electrochemical studies, Langmuir adsorption isotherm, acid medium

1. INTRODUCTION

Extracts of plant materials are low cost and environmentally friendly. They contain many active ingredients. The molecules of these ingredients may contain hetero or polar atoms such as sulphur (S), nitrogen (N), oxygen (O), phosphorous (P) etc. The lone pair of electrons present on these atoms is pumped on to the metal surface. Thus loss of electrons from the metal surface can be avoided and corrosion inhibition takes place. Because of adsorption of inhibitor molecules on metal surface, protective film is formed on metal surface and corrosion is controlled.

Corrosion is a spontaneous and thermodynamically favourable process. Because of corrosion, every year five percentage GNP of any country is lost. However fifty percentage of corrosion loss can be avoided by the available knowledge. There are many methods used to control corrosion process. One such process is use of inhibitors. Due to their toxic nature chromates, as corrosion inhibitors

have been banned by environmental scientists. So researchers are looking for environmental friendly corrosion inhibitors such as extracts of plant materials. Several plant materials have been used for this purpose. [1-10]

Extracts of plant materials contain many active principles. They contain polar atoms such as S, N, O, P etc. Because of this nature, the lone pair of electrons present on these atoms is pumped on to the metal surface. Thus loss of electrons from the metal surface can be avoided. Hence corrosion inhibition takes place. Because of adsorption of inhibitor molecules on metal surface, protective film is formed. Thus corrosion is controlled. Various extracts of plant materials have been used to prevent a variety of metals immersed in various medium at different temperatures in presence and absence of many additives. Many methods have been employed (such as weight loss method, electrochemical studies etc) to evaluate corrosion inhibition efficiencies of inhibitors. The protective film has been analyzed by various surface analyses techniques.

Metals

Extracts of plant materials have been used to control corrosion of various metals such as steel mild steel [1-9], aluminium and its alloy, zinc and copper.

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Medium

Extracts of plant materials have been used to prevent corrosion of metals and alloys immersed in various medium such as acidic medium [1,3,5-7] basic medium and neutral medium.

Temperature

The experiments have been conducted at various temperatures [8,9].

Additives

Mixture of inhibitors shows better inhibition efficiency than individual members. This is called synergistic effect. For this purpose many additives have been used to improve the inhibition efficiency of plant extracts. For this purpose halide, sulphide and phosphonic acid have been used.

Methods

To evaluate the corrosion inhibition efficiency of various plant extracts, several methods such as weight loss method [1-4,6] and electrochemical studies (polarization, AC impedance spectra [8]) have been employed.

Surface morphology of protective film

The protective films formed on metal surfaces have been analyzed by various surface analysis techniques FTIR spectroscopy, UV-Visible spectroscopy, SEM, EDAX and AFM.

Adsorption isotherm

The protective film formed on the metal surface by adsorption of active principles of various plant extracts on the metal surface. The adsorption isotherms are usually Freundlich adsorption isotherm, Temkin adsorption isotherm and Langmuir adsorption isotherm[1,2,5,6].

Thermodynamic parameters

From the adsorption isotherms various thermodynamic parameters such as changes in free energy, entropy, enthalpy, and activation energy [2] have been calculated.

Plant materials

Extracts of various parts of the plant have been used as corrosion inhibitors. Fruit leaves [1,5,8], roots, barks, flowers, seeds, stem, gum, husk and peel have been used as corrosion inhibitors.

Extracts

The plant materials have been extracted by making use of alcohol [1], acid and water [2,3]. Various inhibitors used and methods employed in evaluating their corrosion inhibition efficiencies are summarized in Table1.

In the present study an alcoholic extract of a sea weed, *Sargassum muticum*, has been used to control corrosion of mild steel in 0.5N HCl. Electrochemical studies such as polarization study and AC impedance spectra have been used.

Table 1. Corrosion inhibition by plant extracts

Tabela 1. Inhibicija korozije biljnim ekstraktima

S. No	Metal	Medium	Inhibitor	Additive/ temperature	Method	Findings	Ref.
1	X60 carbon steel	15% HCl solution	Ethanolic extracts of date palm leaves and seeds		Weight loss, electrochemical Techniques and photochemical screening	Inhibition efficiency increased with increase in concentration of the extracts and temperature. Mixed type inhibitors. Langmuir adsorption isotherm model	[1]
2	Carbon steel	Saline formation water	Centaurea cyanus aqueous extract		Weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques	Mixed-type inhibitor, Langmuir adsorption isotherm	[2]
3	Mild steel	HCl aqueous solution	Gorse aqueous extract		Weight-loss measurements, potentiodynamic polarization curves, electrochemical impedance spectroscopy and scanning electron microscopy	Reducing both the anodic and cathodic current density	[3]

4.	Carbon steel API 5LX	Hypersaline environments	Neem extract		Weight loss, electrochemical studies, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction spectroscopy (XRD)	Inhibit corrosion process	[4]
5.	Mild steel	1 M H ₂ SO ₄ solution	Acacia cyanophylla leaves extract		Polarization techniques and electrochemical impedance spectroscopy	Mixed inhibitor, Langmuir isotherm model	[5]
6.	Mild steel	Hydrochloric acid solution	Alpinia galanga		Weight loss method, scanning electron microscopy	Langmuir adsorption isotherm	[6]
7.	Mild steel	15 and 20% HCl solutions	Coal-tar distillation products [CTDP] and the aqueous extract of ginger		Weight loss of the steel	Decrease of corrosion rate and increase of inhibition efficiency	[7]
8.	Carbon steel	Carbon dioxide saturated chloride carbonate solution	Olive leaf extract	25°C and 65°C	Linear polarization resistance technique, electrochemical impedance spectroscopy, scanning electron microscopy and Fourier transform infrared spectroscopy	The adsorption of olive leaf extract on the carbon steel surface	[8]
9	Mild steel	15 wt.% HCl	Durum wheat	Temperature (20-60°C) and immersion time (5-24h)	Weight losses, Fourier transform infrared spectroscopy (FTIR), SEM, EDS spectroscopy and surface profilometry	Langmuir adsorption isotherm	[9]
10	J55 steel	CO ₂ -saturated 3.5 wt. % NaCl solution	Tangerine peel extract		-	Mixed type green inhibitor, the Langmuir isothermal absorption model and the El-Awady dynamic model	[10]

2. MATERIALS AND METHODS

The present investigation deals with the analysis of mild steel corrosion in 0.5N HCl and the inhibitive effect of a seaweed extract (SWE) by weight loss and electrochemical techniques.

Mild steel specimen

The mild steel specimens used for weight loss and surface examination studies were composed of C - 0.079%, P - 0.025%, Mn - 0.018%, S - 0.021% and the remainder Fe and of dimension 5.0 cm x 1.0 cm x 0.05 cm. For electrochemical techniques, mild steel rod of above said composition encapsulated in Teflon with an unprotected area of 1cm² was used. Prior to each experiment, the metal specimens were polished to mirror finish with different grades of emery sheets, washed with double distilled water, degreased using acetone; air dried and preserved. All the corrosive electrolytes

(0.5N HCl) were prepared by distilled water and standardized.

Seaweed Extract (SWE) preparation

The sea weed chosen for the study was identified as *Sargassum muticum*, Figure 1. The seaweed used for this study was collected from Ramanathapuram, Tamilnadu, India.

Sargassum muticum, commonly known as Japanese wire weed, is a large brown seaweed of the genus *Sargassum*. It is an invasive seaweed with high growth rate (up to 10 cm per day during spring). It has an efficient dispersion thanks to its floats [11].

The sea weed was dried completely, powdered and weighed. The extract was prepared by refluxing 5g of powdered sea weed in ethanol medium for 8 hours (Figure 2). Then the extract was filtered after one day and placed in an air tight container.

Figure 1: *Sargassum muticum*Slika 1: *Sargassum muticum*

Based on literature review, the *Sargassum muticum*, was selected for the study due to the presence of the active components. The components of the sea weed extract (Figure 2) of *Sargassum muticum* was found to contain the following 12 compounds, namely geranyl isovalerate, oleic acid, 17-octadecynoic acid, 9,12,15-octadecatrienoic acid, 2,3-dihydroxypropyl ester (zzz), n-hexadecanoic acid, trans-13-octadecenoic acid, methyl ester, 6,9,12,15-

docosatetraenoic acid, methyl ester, gibberellic acid, fenretinide, 9,10-secocholesta, 5,7,10(19)-triene-3,24,25-triol, cholestane-3-O1,2-methylene. Structures of some important compounds are shown in Figure 3.

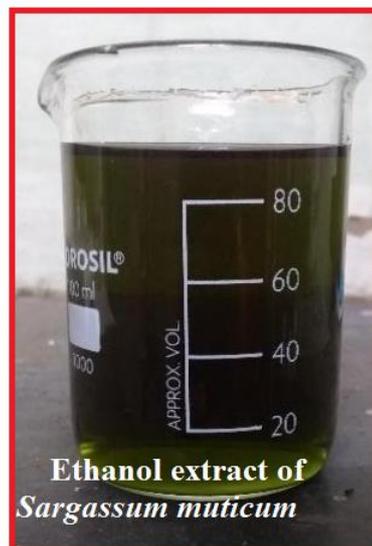
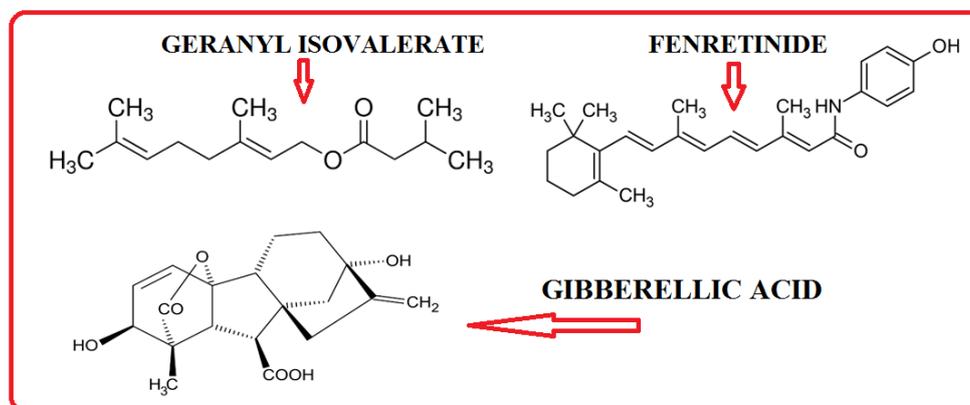
Figure 2: Ethanol extract of *Sargassum muticum*Slika 2: Alkoholni ekstrakt *Sargassum muticum*

Figure 3. Structures of some important active principles

Slika 3. Strukture nekih važnih aktivnih principa

Gravimetric method (Weight loss method)

The pre weighed mirror polished mild steel rods were suspended in 100mL of each of the aggressive environment, 0.5N HCl with and different SWE concentrations. After 52 hrs immersion period, the specimens were removed, washed, dried and re-weighed using ACCULAB Electronic top loading, analytical balance. From the weight loss inhibition efficiency and corrosion rate was calculated as

$$\text{Inhibition efficiency (\%)} = [(W_0 - W_i) / W_0] \times 100 \quad (1)$$

$$\text{Corrosion rate (mmpy)} = 87.6 W / Atd \quad (2)$$

Where W_0 and W_i are the loss in weight of the metal sheet exposed with SWE respectively and W is the mass loss. A , t and d respectively symbolise the exposed area of metal rod in cm^2 , time of exposure in h and density of mild steel in g/cm^3 .

The analyze impact of temperature on the efficiency of SWE, the same gravimetric technique

was executed at the Room temperature range of 303 K for 100 ppm of SWE.

Electrochemical Techniques

Electrochemical measurements were performed in an Ivium compact-stat electrochemical measurement unit. Impedance and polarisation measurements were carried out using a classical three electrode pyrex glass cell set up with a capacity of 100 mL. A platinum wire and a mild steel rod with 1 cm² exposed surface area were employed as counter electrode and working electrode respectively (Figure 4). All the potential data were recorded with reference to saturated calomel electrode. Prior to each measurement, the mild steel working electrode was immersed in the test electrolyte at OCP to attain the stable state.

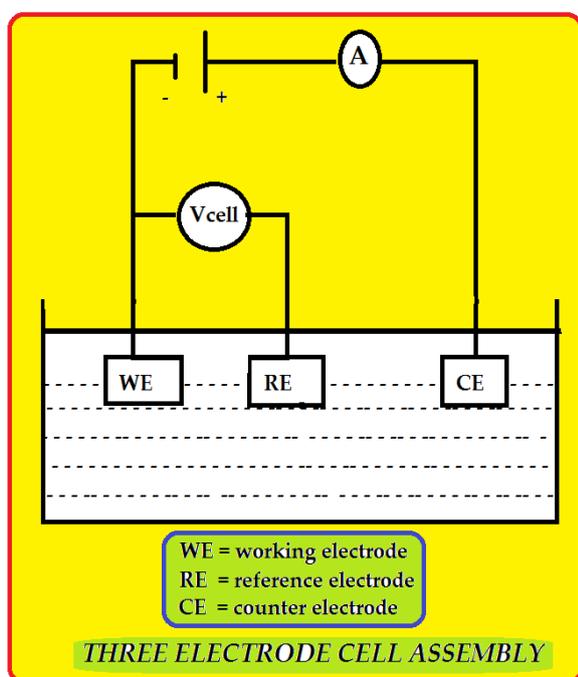


Figure 4. Three electrode cell assembly

Slika 4. Sklop ćelije sa tri elektrode

Electrochemical impedance study (EIS)

The AC impedance measurement was performed at corrosion potentials over a frequency range 0.01 Hz to 10 KHz with 25 mV peak-peak to voltage excitation per second. Electrochemical resistance, R_t and double layer capacitance, C_{dl} were computed from the Z_{real} Vs $Z_{imaginary}$ plot. From R_t data the inhibition efficiency of SWE was figured using the formula,

$$\text{Inhibition efficiency (\%)} = [(R_{ct(i)} - R_{ct(b)}) / R_{ct(i)}] \times 100 \quad (3)$$

where, $R_{t(i)}$ and $R_{t(b)}$ are the electrochemical resistance in the presence and absence of SWE.

Polarisation technique

The Tafel polarization measurements were executed immediately after EIS at a sweep rate of 1mV/sec over potential range of -200 mV to +200 mV pertaining to open circuit potential. The corrosion potential, E_{corr} , corrosion current, I_{corr} and slope for the cathodic and anodic Tafel curves, b_c and b_a were generated with Ivium soft software. The inhibition efficiency was computed as,

$$\text{Inhibition efficiency (\%)} = [(I_{corr(b)} - I_{corr(i)}) / I_{corr(b)}] \times 100 \quad (4)$$

where, $I_{corr(b)}$ and $I_{corr(i)}$ refer the corrosion current with and without SWE.

Equivalent circuit (RC circuit) diagram

An Equivalent circuit diagram is a circuit (Figure 5) with both a resistor (R) and a capacitor (C). RC circuits are frequent element in electronic devices. They also play an important role in the transmission of electrical signals in nerve cells. The crucial parameter that describes the time dependence is the "time constant" RC. This transient response time T , is measured in terms of $\tau = R \times C$, in seconds, where R is the value of the resistor in ohms and C is the value of the capacitor in Farads. This then forms the basis of an RC charging circuit were $5T$ can also be thought of as "5 x RC".

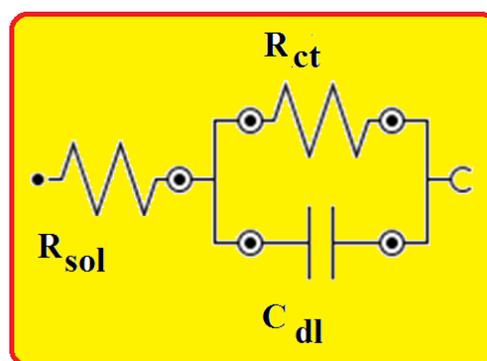


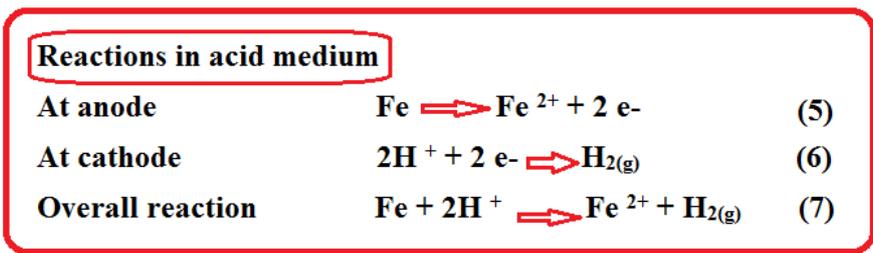
Figure 5. Electrical equivalent circuit proposed for simulate the impedance diagram

Slika 5. Predloženo električno ekvivalentno kolo za simulaciju impedansnog dijagrama

3. RESULTS AND DISCUSSION

Method of metal weight loss

The electrochemistry of any corroding metal in acid medium encompasses partial anodic metal dissolution and partial cathodic hydrogen evolution in accordance with the following Scheme 1.



Scheme1. Anodic and Cathodic reactions in acid medium

Shema 1. Anodne i katodne reakcije u kiseloj sredini

In line with Equation 7 corrosion rate of the metal can be determined by non electrochemical methods like, weight loss, hydrogen evolution, measurement of dissolved Fe²⁺ concentration and change in pH of the electrolyte. Among these the most widely used weight loss method, due to its simplicity and reliability of the measurement, becomes the baseline method in many corrosion monitoring programs. In the present study the corrosion inhibitive ability of SWE obtained for mild steel exposed to 0.5N HCl composed of 100ppm, 200ppm, 300ppm, 400ppm, 500ppm at 303K for 52 h (3 days) was presented. Inspection of data reveals a steady decrease in metal loss as well as corrosion rate and increase in efficiency with SWE concentration. This aspect results from the movement of SWE (sea weed extract) components from the bulk electrolyte onto the mild steel surface and adsorb as a thin film which shields the metal surface from the aggressive acid environment. The enhanced efficiency at 100 ppm concentration may be attributed to the greater coverage by more number of components of SWE on the mild steel surface thereby blocking active sites of the electrode surface at the electrode - acid interface

and the corrosion occurs at the unblocked electrode sites. The increase of inhibition efficiency of mild steel alloy which controls the corrosion is calculated in Table 2. As the concentration of inhibitor increases, corrosion rate decreases and inhibition efficiency increases (Figure 6).

Table 2. Inhibition efficiency at various concentration of SW extract for mild steel corrosion in 0.5 HCl

Tabela 2. Efikasnost inhibicije pri različitim koncentracijama ekstrakta SW za koroziju mekog čelika u 0,5 HCl

Concentration (ppm)	Weight loss (g)	Corrosion Rate (mmpg)	Surface Coverage (θ)	IE %
Blank	0.1734	5.47	-	-
100ppm	0.0197	0.62	0.8864	88.64
200ppm	0.0188	0.59	0.8916	89.16
300ppm	0.0131	0.41	0.9245	92.45
400ppm	0.0038	0.12	0.9781	97.81
500ppm	0.0013	0.04	0.9925	99.25

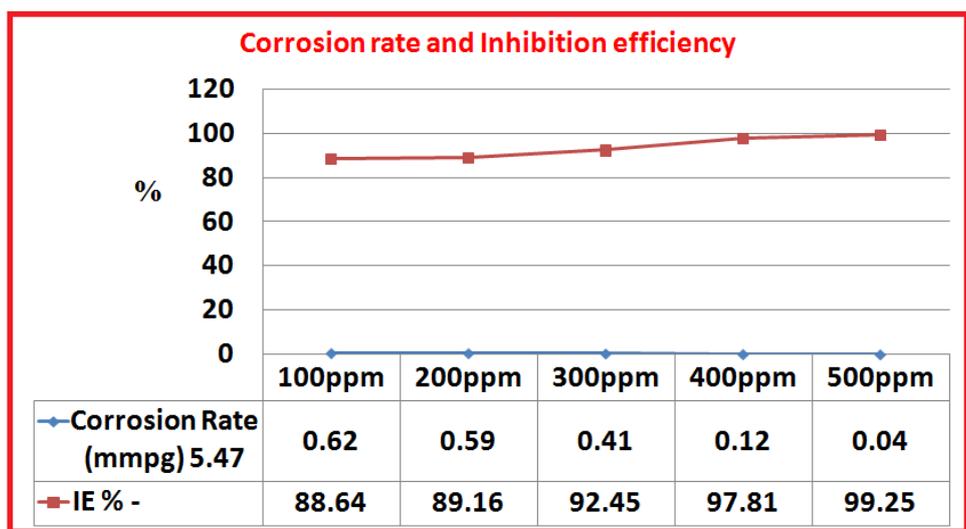


Figure 6. Corrosion rate and inhibition efficiency

Slika 6. Brzina korozije i efikasnost inhibicije

Langmuir Adsorption Isotherm

A plot of C vs C/θ gives a straight line is obtained with very high correlation coefficient R^2 (0.997). This indicates that the adsorption of active principle molecules on the metal surface takes place by Langmuir adsorption isotherm (Figure7). There is formation of monolayers. The C (concentration in ppm) and C/θ values are given in Table 3.

Table 3. The C (concentration in ppm) and C/θ values for Langmuir adsorption isotherm

Tabela 3. Vrednosti C (koncentracija u ppm) i C/θ za Langmuirovu adsorpcionu izoterma

C , ppm	Surface coverage θ	C/θ
100	0.8864	113
200	0.8916	224
300	0.9245	325
400	0.9781	409
500	0.9925	504

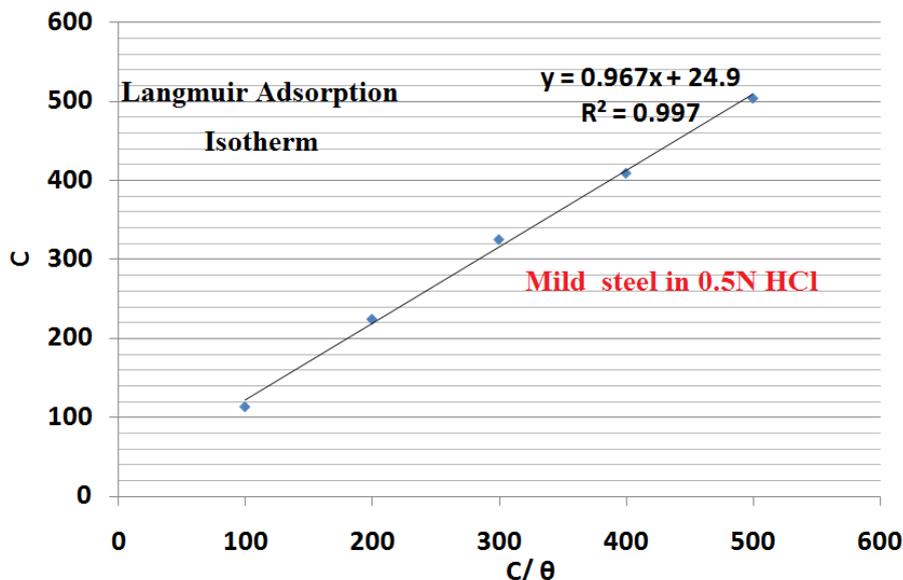


Figure 7. Langmuir adsorption isotherm

Slika 7. Langmuir-ova adsorpciona izoterma

Electrochemical Measurements

Electrochemical studies such as polarization study and AC Impedance spectra have been widely used in corrosion inhibition study [12-16]. If there is corrosion protection, linear polarization resistance increases, corrosion current decreases, charge transfer resistance increases, double layer capacitance decreases, impedance value increases and phase angle value increases.

Electrochemical impedance spectroscopy (EIS) (AC Impedance spectra)

EIS is a sophisticated technique, widely employed to study the corrosion behaviour of mild steel and also the adsorption phenomena. EIS measurements of mild steel electrode was performed at is open circuit in blank 0.5N HCl electrolyte and also in the presence of SW extract concentrations. The corresponding Nyquist, Bode modulus and phase angle representations of EIS are portrayed in Figures 8-10, for mild steel after the addition of SW extract.

Table 4. Corrosion parameters for mild steel at various concentrations of SW extract by Impedance method for 52h

Tabela 4. Parametri korozije za meki čelik pri različitim koncentracijama SW ekstrakta metodom impedancije tokom 52h

Inhibitor ppm	OCP V	R_{ct} Ohm cm^2	C_{dl} mF/ cm^2
Blank	-0.389	11.174	19
100ppm	-0.385	17.721	17.3
200ppm	-0.379	34.945	17.1
300ppm	-0.372	27.421	16.9
400ppm	-0.368	92.31	16.7
500ppm	-0.355	94.31	16.5

Only a single depressed capacitive semicircle is seen in all the cases at high frequency with deviation of their centers from the real axis. The EIS parameters, charge transfer resistance (R_{ct})

and capacitance of the double layer (C_{dl}) were simulated by the simple equivalent circuit. Charge transfer resistance, R_{ct} indicates the degree of electron transfer across the surface. It is inversely proportional to corrosion rate. Efficiency of inhibitor is computed from charge transfer resistance in the presence ($R_{ct(i)}$) and absence ($R_{ct(b)}$) of inhibitor as

$$\text{Inhibition efficiency (\%)} = [(R_{ct(i)} - R_{ct(b)}) / R_{ct(i)}] \times 100 \quad (3)$$

As presented in Table 4, R_{ct} values increased with extract concentration which leads to the reduction in mild steel corrosion rate and increase

in inhibition efficiency. SW extract shows greater efficiency in 0.5N HCl. The higher efficiency in HCl indicates greater adsorption of inhibitor. This might be due to the specific tendency of Cl^- ions to strongly adsorb on the steel surface. It is observed from the Figures 8-10 that as the concentration of inhibitor increases, impedance value increases and also phase angle value increases (Figure 11).

Corrosion parameters from AC impedance spectra are compared in Figure 12. The inhibition efficiency calculated from R_t values (equation 3) is 88.16%, calculated for the 500 ppm of inhibitor system.

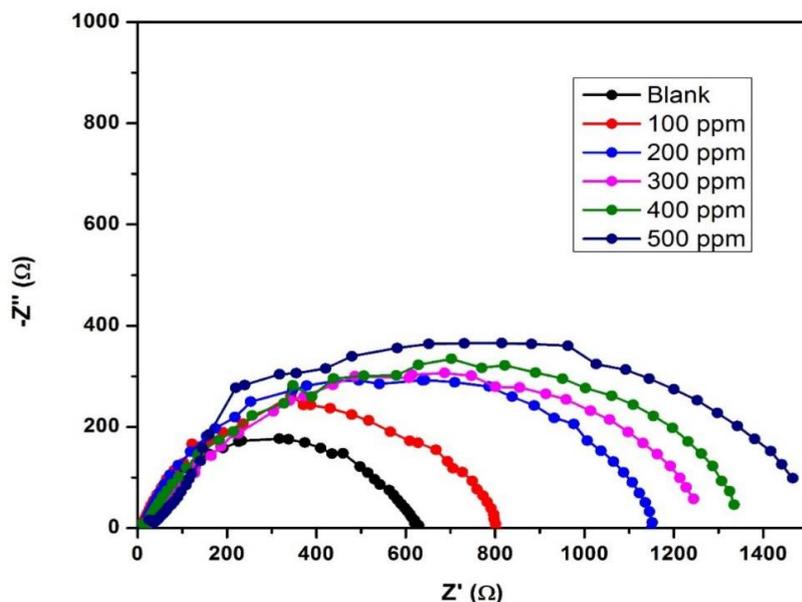


Figure 8. Nyquist plots

Slika 8. Nyquist-ove krive

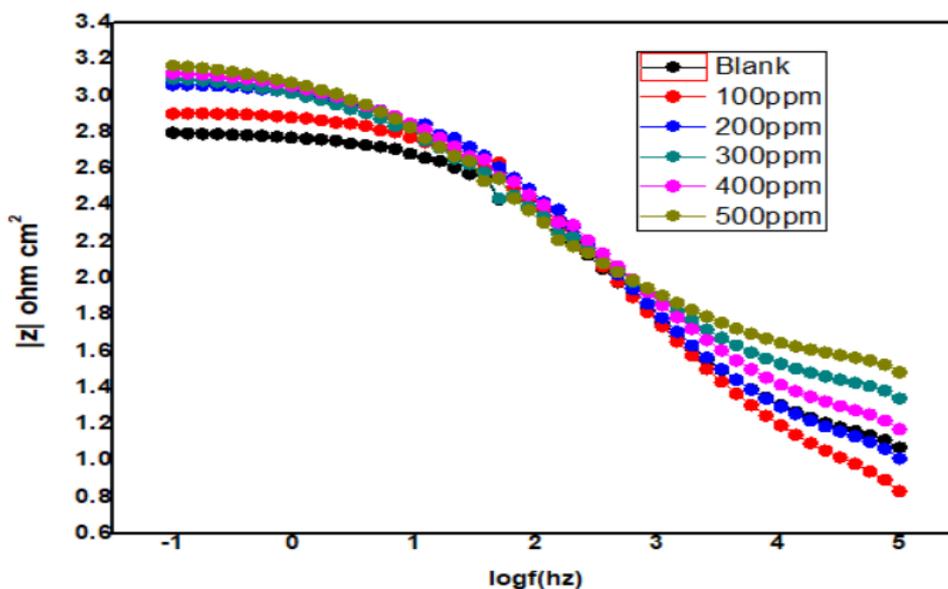


Figure 9. Bode impedance plots

Slika 9. Bode-ove krive impedance

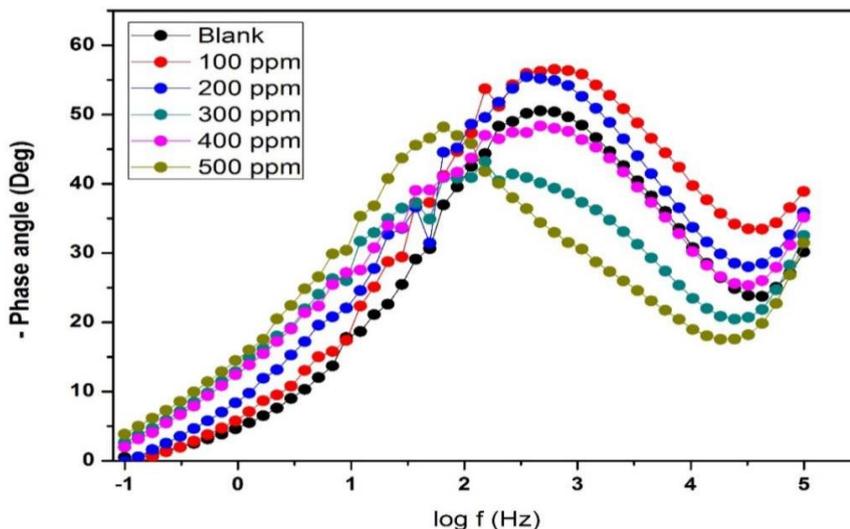


Figure 10. Bode phase angle plots

Slika 10. Bode-ove fazne krive

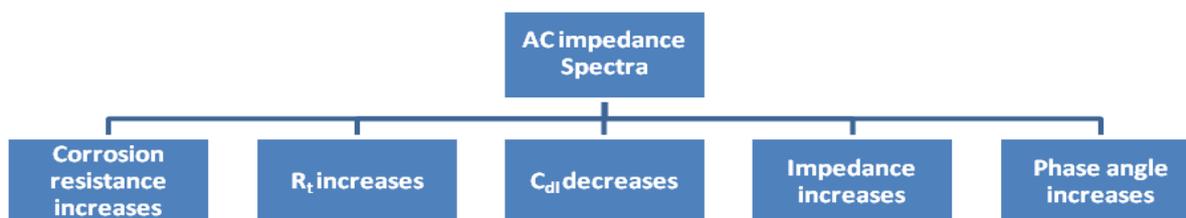


Figure 11. Correlation among corrosion parameters in AC impedance spectra

Slika 11. Korelacija parametara korozije u spektrima impedance naizmjenične struje

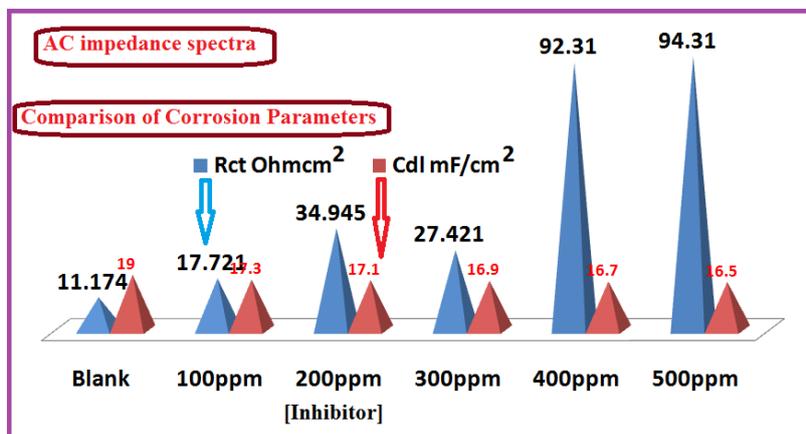


Figure 12. Comparison of corrosion parameters from AC impedance spectra

Slika 12. Poređenje parametara korozije iz spektra impedance naizmjenične struje

Tafel polarization studies Tafel potentiodynamic polarization study is used to explore the corrosion inhibition (CI) of alloys and metals. When corrosion rate decreases, there is increase in linear polarization resistance (LPR) and decrease of corrosion current (I_{corr}) (Figure 13).

Hence, when anodic reaction is predominantly controlled, there is shift in corrosion potential (E_{corr}) to anodic side-noble side (less -ve side or +ve side) and when cathodic reaction is predominantly controlled, there is shift of E_{corr} to active side (more -ve side). If both, anodic and cathodic reactions are predominantly controlled, then the shift in E_{corr} is less (within 50 mV/decade).Figure 14 illustrates

the polarization curves (Tafel plots) of MS alloy evaluated in different concentrations of inhibitor at a room temperature. To study the effect of SWE (Seaweed Extract) on the corrosion process of mild steel, anodic and cathodic polarization behaviour in 0.5N HCl was recorded for different inhibitor concentrations (Table 5).

Table 5. Corrosion parameters of MS Alloy in SW Extract Solution in 52h for Polarization Study

Tabela 5. Parametri korozije MS legure u rastvoru ekstrakta SW u toku 52h za studiju polarizacije

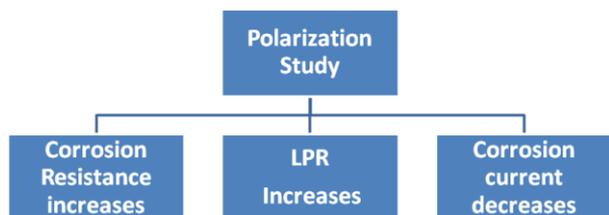


Figure 13. Correlation among corrosion parameters of polarisation study

Slika 13. Korelacija među parametrima korozije pri polarizacionoj studiji

Inhibitor ppm	E _{corr} mV/SCE	LPR Ohmcm ²	I _{corr} A/cm ²
Blank	-533	49.051	2.66 x10 ⁻⁰³
100ppm	-550	194.15	0.327 x10 ⁻⁰³
200ppm	-548	463.25	0.300 x10 ⁻⁰³
300ppm	-540	868.0	0.162 x10 ⁻⁰³
400ppm	-520	1493.9	0.0117 x10 ⁻⁰³
500ppm	-514	1950.3	0.00293 x10 ⁻⁰³

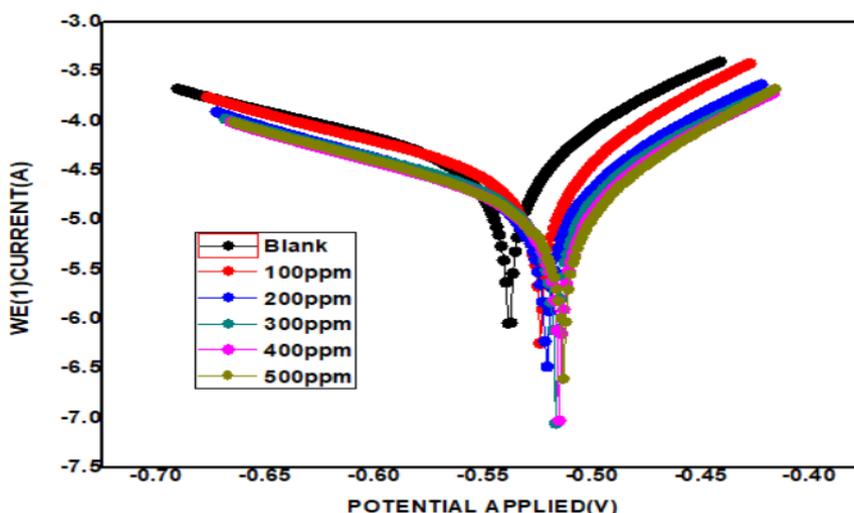


Figure14. Tafel behavior of mild steel in 0.5N HCl with different concentrations of SWE for 52h

Slika 14. Tafel-ove krive mekog čelika u 0,5N HCl sa različitim koncentracijama SWE tokom 52h

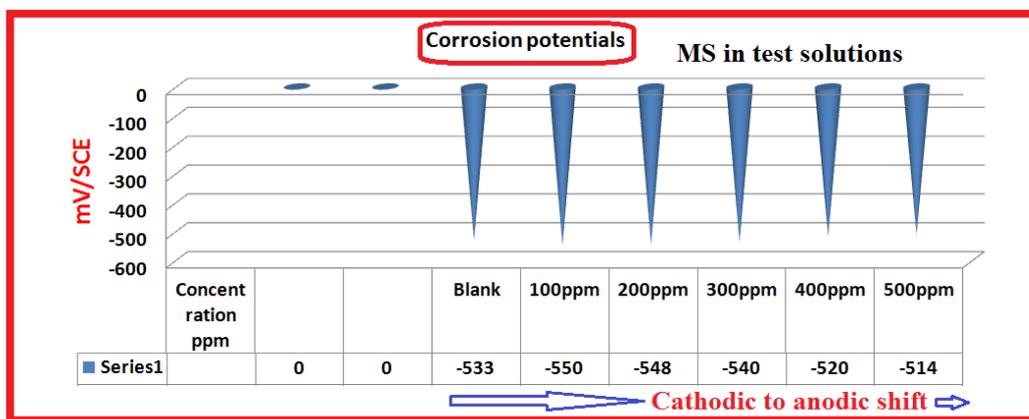


Figure15. The corrosion potential

Slika 15. Potencijal korozije

Corrosion parameters of MS Alloy in SW Extract Solution for 52h obtained by Polarization Study

When MS Alloy immersed in 0.5N HCl medium for 52 h, LPR value is 49.051 Ohmcm². The corrosion current (I_{corr}) value is 2.66×10^{-03} A/cm². The corrosion potential (E_{corr}) value is -533mV vs SCE.

When MS Alloy immersed in 0.5N HCl medium for 52 h, in presence of inhibitor (500ppm), LPR value is 1950.7 Ohmcm². The corrosion current (I_{corr}) value is 0.293×10^{-5} A/cm². The corrosion

potential (E_{corr}) value is -514 mV vs SCE. Thus the polarization study leads to the conclusion that corrosion resistance of MS in 0.5N HCl medium increases in presence of inhibitor (500ppm). The corrosion potential shifts to the anodic side (Figure 15). There is increases in LPR value (Figure 16) and decrease in corrosion current value (Figure 17). The corrosion inhibition efficiency calculated from polarization parameters (equation 4) is 97.48%.

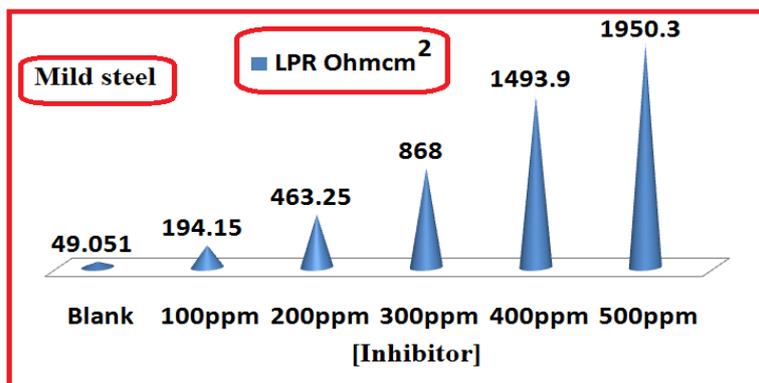


Figure 16. Comparison of LPR values

Slika 16. Poređenje vrednosti LPR –a

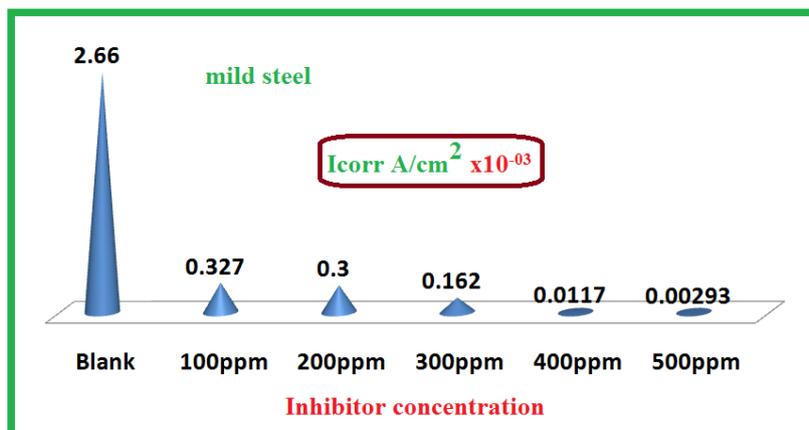


Figure 17. Comparison of corrosion current values

Slika 17. Poređenje vrednosti struje korozije

4. CONCLUSION

- An alcoholic extract of a sea weed *Sargassum muticum* has been used to control corrosion of mild steel in 0.5N HCl.
- Weight loss method and Electrochemical studies have been used in this study. Weight loss study reveals that 500 ppm of the inhibitor offers 99.25% inhibition efficiency.
- Polarization study reveals that the inhibitor functions as an anodic inhibitor at higher concentration. The AC impedance spectra

confirm the formation of a protective film on the metal surface. Adsorption of inhibitor molecules on the metal surface follows Langmuir adsorption isotherm.

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IZVOD

Inhibicija korozije mekog čelika alkoholnim ekstraktom algi *Sargassum muticum*

Alkoholni ekstrakt morske trave Sargassum muticum korišćen je za kontrolu korozije mekog čelika u 0,5N HCl. U ovoj studiji su korišćene metode gubitka težine i elektrohemijske studije. Studija gubitka težine otkriva da 500 vodppm inhibitora daje 99,25 % efikasnost inhibicije. Studija polarizacije otkriva da inhibitor funkcioniše kao anodni inhibitor u većoj koncentraciji. Spektar impedanse naizmenične struje potvrđuje stvaranje zaštitnog filma na površini metala. Adsorpcija molekula inhibitora na površini metala prati Langmuirovu izotermu adsorpcije.

Ključne reči: inhibicija korozije, meki čelik, morski korov, *Sargassum muticum*, elektrohemijske studije, Langmuirova izoterma adsorpcije, kiseli medijum

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