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ORIGINAL PAPER

An eco-friendly green biopolymer blend for copper corrosion inhibition

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Abstract

Copper is a fascinating metal with wide applications since ancient time. Although Copper is resistant to certain environmental factors and several chemicals, aggressive medium could deteriorate the metal leading to its complete damage. The need for an eco-friendly corrosion inhibitor is much relevant in the present scenario. The inhibition efficiency of gum arabic (GA), sodium alginate (SA) and its blend is investigated using weight loss method, potentiodynamic polarization and electroscopic impedance spectroscopy (EIS) analysis in 1.0 M HCl solution. Higher inhibition efficiency is obtained at room temperature for the blend with 6666 ppm GA and 3333 ppm SA. The values of inhibition efficiency obtained are 88.8%, 80.5% and 86.2% using weight loss, potentiodynamic polarization and EIS analysis, respectively. The investigations are complemented by atomic force microscopy and field emission scanning electron microscopy which helped to analyze the physical adsorption of the biopolymer on the metal surface. The adsorption of the biopolymer on Copper obeyed Langmuir isotherm and inhibition efficiency has an inverse relation with temperature.

Keywords Biopolymer blend · Copper · Corrosion inhibition

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Introduction

Copper metal is extensively used in construction, electrical and transportation owing to its high thermal and electrical conductivity [1]. Copper is having face-centered cubic crystal structure with a thermal conductivity of 401 W/mK [2]. Corrosion adversely affects the performance of metal and periodic cleaning is necessary to maintain its efficiency. The cleaning of these oxide layers is done in industries by acid pickling [3]. Acidic medium for cleaning metals destroys its intrinsic properties. This can be prevented by addition of corrosion inhibition substances along with the cleaning medium [4].

Corrosion inhibitors are generally classified into anodic inhibitors, cathodic inhibitors and mixed inhibitors. Most anodic inhibitors contain CrO_4^{2-}, NO_2^- or MoO_4^{2-} that forms a passive layer on the surface of anode [5]. This type is not always recommended, because it may increase the corrosion rate if the treatment rate is not sufficient. Cathodic inhibitors are oxygen scavengers, cathodic poisoner or cathodic precipitates that precipitates on cathodic surface by limiting the cathodic chemical reaction. Mixed inhibitors work by adsorbing on metal surface by chemisorption or physisorption. Most used corrosion inhibitors are mixed type like sulfur-containing compounds, amines, mercaptobenzothiazole, imidazoline or nitrogen containing compounds [6]. Inorganic and organic coatings were widely used as corrosion inhibitors. However, the wide use of these coatings in contact with the environment creates severe environmental pollution [7]. These problems with synthetic or chemical based corrosion inhibitors can be solved by the use of environmental friendly materials as corrosion inhibitors [8–10]. The use of polymer, polymer blends or copolymers for various applications is not new [9, 11, 12]. In the present study, biomaterials like gum arabic (GA) [13]and sodium alginate (SA) [11, 14] are used as corrosion inhibitors and their anti-corrosion activity is attributed to the existence of heteroatoms like nitrogen, oxygen and cyclic rings in their heterostructures.

GA is a natural gum obtained from the hardened sap of Acacia trees belonging to Leguminosae family. Water soluble GA is made up of a mixture containing arabinogalactan, oligosaccharides, polysaccharides and glycoproteins [15]. Functional groups in GA form metal complexes with copper and behave as a protective coating shielding it from corrosion. Sucrose, polysaccharides, arabinogalactan, oligosaccharides and glycoprotein present in GA helps in adsorbing to the metal surface. Shen et al. recently reported the corrosion inhibition efficiency of GA in oil industry for carbon steel. GA forms a film on carbon steel by means of chemisorption and thereby prevents corrosion in the oil-filled synthetic brine environment achieving 94% corrosion inhibition efficiency at room temperature [12]. GA was also used to inhibit the corrosion caused by NaOH on aluminum. The results showed that the inhibition is caused by the adsorption of GA and followed Langmuir and Freundlich adsorption isotherms [13]. Umoren et al. studied the corrosion behavior of mild steel and aluminum under acidic medium in the presence of GA. Physical adsorption was observed for GA with aluminum and chemical adsorption was observed with mild steel. The inhibition efficiency increased with an increase in GA concentration at 0.5 g/L which results in 37.88% at 60 °C for mild steel and 79.69% at 30 °C for aluminum [16].

SA is a biopolymer obtained from the cell walls of brown algae which grows in sea, such as Laminaria or Fucus [17]. Obot et al. showed the inhibition effect of SA on the corrosion of API X60 steel in 3.5% NaCl solution [14]. Jmiai et al. reported that alginate biopolymer inhibited the corrosion of copper in 1 M HCl solution. They studied that alginate biopolymer adsorbed physically on copper surface with an inhibition efficiency of 83% at 0.1 mg/L^{-1} [18].

Separate works are available for the inhibition effect of SA and GA on various metals both under acidic and alkaline medium. The present study introduced a green polymer blend comprising of GA and SA as a corrosion inhibitor of the copper in dilute HCl (1.0 M). A single miscible phase of GA and SA is formed as a corrosion inhibitor and inhibition efficiency is compared with pure GA and SA. The corrosion inhibition efficiency was studied by carrying electrochemical analysis including electrochemical impedance spectroscopy (EIS). AFM and FE-SEM studies were performed to understand the morphology and adsorption effect of blend on the metal surface.

Methodology

Materials

Copper sheet of 35 Gauge (0.191 mm thickness) was purchased from ART IFACT company, India. Hydrochloric acid (37% w/w) was purchased from Sisco Research Laboratories, Mumbai. SA, GA, methanol (> 99.8%) and acetone (> 99%) were purchased from Sigma Aldrich, USA. Deionized (DI) water obtained from Isochem laboratories, Cochin, was used for preparing the solutions.

Preparation of solutions

1.0 M HCl is prepared by diluting 4.1 ml concentrated HCl in 45.9 ml DI water and stirred well using a glass rod. GA and SA in required concentration as mentioned in Table 1 is added to 50 ml of 1.0 M HCl solution and stirred continuously for about 1 h using a magnetic stirrer. Thus, copper coupons are dipped in this prepared solution for performing the potentiodynamic polarization studies and EIS analysis.

Material characterization

The electrochemical measurements were analyzed by CH Instruments Software version 18.01. AFM images were obtained with Park Systems XE-70, Germany, in non-contact mode using a cantilever tip. All the electrochemical measurements were taken in Electrochemical Workstation, 604 D, CH Instruments, USA. Morphological analysis of the copper coupons before and after corrosion was performed using FE-SEM integrated with EDS/EBSD, Supra 40 VP (Carl Zeiss), Germany.

Table 1 Concentration of GA and SA in 50 ml of 1.0 M HCl solution

Sl. no	Sample code	SA (ppm)	GA (ppm)
1	Blank	0	0
2	SA1	50	0
3	SA2	100	0
4	SA3	500	0
5	SA4	1000	0
6	SA5	10,000	0
7	GA1	0	50
8	GA2	0	100
9	GA3	0	500
10	GA4	0	1000
11	GA5	0	10,000
12	GASA1	5000	5000
13	GASA2	3333	6666
14	GASA3	6666	3333

Gravimetric corrosion measurements

Before performing all experiments, copper coupon was washed with distilled water and acetone followed by degreasing with methanol and dried at 50 °C for 5 min.

For mass loss experiment, copper coupon of dimensions (1 cm × 1 cm) was cut from the copper sheet with an exposed surface area of 1.0 cm^2 by masking the other surface and used for the all experiments. The masses were measured using a Shimadzu electronic weighing balance of model ATY224 with a resolution of 0.0001 mg. The initial mass (M_i) of copper coupon after proper cleaning are obtained using the electronic balance. Copper coupons are then immersed in 1.0 M HCl for 24 h with and without the presence of GA, SA and blend. After immersion, copper coupon is removed from the solution, washed with distilled water, cleaned with methanol and dried at 50 °C. The final mass (M_f) is measured and the corrosion rate (CR) from mass loss is calculated from the equation given below.

$$\mathrm{CR} = \left(M_i - M_f\right)/\mathrm{ST} \tag{1}$$

where S is area of the copper coupon (1 cm^2), and T is the time period of immersion (h).

The inhibition efficiency is evaluated by,

$$\mathrm{IE\%} = \left[\left(\mathrm{CR} - \mathrm{CR}_{(\mathrm{inh})}\right) \times 100\right]/\mathrm{CR} \tag{2}$$

where CR is the corrosion rate without inhibitor and $\mathrm{CR}_{(\mathrm{inh})}$ is the corrosion rate with inhibitor.

Electrochemical corrosion measurements

The working electrode, counter electrode and reference electrode used were copper coupon, platinum wire and Ag/AgCl rod, respectively. 1.0 M HCl solution with different concentration of blend was used as electrolyte in which the electrodes were immersed. The solutions were bubbled with nitrogen gas (99.99% purity) at the flow rate of 50 ml/min for 30 min. The working electrode after proper cleaning is connected to the workstation. The platinum electrode was polished with 1.0 µm, 0.3 µm and 0.05 µm α-alumina powder before each experiment. The electrochemical corrosion analysis was carried out between the potential range of 0.0 mV and − 0.2 mV at a scan rate of 10.0 mVs^{-1}. Electrochemical impedance spectra were recorded in the range 10^5–1 Hz with an ac voltage amplitude of 0.005 V.

The CR was evaluated from the following equation

$$\mathrm{CR} = \left[0.13 I_{\mathrm{corr}}(\mathrm{ew})\right] / \mathrm{d}A \tag{3}$$

where "ew" is the equivalent weight in grams/equivalent, "A" is the area in cm^2, "d" is the density in $\mathrm{g/cm}^3$ and I_{corr} is the corrosion current density in $\mu\mathrm{A/cm}^2$.

Results and discussions

Gravimetric analysis of corrosion rate

Effect of concentration

The CR, surface coverage and inhibition efficiency of GA, SA and blends on copper after an immersion time of 24 h at room temperature (29.85 °C) are shown in Table 2. The results proved that CR decreased with increase in inhibitor concentration and least value of CR is obtained for GASA3. The inhibition rate of SA investigated by Jmiai et al. on copper in 1.0 M HCl was 78% at a concentration of 10^{-1} mg/L [18]. The IE% obtained for 1 g/L of GA on mild steel in 1.0 M HCl is 95% at 303 K [10]. The ability to adsorb on metal surface has increased on blend formation. The changes happened to the spectral bands, crystallinity and intensity peaks on blend formation have been discussed in our previous work [19]. The biopolymers exhibit polar grouping nature and form metal complexes with copper coupon. The metal complexes formed increases with increase in concentration of biopolymers and are adsorbed on copper coupon preventing further deterioration [20].

Effect of temperature on corrosion activation energy

The corrosion activation parameters with and without the presence of inhibitor are investigated by gravimetric method for an immersion time of 24 h at different temperatures of 303 K, 308 K, 313 K and 318 K in a hot air oven. The results

Table 2 Corrosion parameters obtained for copper coupon immersed in 1.0 M HCl with different concentrations of SA, GA and blends after 24 h by weight loss method

Medium	CR (mg cm^{-2} h^{-1})	Inhibition efficiency (IE%)	Surface coverage (θ)	C/θ (*10^4)
Blank solution without inhibitor	0.0722	–	–	
SA1	0.0611	15.37	0.1537	32.5309
SA2	0.0444	38.5	0.385	25.9740
SA3	0.0347	51.94	0.5194	96.2649
SA4	0.0179	75.21	0.7521	132.961
SA5	0.0159	77.98	0.7798	1282.38
GA1	0.0418	42.12	0.4212	11.871
GA2	0.0403	44.18	0.4418	22.635
GA3	0.0375	48.06	0.4806	104.037
GA4	0.0219	69.67	0.6967	143.534
GA5	0.0181	74.93	0.7493	1334.579
GASA1	0.0132	81.72	0.8172	–
GASA2	0.0097	86.57	0.8657	–
GASA3	0.0081	88.78	0.8878	–

Table 3 Corrosion parameters obtained at different temperatures after 24 h of immersion time in 1 M HCl solution with and without inhibitor

Medium	Temperature (K)	CR (mgcm^{-2} h^{-1})	IE%	Surface coverage (θ)
Blank solution without inhibitor	303	0.0722	–	–
	308	0.0934	–	–
	313	0.135	–	–
	318	0.1592	–	–
SA5	303	0.0159	77.98	0.779
	308	0.0248	73.45	0.735
	313	0.0485	64.07	0.641
	318	0.0676	57.53	0.575
GA5	303	0.0181	74.93	0.749
	308	0.0183	80.4	0.804
	313	0.0603	55.33	0.553
	318	0.1086	31.78	0.318
GASA3	303	0.0081	88.78	0.888
	308	0.0184	80.3	0.803
	313	0.067	50.37	0.504
	318	0.08	49.74	0.497

are summarized in Table 3 showing the inhibition efficiency of prepared samples decreases with increase in temperature which can be attributed to the desorption of inhibitor from copper coupon and thereby increasing the probability of acid attack leading to dissolution of the metal [21]. The activation energy value (E_a) was calculated from graphical plot of Log CR versus 1000/T as shown in Fig. 1a using the following form of Arrhenius equation

$$\text{Log CR} = \left(-\frac{E_a}{2.303\text{RT}}\right) + C \tag{4}$$

where T is the absolute temperature in Kelvin (K), R is the molar gas constant (8.314 J/mol·K) and C is the Arrhenius constant.

The value of Ea calculated from the plot is 24.409 kJ/mol for blank medium without inhibitor after 24 h of immersion time. Ea obtained for GA5, SA5, and GASA3 is found to be 45.56 kJ/mol, 34.89 kJ/mol and 56.93 kJ/mol, respectively. The minimum activation threshold energy needed for chemical adsorption was reported to be 80 kJ/mol [22]. The results obtained for Ea in the presence of inhibitor is greater than that without inhibitor. The molecules of polymer get physically adsorbed on the active sites of copper and form as a barrier preventing it from further corrosion [23]. It is observed that an increase in temperature increases the corrosion rate which is attributed to the faster electrochemical reaction at higher temperatures. The chemical bonds which join the inhibitor molecule to the metal surface gets impaired at higher temperature due to the rise in enthalpy and Gibbs free energy value [16]. The stability of the film formed on the surface of the metal gets reduced as a result of this. Increase in temperature adds on energy to the chemical reaction and thereby leads to higher corrosion rate.

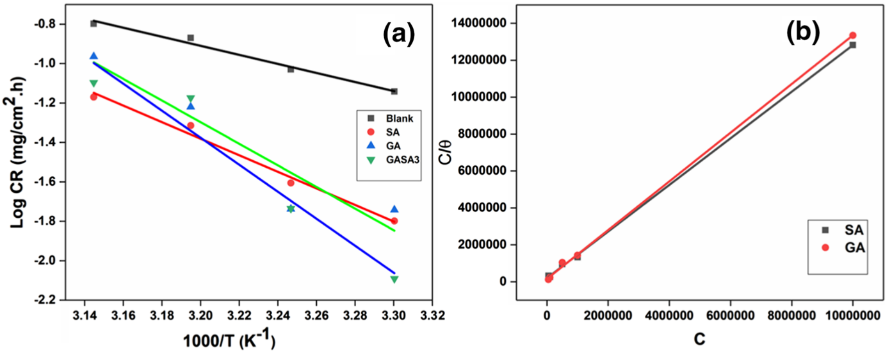


Fig. 1 **a** Arrhenius plot showing variation of CR with temperature for GA5, SA5, GASA3. **b** Langmuir isotherm plot for SA and GA in 1 M HCl solution with and without the presence of inhibitor

Fig. 2 SEM micrograph and corresponding EDS spectra of **a**, **a'** copper coupon, **b**, **b'** after immersion in 1 M HCl solution without the presence of inhibitor, and copper coupon after immersion in 1 M HCl in the presence of **c**, **c'** GA5, **d**, **d'** SA5, **e**, **e'** GASA3 ▶

Adsorption isotherm

In order to understand and investigate the adsorption of inhibitor medium on copper coupon, it is necessary to study the adsorption isotherm which is shown in Fig. 1b. There exist different adsorption isotherm plots like Freundlich, Langmuir, BET, Frumkin, etc., among which Langmuir adsorption fits best with the experimental data and provides a satisfactory explanation for adsorption of polymers on copper coupon in the present study. Adsorption of biopolymer molecules on copper coupon is the most probable technique by which metal corrosion is prevented. The Langmuir adsorption isotherm in its linear form is given by,

$$\frac{C}{\theta} = \left(\frac{1}{K_{\mathrm{ads}}}\right) + C \tag{5}$$

where K_{ads} is the adsorption/desorption equilibrium constant, C is the concentration and θ is the degree of surface coverage given in Table 2. The graph of C/θ versus C plot fitted best with the experimental data at 303 K.

Gibbs adsorption energy (ΔG) provides information about the nature of adsorption of molecules.

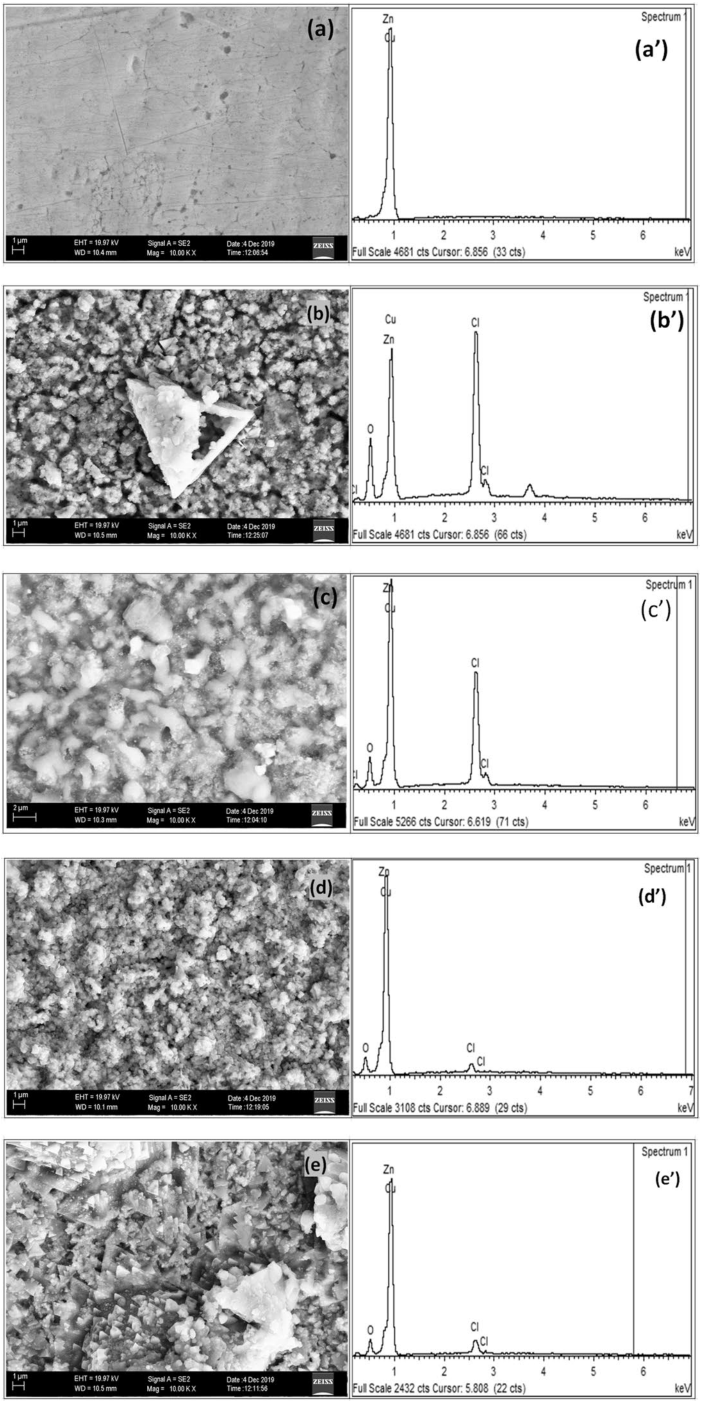
$$\Delta G = -\mathrm{RT}\ln\left(55.5K_{\mathrm{ads}}\right) \tag{6}$$

where R is the gas constant and T is the absolute temperature (K) and 55.5 is the molar concentration of water.

The sign of ΔG obtained greatly influence the corrosion behavior of the metal surface in the presence of inhibitor medium. When the anodic potential exceeds the cathodic potential, the reaction becomes endergonic and ΔG is positive for such reactions. The corroding behavior can be suppressed only when ΔG is positive and corrosion potential (E_{corr}) value is an indicator for the stability of copper coupon against corrosion without the presence of an external current [24]. The values obtained for ΔG are 20.06 kJ/mol and 20.64 kJ/mol for SA and GA, respectively, indicating physical adsorption.

Morphological analysis of copper coupon

The surface and morphological analysis of copper coupon before and after immersion with and without the presence of inhibitor in 1.0 M HCl medium was investigated using FE-SEM analysis. The FE-SEM image of cleaned copper coupon before immersion shows smooth and clear surface, whereas the image after immersion shows abrasions on the surface. Figure 2a shows the image of copper coupon before immersion and Fig. 2b shows the image of corroded surface with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1 µm
EHT = 19.97 kV
WD = 10.4 mm
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WD = 10.5 mm
Signal A = SE2
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small pits and rough scratches created by acidic medium. The highly corroded surface has triangular shaped crystalline aggregates in the absence of inhibitor medium. However, the presence of inhibitor relatively reduces abrasion marks and small pits created by the acidic medium. Copper coupon retrieved after immersing in the acidic medium containing inhibitor shows relatively smooth surface with less abrasions. The aggregates of inhibitor polymer molecules on metal surface are clearly visible in Fig. 2c–e.

The EDS spectra obtained provide information about the elementary composition of copper coupon before and after immersion in the acidic medium with and without the presence of inhibitor. The spectra of copper coupon prior to immersion in Fig. 2a show the presence of copper and zinc. Abraded copper coupon after immersion shows the presence of chlorine and oxygen in addition to copper and zinc. The percentage of chlorine is found to decrease in the presence of

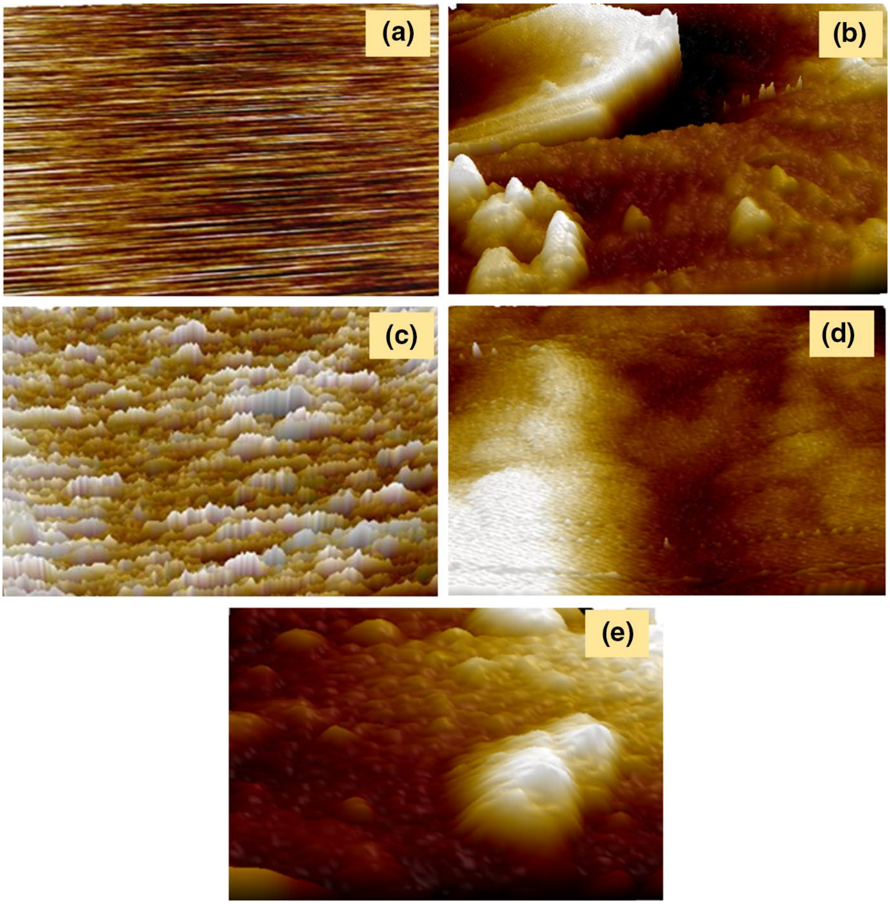

Fig. 3 AFM of copper coupon before immersion (**a**), and after immersion in the acidic medium (**b**), after immersion in the presence of SA (**c**), GA (**d**), GASA3 (**e**)

inhibitor (1.81 weight% for GASA3), whereas it is very high for metal coupon immersed in HCl (18.22 weight%) alone.

Figure 3 shows the AFM image of copper coupon with and without the presence of inhibitor after immersion in 1.0 M HCl solution. This technique provides information on the extend of corrosion and roughness of the metal surface. Figure 3a shows the image of smooth surface of copper coupon before immersion in the acidic medium and Fig. 3b shows the image of abraded copper surface after immersion in the acidic medium. Figure 3c–e shows the image of physically attached polymers on the surface of copper coupon.

Electrochemical method for corrosion parameters

The potentiodynamic polarization curves of SA, GA, and its blend at different concentrations are shown in Fig. 4. The observed values of I_{corr}, E_{corr}, CR and IE% for all the samples are depicted in Table 4. I_{corr} value is obtained using CH Instruments Software version 18.01 from their respective plots. The polarization curve permits us to understand and analyze the variation in corrosion parameters with and without the addition of inhibitors at different concentration. The corrosion current is directly related to the rate of corrosion by Eq. (3).as follows

The corrosion inhibition efficiency is calculated by,

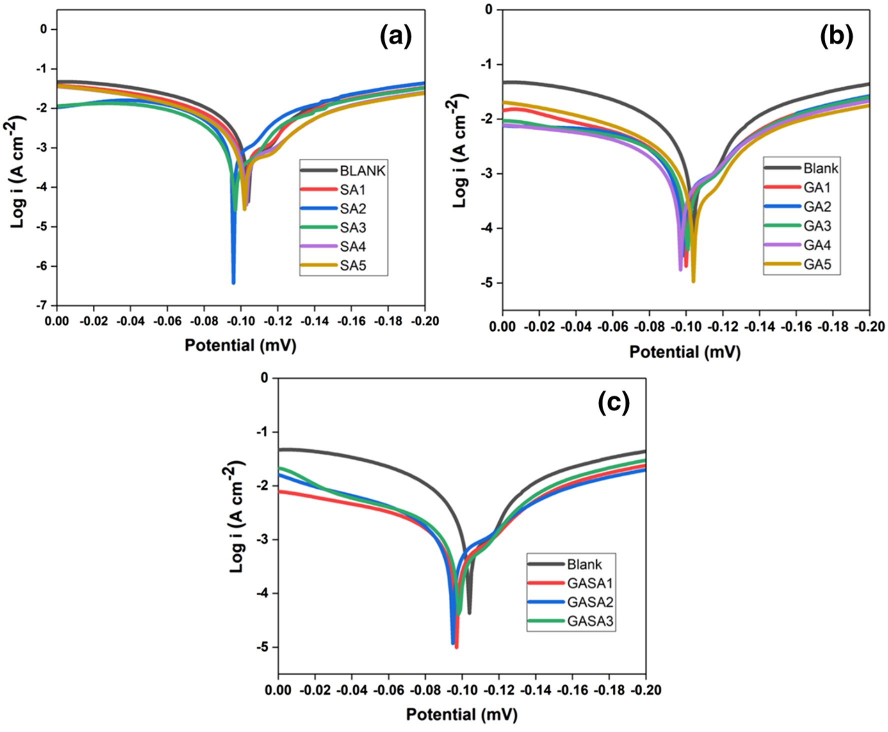

Fig. 4 Potentiodynamic polarization curve of SA (**a**), GA (**b**), blend (**c**), GA, SA and blend

Table 4 Potentiodynamic polarization parameters of copper coupon in 1 M HCl solution in presence and absence of SA and GA and blends as inhibitor at different concentrations

Medium	I_{corr} (μAcm^{-2})	E_{corr} (mV)	CR (mpy)	IE (%)
Blank solution without inhibitor	139.9	86	6.385	–
SA1	93.73	102	4.277	33
SA2	83.48	96	3.847	40
SA3	57.17	97	2.635	59.1
SA4	56.38	103	2.57	59.7
SA5	50.55	102	2.307	63.87
GA1	62.83	100	2.867	55.1
GA2	53.58	98	2.445	61.7
GA3	43.41	101	1.981	68.98
GA4	42.23	97	1.927	69.67
GA5	37.93	104	1.731	72.89
GASA1	30.15	97	1.376	78.44
GASA2	28.40	95	1.296	79.7
GASA3	27.22	98	1.242	80.54

$$\text{IE\%} = \left[\frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \right] * 100 \tag{7}$$

where I_{corr} and $I_{corr(inh)}$ are the corrosion current density in the absence and presence of inhibitor medium, respectively. The results obtained from Fig. 4 show that anodic and cathodic current densities decrease with increase in the addition of inhibitors and are shown in Table 5. It was reported that GA and alginate derivatives behaves as mixed type inhibitors [25, 12]. From the Tafel plot analysis of the GASA1, GASA2 and GASA3, it is clear that the addition of inhibitor medium shifted both cathodic and anodic curves to lower values of current density. This indicated that the three blend samples behave as mixed type of corrosion inhibitor. From Table 4, the least value of corrosion current is obtained for GASA3 indicating that it adsorbs more thereby decreasing the corrosion kinetics on the copper surface than GASA2 and GASA3. Thus, the improved inhibition efficiency of GASA3 is attributed to its amphiphilic nature due to the presence of GA and the subsequent formation of

Table 5 Parameters obtained after fitting the equivalent circuit with the electrochemical impedance measurement data with and without the presence of inhibitor medium in 1 M HCl solution

Medium	R_S	R_F	R_P	R_T	C_F	C_{DL}	IE%
Blank solution without inhibitor	1.043	2.162	34.56	36.722	61.01	–	–
GA5	0.9579	0.032	124.98	125.012	70.04	55.08	71%
SA5	1.84	2.306	130.87	133.176	21.09×10^6	36.64×10^6	72.4%
GASA3	1.124	3.008	263.54	266.548	44.04	42.95×106	86.2%

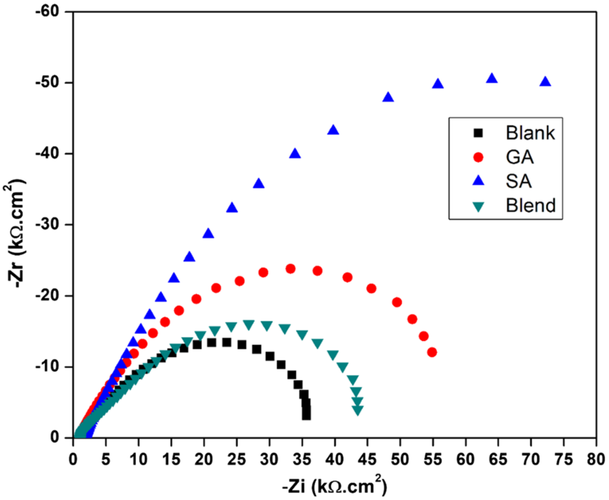

Fig. 5 Nyquist plot for blank sample, GA, SA and blend

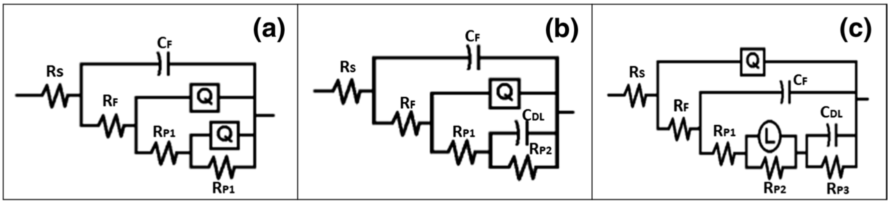

Fig. 6 Equivalent circuits used to fit the obtained EIS data of blank (**a**), SA5 and GASA3 (**b**), and GA (**c**)

protective stable layer which prevented the exposure of metal surface to the acidic solution [12].

Electrochemical impedance measurements for inhibition efficiency

Electrochemical impedance spectroscopy measurements were carried out for determining the impedance characteristics of the metal/electrolyte interface. The Nyquist plot of copper coupon after 24 h of immersion time in GA5, SA5, GASA3 and acidic medium without inhibitor are depicted in Fig. 5. The electronic circuit corresponding to the best fit curve for the experimental data are shown in Fig. 6. The plots give depressed semicircular loops as a result of the non-ideal character of the interface of the metal coupon in the presence of corrosive acidic medium. The diameter of semicircular loops of GA5, SA5 and GASA3 are greater when compared to that of blank copper coupon. The inhibitor medium develops a protective thin coating on copper coupon and thereby increases the impedance of metal–electrolyte interface. The electrochemical parameters are given in Table 5. Chen et al. studied the inhibition rate of GA on carbon steel in synthetic brine and obtained 83.5% at 5 g/L by electroscopic impedance spectroscopy [12]. The inhibition rate obtained for SA on API X60 steel in 3.5% NaCl solution at 1000 ppm was 87.2% at 25 °C [14]. The resistance of electrolytic solution is given by R_S; R_T is the total sum of the resistance of film formed (R_F) and polarization resistance ($R_P = R_{P1} + R_{P2}$) for equivalent circuit in Fig. 6a, b and ($R_P = R_{P1} + R_{P2} + R_{P3}$) for Fig. 6c. Q is called the constant phase element, C_F and C_{DL} are called the film capacitance and double layer capacitance, respectively. The inhibition efficiency is calculated by,

$$\mathrm{IE\%} = \left[1 - \left(\frac{R_T}{R_{T(inh)}}\right)\right] * 100$$

where R_T is the total resistance in the absence of inhibitor medium and $R_{T(inh)}$ is the total resistance in the presence of inhibitor medium. The values of inhibition efficiency calculated using above equation listed in Table 5 are comparable with that obtained from electrochemical corrosion analysis by Tafel plot.

Conclusion

The green biopolymer blend GASA3 exhibited good inhibition efficiency against copper coupon corrosion in acidic medium (HCl) than GA and SA alone. The physical adsorption of biopolymers and its blend were proved from Arrhenius plot and Langmuir isotherm. Copper coupon before immersion shows smooth surface in the SEM image, whereas that after immersion shows rough scratches and pits in the absence of inhibitor medium. Copper coupon after immersion in the acidic medium with the inhibitor shows very less abrasions and scratches. The inhibition efficiency of the biopolymers and the prepared blends were investigated by gravimetric analysis, potentiodynamic polarization and EIS methods. The maximum inhibition efficiency is obtained for GASA3 which are 88.8%, 80.5%, 86.2% after gravimetric method, potentiodynamic polarization and EIS methods respectively.

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Code availability All data are available online in Mendeley dataset through the given code: 10.17632/mj6jd2cp75.4.

Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest.

Availability of data and material Required data or original images obtained during the study will be available from the corresponding author on request.

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