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Green inhibitors for corrosion protection in acidizing oilfield environment

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Abstract Tafel extrapolation method has been employed to determine the corrosion resistance of super austenitic stainless steel (UNS S31254) in a CO₂-saturated acidizing oilfield environment. Green inhibitors (*Tridax procumbens* and *Chromolaena odorata* extracts) were employed for protection of the alloy in the environment. Over 90% inhibition efficiency was achieved at inhibition dosage of 100 ppm for one of the inhibitors. Results showed that both inhibitors are effective for protecting the alloy in the acidizing environment. The result of the adsorption isotherm showed that the adsorption of the extracts on the surface of UNS S31254 is a monolayer and consistent with the Langmuir isotherm.

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1. Introduction

Acidization is an oil-well stimulation process which is carried out by the use of hot solution of acid to enhance oil production (Yadav et al., 2013). The use of hot 15–28% hydrochloric acid for such oil well stimulation process results in corrosion attack on the production tubing (Yadav et al., 2013; Quraishi and Jamal, 2000a,b; Ansari et al., 2015). Sometimes a mixture of acids such as sulphamic, sulphuric, phosphoric methanesulphonic, nitric, citric and chloroacetic are employed for such operations (Quraishi and Jamal, 2000a,b; Quraishi et al., 2002; Migahed and Nasar, 2008). As a result of the use of such acids the corrosion rate of carbon steels in such environment can be as high as 100 mm/year (Finsgar and Jackson, 2014).

To mitigate the effect of such highly corrosive acids, inhibitors are added (Ansari et al., 2015; Samuel and Sengul, 2003). Selection of suitable inhibitors for such environments put into consideration parameters such as acid type, temperature and flow velocity of the fluid (Sastri, 2001). Some of the inhibitors that are commonly used are acetylenic alcohols, alkenyl phenones, aromatic aldehydes, nitrogen containing heterocyclics, quaternary salts and condensation products of carbonyls and amines. However, these inhibitors are effective only at high concentrations and they are harmful to the environment.

It is therefore important to search for nontoxic, eco-friendly and effective organic corrosion inhibitors for acidizing oilfield system. In this regard, natural plant extracts are becoming useful. Bammou et al. (2014) studied the corrosion of carbon steel in 0.5 M sulphuric acid in the presence of *Che-nopodium ambrosioides* extract and found the inhibitor to exhibit up to 94% efficiency. Ostovari et al. (2009), used *henna* extract (*Lawsonia inermis*), and they found that the extract is

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effective in preventing corrosion of mild steel in 1 M HCl. Satapathy et al. (2009), tested *Justicia gendarussa* plant extract in 1 M HCl at 25–70 °C. Other plants that have been used are: *Jatropha curcas*, *Moringa oleifera*, *Nicotiana tabacum*, *Aloe vera*, *Rice husk*, *Hunteria umbellata* (Olusegun et al., 2013; Olasehinde et al., 2013; Mehdipour et al., 2015; Alaneme et al., 2015a, 2015b; Singh et al., 2012). These authors claimed that the extract was effective as corrosion inhibitor.

Other plant extracts that have also found application as corrosion inhibitor is *Chromolaena odorata* (Obot et al., 2012; Obot and Obi-Egbedi, 2010). *Chromolaena odorata* is a species of the flowering shrub in the sunflower family-Asteraceae. *Chromolaena odorata* leaf extracts have been found to be good corrosion inhibitors because of the presence of active ingredients such as essential oils, steroids and triterpenes (Obot et al., 2012; Obot and Obi-Egbedi, 2010). Active ingredients in *Chromolaena odorata* include flavanones, perisicogenin, chalcones, flavones and luteolin (Obot et al., 2012). These compounds are heterogeneous organic compounds containing nitrogen, oxygen and sulphur or/and aromatic ring in their molecular structures. Thus, the adsorption of these compounds on the surface of the metal is assumed to be mostly responsible for the inhibition of the corrosion reaction. *Tridax procumbens* on the other hand is a common weed found in the tropics that grows primarily during the rainy season. *Tridax procumbens* has also been found to be a potential green inhibitor for protecting mild steel in acidic environment (Kumar et al., 2014).

2. Materials and methods

2.1. Material

Alloy used for this research is a super austenitic stainless steel (UNS S31254) with chemical compositions shown in Table 1. The alloy was solution annealed as received.

2.2. Methods

2.2.1. Alloy preparation

The Alloy sample was sectioned into 10 mm × 10 mm. To ensure good electrical contact, conductive aluminium tape was used to fasten a copper wire onto the surface of the working electrode. The sample was then mounted using epoxy resin and thereafter grounded using grinding papers ranging from 220 to 1200 grits. The sample was then degreased with acetone, washed in a stream of water and dried with air and then immersed into the electrolyte.

2.2.2. Brine preparation

Meanwhile, the acidizing oilfield environment was simulated by adding 4 M HCl and a CO₂-saturated 3.5% NaCl solution in ratio 1:1 (to mimic spent acid environment) to make a one-litre solution. CO₂ gas was also used to purge the environment

throughout the duration of the experiment. *Chromolaena odorata* and *Tridax procumbens* leaf extracts were used as inhibitors in concentrations of 100, 200, 300, 400 ppm. All experiments were carried out at a temperature of 40 °C.

2.2.3. Electrochemical measurements

The sample was left at open circuit potentials for 30 min before polarisation. Tafel polarisation tests were conducted using AUTOLAB PGSTAT 204 N with Ag/AgCl reference electrode and a platinum counter electrode. The surfaces of the specimen were polarized from –250 mV below OCP to +250 mV above OCP at a scan rate of 0.25 mV/s. Corrosion current density was determined as the intersection between the anodic and cathodic extrapolation of the Tafel plot. This was achieved by fitting the Tafel slopes using NOVA 1.8 software.

2.2.4. Inhibitor preparation and inhibition efficiency

The leaves were washed, cut into pieces and dried under the sun for 3 days. They were then grounded and sieved into a powdery form. 100 g each of the powder was put into flat bottomed flask containing 1000 ml of ethanol. The resulting solution was left for 72 h before it was carefully filtered. The stock solution was prepared from the filtrate which was evaporated and then used to make solutions of 100, 200, 300, and 400 ppm concentrations of the green inhibitor.

Meanwhile, phytochemical screening for *Chromolaena odorata* revealed the presence of tannins, steroids, terpenoids, flavonoids, phenols, saponins and glycosides (Vijayaraghavan et al., 2013; Obot et al., 2012). *Tridax procumbens* on the other hand has been reported to contain high flavonoids, alkaloids, hydroxycinnamates, tannins and phytosterols and moderate benzoic acid derivatives and lignans (Ikewuchi et al., 2015).

The inhibition efficiency was obtained from the corrosion current density at different concentrations of inhibitor at a test temperature of 40 °C. The inhibitor efficiencies (IE) were calculated from the corrosion current density according to Eq. (1)

$$IE (\%) = [(i_o - i_{inh})/i_o] * 100\% \quad (1)$$

where i_o and i_{inh} are the corrosion current density of the mild steel in the absence and presence of inhibitor, respectively.

3. Results and discussion

3.1. Tafel plots

Figs. 1 and 2 show the Tafel plots for UNS S31254 in the presence of the green inhibitors. Corrosion rate for the alloy in the uninhibited solution is higher than the inhibited solution as expected (Figs. 1 and 2). Both inhibitors also seem to be anodic in nature from the observation of the anodic branches (Anodic reaction is suppressed from the nature of the Tafel). This is dominant at higher inhibition dosage of 200–400 ppm. The addition of both inhibitors shifts the corrosion potentials

Table 1 Chemical composition (weight %) of the alloys.

C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu	Fe
0.012	0.36	0.51	0.02	0.001	20.06	17.76	6.02	0.20	0.72	Bal.

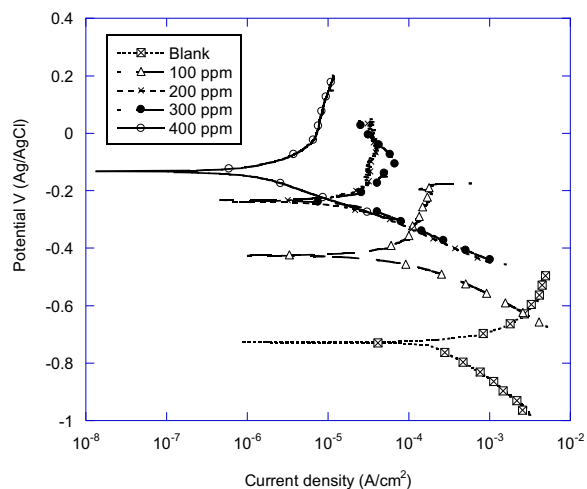


Figure 1 Tafel plots for UNS S31254 in acidizing oilfield brine in the presence of *Chromolaena odorata* inhibitor at 40 °C.

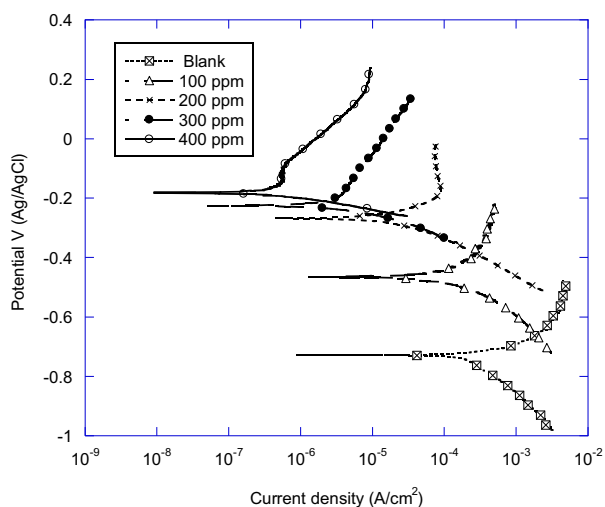


Figure 2 Tafel plots for UNS S31254 in acidizing oilfield brine in the presence of *Tridax procumbens* inhibitor at 40 °C.

towards the anodic direction (Figs. 2 and 3). The significant shift in the anodic and cathodic curves which resulted in the reduction of corrosion rate could be attributed to film formation (Pessu et al., 2016).

3.2. Corrosion behaviour

The corrosion rates for UNS S31254 steel samples in acidizing oilfield brine in the presence and absence of *Chromolaena odorata* and *Tridax procumbens* extracts at 40 °C are also shown in Tables 2 and 3 respectively. Addition of the green inhibitors reduced the corrosion rate considerably and the rate decreases with increase in the inhibitor concentration. The uninhibited sample of UNS S31254 corroded at the rate of 18.205 mm/year while 400 ppm concentrations of *Tridax procumbens* and *Chromolaena odorata* extract reduced the corrosion rates to 0.009 mm/year and 0.022 mm/year respectively.

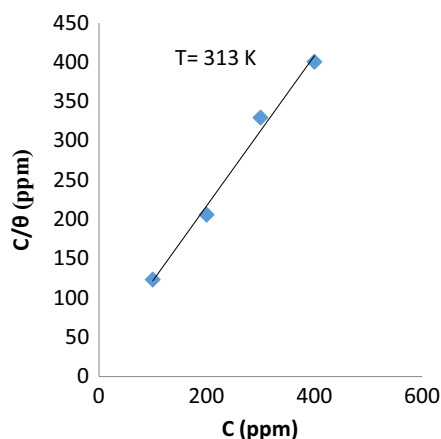


Figure 3 Langmuir adsorption isotherm plot for the adsorption of *Chromolaena odorata* extract on UNS S31254.

3.3. Inhibition efficiency

Higher inhibition efficiency was observed at higher inhibition dosage (Tables 2 and 3). Inhibition efficiencies of 82.03% and 95.06% were observed for *Tridax procumbens* and *Chromolaena odorata* respectively at 100 ppm dosage. Moreover as the concentration increases to 200 ppm the corrosion performance was above 90% which is the standard in the oil industry (Marsh and Teh, 2007).

3.4. Adsorption isotherm

The degree of surface coverage (θ) that was used for the plot of the isotherm was calculated from the corrosion rate values.

$$\theta = 1 - \frac{CR_{inh}}{CR_{blank}} \quad (2)$$

where, CR_{inh} is the corrosion rate with the addition of inhibitor and CR_{blank} is the corrosion rate in the blank solution (without inhibitor). The calculated surface coverage (θ) was fitted into different isotherms. An inhibitor is said to obey Langmuir if the plot of C/θ vs C is linear. Similarly, for Temkin the plot of θ vs $\log C$ and for Freundlich the plot of $\log \theta$ vs $\log C$ should be linear. From the correlation coefficients obtained as shown in Table 4; Langmuir was found to be best applicable by the following equation:

$$\frac{C}{\theta} = \frac{1}{k_{ads}} + C \quad (3)$$

where C is the inhibitor concentration, θ is the surface coverage and k_{ads} is the adsorption equilibrium constant.

The plot of C/θ against C is linear as shown in Figs. 3 and 4 indicating that the adsorption of the two inhibitors on the surface of UNS S31254 is consistent with Langmuir isotherm and the slopes obtained are closed to unity. The correlation coefficient (r^2) of the adsorption isotherm data (Table 4) showed that Langmuir isotherm is fitted into the experiment with r^2 of 0.9994 and 0.9989 for *Chromolaena odorata* and *Tridax procumbens* respectively at 313 K (40 °C) temperature (Table 4).

Table 2 Corrosion parameters for UNS S31254 in the presence of *Chromolaena odorata*.

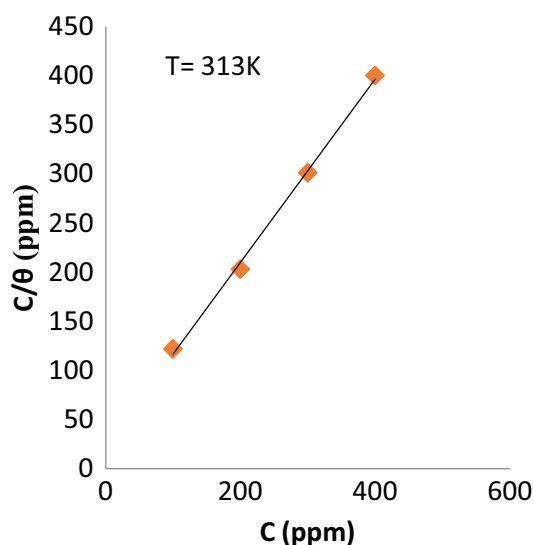
S/N	Inhibitor dosage (ppm)	Corrosion current density (A/cm ²)	Corrosion rate (mm/year)	Corrosion Potential (V)	Inhibition Efficiency (%)
1	Blank	0.0015670	18.2050	-0.7249	
2	100	0.0000774	0.8999	-0.4253	95.06
3	200	0.0000451	0.5236	-0.2375	97.12
4	300	0.0001400	1.6289	-0.2326	91.05
5	400	0.0000018	0.0219	-0.1302	99.88

Table 3 Corrosion parameters for UNS S31254 in the presence of *Tridax procumbens*.

S/N	Inhibitor dosage (ppm)	Corrosion current density (A/cm ²)	Corrosion rate (mm/year)	Corrosion potential (V)	Inhibition efficiency (%)
1	Blank	0.0015670	18.2050	-0.7249	
2	100	0.0003659	3.2700	-0.4638	82.03
3	200	0.0000233	0.2705	-0.2635	98.51
4	300	0.0000068	0.0790	-0.2229	99.57
5	400	0.0000008	0.0090	-0.1871	99.95

Table 4 Adsorption Isotherms parameters at 313 K.

Extract	Langmuir		Temkin		Freundlich	
	r ²	Slope	r ²	Slope	r ²	Slope
<i>Chromolaena odorata</i>	0.9948	0.9549	0.8343	0.1157	0.8401	0.1296
<i>Tridax procumbens</i>	0.9989	0.9311	0.9116	0.1315	0.9091	0.1450

**Figure 4** Langmuir adsorption isotherm plot for the adsorption of *Tridax procumbens* extract on UNS S31254.

4. Conclusion

Tridax procumbens and *Chromolaena odorata* extracts have been found to be good inhibitors for the protection of super austenitic stainless steel UNS S31254 in acidizing sweet oilfield

environments. Inhibition efficiency higher than 90% was achieved which is in line with the standard in oilfield (Marsh and Teh, 2007). The result of the adsorption isotherm showed that the adsorption of the extracts on the surface UNS S31254 is monolayer and consistent with the Langmuir isotherm.

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