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# *Murraya Koenigii* as Green Corrosion Inhibitor for Mild Steel in $CO_2$-saturated 3.5% NaCl Medium†

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Green corrosion inhibitor is one of the recent emerging remedy to prevent oil and gas pipeline corrosion. In this study, the leaf extract of *Murraya koenigii* (curry leaf tree) has been tested as a corrosion inhibitor for mild steel corrosion in $CO_2$-saturated 3.5% NaCl medium. Standard corrosion evaluation techniques viz., weight loss method and electrochemical technique (potentiodynamic polarization) were employed to study the corrosion inhibition properties. The changes of surface morphology on mild steel specimens before and after corrosion studies were screened through scanning electron microscopy (SEM) combined with energy dispersive X-Ray analyzer (EDX). In addition, Fourier Transform Infrared (FTIR) Spectroscopy was used to characterize the leaf extract and the corrosion protective film formed over the mild steel surfaces. Results showed that *Murraya koenigii* leaf extract successfully reduced the corrosion rate through adsorption process, which followed the Langmuir adsorption isotherm.

**Key words**: Green corrosion inhibitor; mild steel; *Murraya koenigii*; potentiodynamic polarization; SEM

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In today's world, various petroleum products such as petrol, diesel, and several other hydrocarbons govern the economy of a country. The exploration of crude oil in deep oceans or barren deserts while passing through different layers of soil could pose some huge challenges to transport the crude oil [1]. The main problem is crude oil is flammable and volatile. Thus, any leakage can lead to severe accident, causing a polluted ocean or explosion on a platform. Hence, the method employed in transporting crude oil would involve pipelines.

Generally, the pipeline materials will be derived from carbon steel because it is economical, durable, and competent in strength. However, steel is known to rust easily and corrosion is completely unavoidable. Hence, it creates a great loss to the industry every year. Corrosion is a main degradation reaction that affects the long-term dependability and principle of metallic underground pipelines [1]. According to Ameh *et al.* [2], both internal and external of pipelines suffer from corrosion. In the pipeline streams, the presence of carbon dioxide, hydrogen sulfide, and moisture, which are commonly trapped as brine from the sea can cause internal corrosion. As for the external of pipelines, the main problem is due to the corrosive nature of soil.

There are many methods of corrosion protection in oil and gas pipelines, which have widely being used since 1940s until now. During the period from 1940s to 1950s, vinyl tape, coal tar, and wax were used and followed by asphalt in 1960s. The cathodic protection was introduced later. Thus, the new pipeline system, which includes steel quality, surface condition and treatments, coating application, and cathodic protection system is now being considered in the process [3].

Another method is by introducing corrosion inhibitors to a corroding system as they can be changed without busting the process. The inhibitors can be introduced in very minimum quantities and can be easily monitored. Besides, the corrosion inhibitors are usually adsorbed on metal surfaces to form protective films, which protect the metal surfaces from aggressive corrosive agents. After forming the protective films over the metal surfaces, it will slow down process of corrosion through interfering reactions such as anodic or cathodic polarization or resistance for diffusion of ions to or from metal surface, and hence decrease the rate of corrosion [4].

Generally, corrosion inhibitors used in gas/oil

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industries are organic compounds having electron rich heteroatoms (P, S, N, and O) and possess π-electronic clouds; for instance, derivatives/series of amines, amides, imidazolines, nitrogenous molecules with carboxylic acids, and polyoxyalkylated nitrogen containing compounds [5-8]. These commercial inhibitors have organic polar functional groups, which can adsorb onto metal surfaces and form protective film barriers.

However, eventhough these synthetic organic compounds show efficient corrosion reduction, most are classified as highly toxic for the environment, as well as human beings [9]. Safety and environmental issues that arise in industries during usage of any synthetic materials have always been a global concern. These synthetic corrosion inhibitors may cause damage to organ systems, including liver and kidneys, and/or disturb enzyme systems in the human body [10].

As such, an intense research on environment-friendly corrosion inhibitors, known as green inhibitors, has been in progress to solve the problem, which involves screening natural extracts of plant tissues, such as roots, stems, leaves, and fruit peels [11]. Green inhibitors are mostly cheap, easily accessible, and environmentally friendly [12]. A few natural extracts had been tested recently, such as fennel (*Foeniculum vulgare*) essential oil [13], *Newbouldia* leaf extract [14], and *Garcinia mangostana* [15] for use as corrosion inhibitors in $CO_2$-saturated NaCl medium. In this study, *Murraya koenigii* leaf extract was tested as a corrosion inhibitor for mild steel corrosion in $CO_2$-saturated NaCl medium.

*Murraya koenigii* (*M. koenigii*), or commonly known as curry leaf tree, is used mostly in tropical countries such as India, Malaysia, and Indonesia. *M. koenigii* acts as a natural flavoring agent and belongs to the citrus family. *M. koenigii* has the potential role of domestic remedy as it contains many vitamins that can treat disorders such as diabetes, cancer, and other diseases. *M. koenigii* is also used in many treatments, such as for stomach ache, headache, influenza, snake bites, and diarrhea [16]. It has been disclosed that *M. koenigii* contains carbazole, which is a strong antioxidant. The presence of phytoconstituents with heteroatoms (N, O, and S) functional groups in this plant is promising for corrosion inhibition potential [3]. According to Shamrmila *et al.* (2010), monoterpene hydrocarbon that exists in *M. koenigii* leaves shows inhibitory efficiency [17]. Hence, this work aimed at investigating the application of *M. koenigii* extract as a corrosion inhibitor for mild steel in $CO_2$-saturated 3.5% NaCl medium. The assessment of corrosion behavior was studied using weight loss method, potentiodynamic polarization method, scanning electron microscopy (SEM), energy dispersive X-Ray analyzer (EDX), and Fourier Transform Infrared (FTIR) Spectroscopy.

## EXPERIMENTAL

### Extraction

Air-dried and powdered leaves of *M. koeginii* (1.0 kg) were used for extraction with ethyl acetate (EtOAc) (3.0 L) at room temperature (72 hours) [18]. The solvent was used directly without purification to understand bottom-line composition of the extract. After 72 hours, EtOAc was removed using a rotary evaporator and the remaining residue was dried / screened for corrosion inhibition potential.

### Preparation of Metal Specimens and Extract Solutions

Mild steel (MS) specimens with the composition: carbon, 0.205%; manganese, 0.55%; silica, 0.06%; sulfur, 0.047%; phosphorus, 0.039%; and Fe as the balance; with an exposed area of 3.14 $cm^2$ were used for the electrochemical study, and specimens with the size of 1.0 cm × 0.2 cm × 3.0 cm (length × width × height) were used for the weight loss study and SEM analysis. The surface preparation of the specimens was carried out using emery papers of different grades (80, 100, 300, 500, 700, 800, 900, and 1000) for weight loss method and surface examination studies. The specimens' initial weight was recorded. Different concentrations of *M. koeginii* extract were prepared by diluting the extract in corresponding volumes of 3.5% NaCl solution and made up to 100 ml for further corrosion analyses.

### Weight-loss Method

Pre-weighed mild steel specimens were immersed in 100 ml of 3.5% NaCl solution, which was purged with $CO_2$ for two hours prior to the experiment. The plant extracts prepared were added to the purged solution and left purging with $CO_2$ for 24 hours. After 24 hours of immersion, the specimens were taken out from the corrosive medium, carefully washed with double distilled water, dried and weighed [19,20]. The corrosion inhibition efficiency (IE) was calculated using equation 1 [13].

$$\text{IE (\%)} = [\frac{W_1 - W_2}{W_1}] \times 100 \quad \text{..... (1)}$$

Where $W_1$ is the weight loss value in the absence of inhibitor and $W_2$ is the weight loss value in the presence of inhibitor. Corrosion rate (CR) was calculated by using equation 2 [21].

$$\text{CR (mpy)} = \frac{534 \times W}{A \times T \times \rho} \quad \text{..... (2)}$$

Where $W$ is the weight loss in mg, ρ is the metal density in g/$cm^3$, $A$ is the area of the metal surface in $inch^2$, and $T$ is the exposure time in hours. Duplicate

measurements were carried out to check the consistency of the results.

**Electrochemical Studies**

Electrochemical studies (potentiodynamic polarization) were carried out using Gamry Instrument reference 600 (potentiostat/galvanostat/ZRA). Electrodes used for this study were working electrode (mild steel), counter electrode (Pt wire), and reference electrode (standard calomel electrode, SCE). The test solution (3.5% NaCl) was purged with $CO_2$ prior to the electrochemical experiments; later the electrodes were immersed in the test solution at $\pm 32$ ℃ for 30 minutes to attain stable open circuit potential (OCP). Further, the Tafel polarization study was carried out by scanning the electrode potential ± 300 mV (vs SCE) from OCP values with scan rate of 0.1 $mVs^{-1}$. Corrosion potentials ($E_{corr}$) of anodic and cathodic curves were extrapolated to obtain corrosion current density ($I_{corr}$) values. Percentage of inhibition efficiency, $\eta$ was calculated using equation 3 [22].

$$\eta\ \% = (1 - \frac{i_{corr(i)}}{i_{corr(0)}}) \qquad \text{….. (3)}$$

Where $i_{corr(i)}$ is corrosion current density of MS with inhibitor and $i_{corr(o)}$ is corrosion current density of MS without inhibitor.

**SEM – EDX Analysis**

To monitor the surface morphological changes and observe the image of mild steel after immersion with 3.5% NaCl, a Carl Zeiss LEO SUPRA 50VP scanning electron microscope with energy dispersive X-ray (SEM-EDX) was utilized at an accelerating voltage of 1.735 keV. The mild steel specimens used before and after the weight loss study were used for this purpose. The mild steel specimens were polished using 1000-grit surface and immersed in 3.5% NaCl medium; without inhibitor and with inhibitor at 500 ppm and 1000 ppm of *M. koenigii* extract. The specimens were left for 24 hours and cleaned with distilled water, dried in open air, and used for analysis.

**Fourier-transform Infrared Spectroscopy**

The plant extract and the respective protective films formed over the MS surfaces were analyzed through FTIR spectroscopy for the identification of the functional groups using KBr pellet method in the IR range of 400 to 4000 $cm^{-1}$. The protective films covered the MS surfaces for 7 days immersion period, and later the films were carefully scratched off the MS surface. The ratio between sample and KBr was 1:10. The mixture was pressed with 8-ton pressure to make the pellet. The pellet was then analyzed using Perkin-Elmer System 2000 FTIR instrument.

## RESULTS AND DISCUSSION

**Weight Loss Method**

Weight loss results obtained are given in Table 1, which present plant extract concentrations and the corresponding responses as inhibition efficiency (% IE) and corrosion rate. As the concentration of green inhibitor increased, weight loss values and corrosion rate values decreased, indicating adsorption played a main role during corrosion inhibition. This was also due to the surface coverage (θ), of inhibitor over mild steel and adsorption amount increased with concentration of inhibitor. Hence, this allowed the MS surface to be efficiently blocked from the aggressive carbonic acid solution. Thus, the maximum % IE obtained was 99.62% and it was optimized at the concentration of 500 ppm.

Figure 1 shows linear plot of log (θ / 1- θ) vs log C in order to understand the corrosion inhibition mechanism wherein the adsorption properties of *M. koenigii* extract has been tested to fit with different adsorption isotherms (Temkin, Langmuir, and Frumkin). The system was found to follow Langmuir adsorption

**Table 1.** Effect of different concentrations of *M. koenigii* extract on MS corrosion in $CO_2$-saturated 3.5% NaCl medium

| Corrosion inhibitor | Concentration (ppm) | % IE | θ | Corrosion rate (mpy) |
|---|---|---|---|---|
| *M. koenigii* | 100 | 65.19 | 0.6519 | 28.58 |
| | 200 | 85.93 | 0.8593 | 11.55 |
| | 300 | 87.41 | 0.8741 | 10.34 |
| | 500 | 99.62 | 0.9962 | 1.82 |
| | 1000 | 98.52 | 0.9852 | 1.22 |

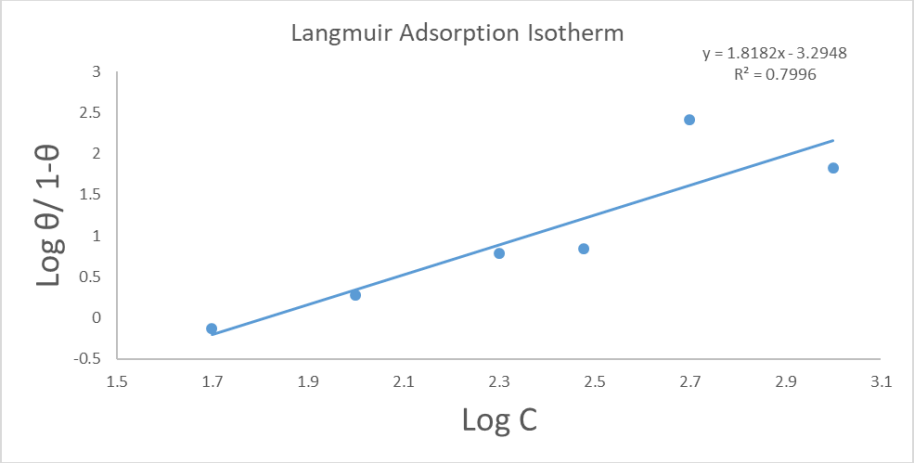


**Figure 1.** Langmuir adsorption isotherm of green inhibitor protection of mild steel in $CO_2$-saturated NaCl medium

isotherm, which showed a linear graph with regression coefficient, R value of 0.80 with deviation from unity. This may be due to the factor that after being adsorbed over the metal surface, inhibitor species may be either mutually repelled or attracted one another that could affect the slope [23].

**Potentiodynamic Polarization Measurements**

Typical potentiodynamic polarization results obtained are depicted as Tafel plots in Figure 2. Various Tafel parameters viz., corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$) and Tafel slope (ba and bc) values obtained are recorded in Table 2. From the results, the addition of plant extract shifted the corrosion potential ($E_{corr}$) to the positive side (100 mV) due to the decrease in anodic reaction. This denoted that the inhibitors succeeded in avoiding metal dissolution reaction and controlled the corrosion due to inhibitors that were absorbed on anodic side of MS surface. However, Tafel slope values (ba / bc) were found to be altered in all the concentrations. This proved that the plant extract adsorbed on anodic and cathodic sites of MS and proceeded through mixed mode of inhibition while predominantly influenced the anodic dissolution reaction. Furthermore, the addition of inhibitors reduced the corrosion current density ($I_{corr}$) values considerably; from 112 to 8 for *M. koenigii*. This resulted in inhibition efficiency of 93% for *M. koenigii* extract at the maximum concentration of 1000 ppm. In addition, *M. koenigii* extract showed better inhibition efficiency in comparison with *Momordica charantia* seed extract, which showed 89% IE for the same concentration [24].

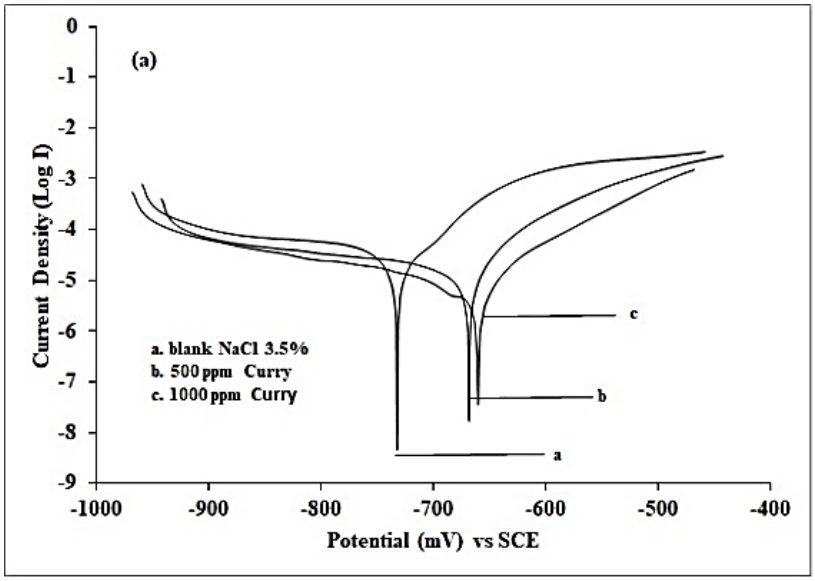


**Figure 2.** Tafel plot of *M. koenigii* extract-inhibited mild steel in $CO_2$-saturated 3.5% NaCl medium

**Table 2.** Effects of different concentrations of *M. koenigii* extract on MS corrosion in $CO_2$-satured 3.5% NaCl medium

| Corrosion inhibitor | Concentration of inhibitor (ppm) | -ba $mVdec^{-1}$ | -bc $mVdec^{-1}$ | $-E_{corr}$ mV (vs SCE) | $I_{corr}$ $\mu Acm^{-2}$ | % of IE |
|---|---|---|---|---|---|---|
| - | 0 | 94 | 124 | -732 | 112 | - |
| *M. koenigii* | 500 | 36 | 97 | -668 | 28 | 75.0 |
| | 1000 | 27 | 39 | -666 | 8 | 92.9 |

**FTIR Studies**

FTIR band values at 2900-3400 $cm^{-1}$ corresponded to the N-H and O-H groups in the plant extract. *M. koenigii* extract showed a positive result for Dragendroff reagent that could confirm the existence of alkaloids. The appearance of a peak at 1600 $cm^{-1}$ assignable to the C=C stretching supported the presence of carbazole alkaloids such as koenioline, murrayazoline, girinimbine, and other related compounds [25,26].

*M. koenigii* extract showed a potent corrosion inhibition potential and the result of FTIR clearly showed that through adsorption an inhibition mechanism proceeded via blockage of mild steel surface by inhibitor molecules. The alkaloid constituents existed as neutral groups. The adsorption of anticorrosion inhibitors occurred through the formation of a bond with Fe, which involved donation of one pair of electrons from alkaloid constituents, such as N-H, C=O, and O-H, present in the neutral alkaloid groups to Fe. Adsorption can occur through electrostatic interactions between negatively charged metal surface and positively charged alkaloid groups. Based on the FTIR spectra of *M. koenigii* leaf extract/protective film (Figure 3), it can be observed that a peak appeared at 2250 $cm^{-1}$, indicating the presence of C=N of nitrile group from the alkaloid group in the plant extract [27].

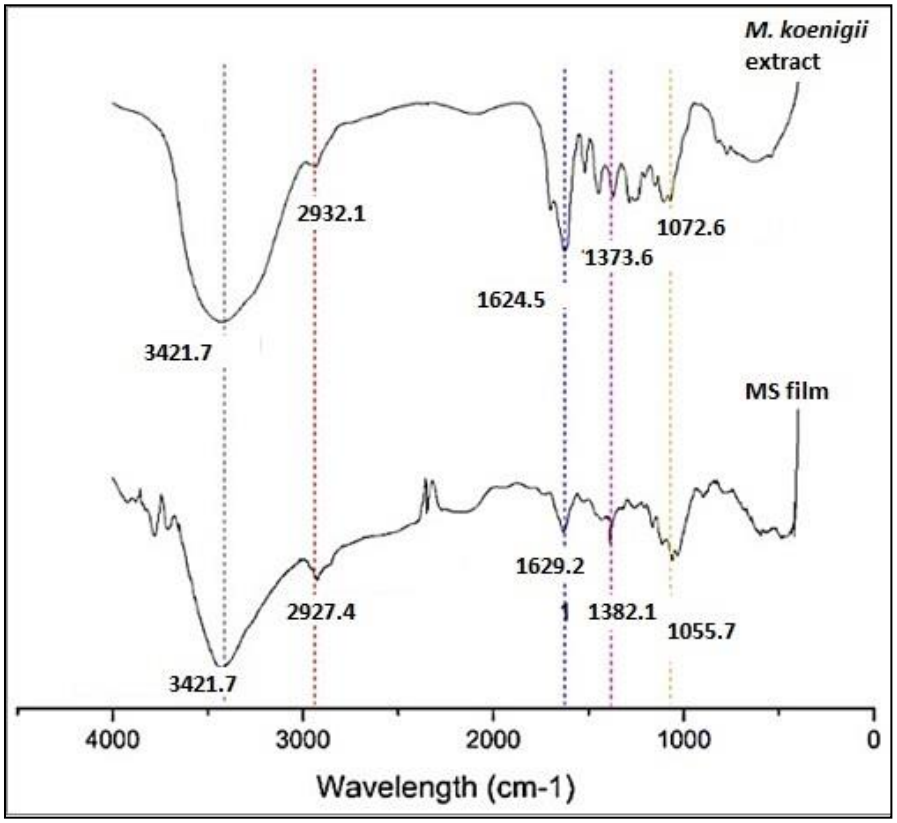


**Figure 3** FTIR spectra of *M. koenigii* leaf extract and *M. koenigii* protective film formed over MS surface

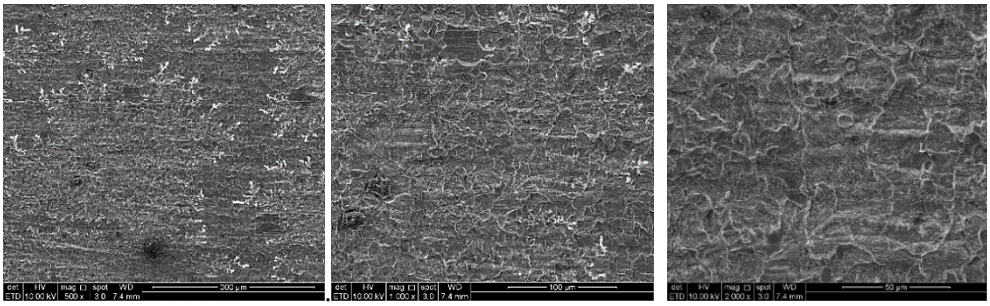

**Figure 4(i).** SEM images of mild steel in $CO_2$-saturated 3.5% NaCl medium at different magnifications of 500×, 1000×, and 2000×

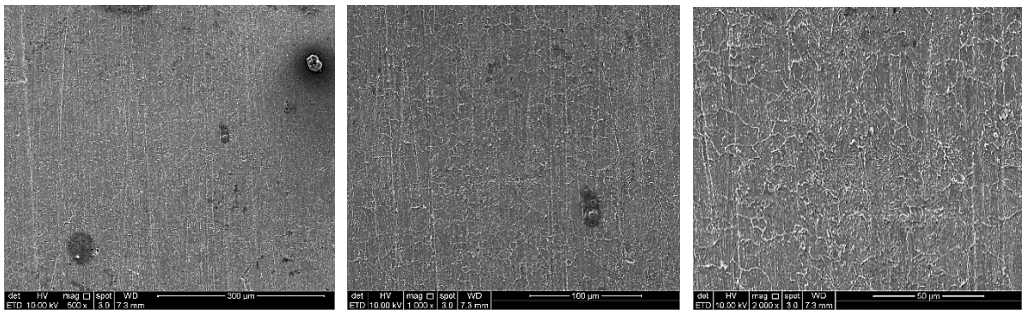

**Figure 4 (ii).** SEM images of mild steel in *M. koenigii* extract in $CO_2$-saturated 3.5% NaCl medium at different magnifications of 500×, 1000×, and 2000×

**Scanning Electron Microscope (SEM) Analysis**

Optical microstructures of mild steel specimens in blank solution ($CO_2$-saturated 3.5% NaCl medium) and 1000 ppm *M. koenigii* extract (in $CO_2$-saturated 3.5% NaCl medium) are shown in Figure 4(i) and (ii), respectively. Figure 4(i) shows viciously abrasive surfaces due to formation of corrosion on the metal, while cracks were found limited/minimized in micrographs of the metal with the plant extract except in the vicinity of the polishing lines. A protecting film covering the metal surface can be seen in Figure 4(ii), indicating the metal surface was well covered by green inhibitor molecules.

## CONCLUSION

The green inhibitor *M. koenigii* extract exhibited a dose-dependent corrosion inhibition in which the inhibition efficiency was found to increase with inhibitor concentration, which at 500 ppm gave 99% IE. The green inhibitor reduced corrosion through adsorption process, which followed Langmuir adsorption isotherm. Polarization studies revealed that the green inhibitor acted through mixed mode of corrosion inhibition while predominantly controlling the anodic dissolution. SEM micrographs have proven the presence of protective layers on the metal surfaces, which were formed by the plant extract chemical components through adsorption. FTIR results supported the presence of alkaloids, carbazoles, which were responsible for potent anticorrosion of the green inhibitor.

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## REFERENCES

1. Khanna, A. S. (2013) Corrosion protection of underground gas/crude pipelines, in *Corrosion and Materials:in the Oil and Gas Industries,* eds. R. Javaherdashti, C. Nwaoha and H. Tan, CRC Press: Boca Raton.

2. Ameh, E. S., Ikpeseni, S. and Lawal, L. S. (2017) A review of field corrosion control and monitoring techniques of the upstream oil and gas pipelines, *Africal Journal Online*, **14**, 67.

3. Khanna, A. S. (2016) Corrosion Protection of Underground Gas/Pipelines, *in Corrosion and*

*Materials in the Oil and Gas Industries*. CRC Press. 204-215.

4. Nathan, C. C. (1973) Corrosion inhibitors. *NACE*, **260**, 18.

5. Desimone, M. P., Grundmeier, G., Gordillo, and G. and Simison, S. N. (2011) Electrochim,. Acta **56**, 2990–2998.

6. Palmer, J. W., Hedges, W. and Dawson, J. L. (2004) The use of corrosion inhibitors in oil and gas production, Maney, London

7. John, D., Blom A., Bailey, S., Nelson, A., Schulz, J., De Marco, R. and Kinsella, B. (2006) The application of neutron reflectometry and atomic force microscopy in the study of corrosion inhibitor films, *Physica B: Condensed Editor Matter*, **385**, 924-926.

8. Reznik, V., Akamsin, V. D., Khodyrev, Yu P., Galiakberov, R. M., Efremov, Yu Ya and Tiwari, L. (2008) Mercaptopyrimidines as inhibitors of carbon dioxide corrosion of iron, *Corrosion Science*, **50**, 392-403.

9. Hamdy, A. and. El-Gendy, N. S. (2013) Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium, *Egypt. Journal. Petroleum*, **22**, 17-25.

10. Pandian, B. R. and Sethuraman, M. G. (2008) Natural products as corrosion inhibitor for metals in corrosive media -A review, *Materials Letters*, **62,** 113–116.

11. Gunavathy, N. and Murugavel, S. (2012) Corrosion inhibition studies of mild steel in acid medium using Musa acuminata fruit peel extract, *Journal of Chemistry*, **9**, 487-4957.

12. Odewunmi, N., Umoren, S. and Gasem, Z. (2015) Watermelon waste products as green corrosion inhibitors for mild steel in HCl solution, *Journal of Environmental Chemical Engineering*, **3**, 286-2968.

13. Lahhit, N., Bouyanzer, A., Desjobert, J. M., Hammouti, B., Salghi, R., Costa, J., Jama, C., Bentiss, F. and Majidi, L. (2011) Fennel (Foeniculum vulgare) essential oil as green corrosion inhibitor of carbon steel in hydrochloric acid solution, *Portugaliae Electrochimica Acta*, **29,** 127-1389.

14. Nnanna, L., Obasi, V. U., Nwadiuko, O. C., Mejeh, K. I., Ekekwe, N. D. and Udensi, S. C. (2012) Inhibition by *Newbouldia leavis* leaf extract of the corrosion of aluminium in HCl and $H_2SO_4$ solutions, *Archives of Applied Science Research*, **4**, 207-217

15. Kumar, K., Pillai, M. and Thusnavis, G. R. (2010) Pericarp of the fruit of *Garcinia Mangostana* as corrosion inhibitor for mild steel in hydrochloric acid medium, *Portugaliae Electrochimica Acta*, **28**, 373-383.

16. Kong, Y. C., But, P. P. H., Ng. K. H., Cheng, K. F., Chang, K. L., Wonga, K. M., Alexander I. G., Waterman, P. G. (1998) The biochemical systematics of *Merrillia*; in relation to *Murraya*, The Clauseneae and the Aurantioideae, *Biochemical systematics and ecology*, **16**, 47-50.

17. Sharmila, A., Prema, A. A., and Sahayaraj, P. A. (2010) Influence of *Murraya koenigii* (curry leaves) extract on the corrosion inhibition of carbon steel in HCl solution, *Rasayan Journal Chemistry*, **3**, 74-81.

18. Beenakumari, K. S. (2010) Inhibitory effects of *Murraya koenigii* (curry leaf) leaf extract on the corrosionof mild steel in 1M HCl, *Green Letters and Reviews*, **4**, 117-120.

19. Mu, G., Li, X., Qu, Q. and Zhou, J. (2006) Molybdate and tungstate as corrosion inhibitors for cold rolling steel in hydrochloric acid solution, *Corrosion Science*, **48**, 445-459.

20. ASTM G1-03 (2011) Standard Practice for Preparing, Cleaning and Evaluating Corrosion Speciments, ASTM G1-03, ASTM International.

21. AN-116 (1999) Corrosion rate calculations from coupons, Rohrback Cosasco System Inc., Application note.

22. Pandian, B. R. and Sethuraman, M. G. (2009) Solanum tuberosum as an inhibitor of mild steel corrosion in acid media, *Iranian Journal of Chemistry and Chemical Engineering* (IJCCE), **28**, 77-8413.

23. Karthikaiselvi, R. and Subhashini, S. (2013) Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol-*o*-methoxy aniline), *Journal of the Association of Arab*

*Universities for Basic and Applied Sciences*, **16**, 74-82.

24. Singh, A., Lin, Y., Liu, W., Ebenso, E. E. and Pan, J. (2013) Extract of *Momordica charantia* (Karela) seeds as corrosion inhibitor for P110SS Steel in $CO_2$ Saturated 3.5% NaCl Solution, *International Journal of Electrochemical Science*, **8**, 12884-12893.

25. Kumar, S. R., Loveleena, D., Godwin, S. (2013) Medicinal property of *Murraya koenigii*-a review, *International Research Journal of Biological Science*, **2**, 80-83.

26. Sethuraman, M. G. and Pandian, B. R. (2005) Corrosion inhibition of mild steel by *Datura metelin* acidic medium. *Pigment & Resin Technology,* **34**, 327–331

27. Fiebig, M., M. Pezzuto, J., D.Soejarto, D., Kinghornet, A. D. (1985) Koenoline, a further cytotoxic carbazole alkaloid from *Murraya koenigii*. *Phytochemistry*, **24**, 3041-3043.