Inhibition of Mild Steel Corrosion using Binary Mixture of Sesame and Castor Oil

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Abstract-
Mild steel is utilized as a prominent metal in the construction of equipment’s such as pipes and storage tanks in the oil and gas industry. It is vulnerable to a high rate of corrosion attack which has led to great losses and damages in the industry. The effect of corrosion attack on mild steel have continued to create a global interest on a means of controlling it. Different research have reported different ways of preventing corrosion, one of which involves the application of inhibitors on these structures. Previous research works have demonstrate the use of corrosion inhibitors as an effective means of reducing corrosion rate. This research study was to explore the efficiency of the binary mixture of castor and sesame oil as an organic corrosion inhibitor at different concentration of brine, volume of binary inhibitor and time. Minitab 17 was used as an optimization tool for the experimental procedure. The highest corrosion rate of 42.20 mm/yr was observed at 0.7 M brine solution, 19 mL volume of the binary inhibitor, over a period of 21 days. The lowest corrosion rate (3.01 mm/yr) was observed at 0.7 M brine solution, 23 ml of binary inhibitor and at 13 days. The results shows that the binary mixture of both castor and sesame oil is an effective and efficient organic inhibitor used in controlling corrosion.

Key words: Mild steel, Brine, Castor oil, sesame oil, Binary inhibitor

1. Introduction
Mild steel is one of the most frequently used raw materials in oil and gas industries. It is commonly used in the construction of pipes, storage units, tools and equipment. It is formed by the alloying of carbon with iron thereby enhancing the corrosion resistance properties of iron [1]. It’s easy to handle and is often used due to its numerous benefits such as low cost, high strength, toughness, malleability, and ductility. The trouble associated with corrosion is predominant in most industries as it results in the gradual destruction and irreversible deterioration of these metals by means of a chemical or electrochemical reaction [2]. It also accounts for the huge expenses spent on preserving the metals from to corrosion degradation [3-4]. Numerous damage resulting from corrosion had led to significant environmental issues due to disclosure of the corroded metallic part, causing the collapse of structures and impromptu plant shutdown [5, 6]. The most economically used means of elongating the useful period of industrial parts and components fabricated using mild steel is the application of chemically produced compounds that can be used to as inhibit corrosion [7]. The most frequently used inhibitors of corrosion is organic chemicals which react by creating a passive layer protecting the surface of the mild steel [8-11].
Different types of organic and inorganic compounds have been used as an inhibitor to shield metals from corrosion assault. Often times, organic inhibitors have a high level of remarkable impact on the effect of adsorption on the outer layer of the metal and consequently can be applied as a good corrosion inhibitor [12 – 14]. The effectiveness of organic inhibitors is associated with the availability of S, O and N atoms as polar function in a molecule, π electrons and heterocyclic compounds [15-17]. The polar function can be considered as the nucleus of reaction where the process of adsorption is established [18]. The use of natural extracts from seeds or leaves have been applied as corrosion inhibitors by various authors. El-Etre [19-23] performed corrosion inhibition using Khillah, Lawsonia, and natural honey on steel, zinc, aluminum and copper surfaces. Oguzie [24] studied the inhibitory properties of Hibiscus sabdariffa, Azadirachta indica, Telferia occidentalis, and Ocimum viridis leave extract. He also studied the use of Garcinia kola seed extract on mild steel in acidic solutions. Variant extracts from plants that have been studied for its corrosion inhibition properties include caffeic acid [25], aminoacids [26], Pennyroyal oil [27], caffeine [28], succinic acid [19] and ascorbic acid [29]. Loto and Olowoyo [10] used a combined mixture of Salvia officinalis and Simmondisa chinensis as corrosion inhibition on mild steel.

Hydrophobic acids are used to produce essential oils from volatile aroma compounds [10]. They are extracted from plants by absolute oil extraction, mechanical extraction, ultrasound extraction, solvent extraction, distillation, microwave assisted extraction among others. Essential oils have a wide range of health advantages and are investigated for the treatment of different types of diseases. This present study investigates the inhibition efficiency of the binary mixture of castor and sesame oil as an organic inhibitor in a brine solution.

2. **Methodology**

2.1 **Metal samples preparation**

Mild steel coupons of dimensions 20mm x 20mm x 3mm were glazed with 120 grade of emery and cleansed with distilled water. Experimental samples used for analysis were prepared by submerging these metal coupons in brine solution of different molarity concentration, the specific volumes of inhibitor solution, and time as stated in Table 1. The coupons were successively withdrawn from the mixture, cleansed using distilled water and the dry weight of the metal was determined.

2.2 **Experimental Procedures**

The mild steel plates were cleaned before being immersed in each of the solution. The specimen initial weight was noted using single pan balance and then immersed into the corrosive medium. The duration of the experiment was in days. After the stipulated no of days each of the specimen was cleaned of any corrosion product and the weight was measured. The weight loss was determined from the initial weight, and the corrosion rate was determined as given in Eqn. 1.

\[
\text{Corrosion Rate} = \frac{87.6 \times W_L}{A \text{ (cm}^2\text{)} \times \rho \times \left(\frac{T}{365}\right)}
\]

Where \(W_L\) is the weight loss of the metal coupons after treatment, \(A\) is mild steel area, \(\rho\) represents the density of metal, while \(T\) represents Time.
2.3 Gas Chromatography-mass spectrometry (GC-MS) analysis

GCMS analysis was carried out using GCMS-QP2010 Plus Shimadzu, Japan. The oven temperature was programmed from 70 to 280 °C at a linear velocity of 49.2 cm/sec and held for a hold up time of 5 min. The injector temperature was kept at 250 °C and column volume temperature was maintained 70 °C. The column flow rate was 1.80 mL/min, at a pressure of 116.9kPa. Helium was used as a carrier gas at a split ratio of 20.0. The Mass spectral ionization and interface temperature was maintained at 200 °C and 250 °C respectively. Mass spectra were within the m/z range 30– 3500 amu. Individual components of the binary inhibitor were identified by WILEY and NIST database matching and by comparison of mass spectra with published data [30, 31].

3. Result and discussions

3.1 Inhibition of corrosion rate in mild steel using RSM

Table 1 shows experimental design executed by Response Surface Methodology (RSM) to determine the corrosion rate as generated by Box Bohnken design Minitab 17. The experiment was carried out over 21-day period at a temperature of 23 °C. This experiment investigate the efficiency of the binary mixture of castor oil and sesame oil as an inhibitor of corrosion. The variables considered in this study include concentration of brine, volume of binary inhibitor, and time. The corrosion rate was determined and from the experimental results the highest corrosion rate was observed at 0.7 M concentration of brine, 19 mL of brine, and at a time of 21 days. This shows that a higher reaction time of 21 days and a low inhibitor volume of 19 mL was responsible for a faster corrosion rate on mild steel. The lowest corrosion rate of 3.01 mm/yr was observed at 0.7 M brine concentration, 23 mL of inhibitor, and at a low reaction time of 13 days. It can be said that the inhibitor creates a protective coating over the mild steel inhibiting the effect of brine on the time duration. Equation 1 shows the regression equation obtained from Minitab 17 statistical software using the second order polynomial.

\[
\text{Corrosion rate} = 158.2 - 91.7 \times \text{Conc. of Brine (M)} - 3.37 \times \text{volume of oil} + 10.541 \times \text{Time} + 33.3 \times \text{Conc. of Brine (M)} \times \text{Conc. of Brine (M)} + 0.0692 \times \text{volume of oil} \times \text{volume of oil} + 0.2800 \times \text{Time} \times \text{Time} - 0.03 \times \text{Conc. of Brine (M)} \times \text{volume of oil} + 2.709 \times \text{Conc. of Brine} \times \text{Time}
\]

(1)

Table 1: Experimental design of the weight loss experiment on mild steel in binary solution.

| Run | Conc. Of Brine (M) | Volume of the Binary Inhibitor (mL) | Time (Days) | Experimental Corrosion rate (mm/yr) | Predicted corrosion rate (mm/yr) |
|-----|-------------------|-----------------------------------|-------------|-------------------------------------|----------------------------------|
| 1   | 0.7               | 23                                | 13          | 3.01                                | 4.03                             |
| 2   | 0.5               | 26                                | 8           | 27.52                               | 24.03                            |
| 3   | 0.7               | 23                                | 13          | 3.70                                | 4.03                             |
| 4   | 0.7               | 19                                | 21          | 42.20                               | 45.68                            |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 5 | 0.9 | 26 | 8 | 17.68 | 14.39 |
| 6 | 0.9 | 19 | 17 | 5.91 | 6.39 |
| 7 | 0.7 | 23 | 13 | 3.05 | 4.03 |
| 8 | 0.9 | 26 | 17 | 5.12 | 4.46 |
| 9 | 0.7 | 30 | 13 | 3.75 | 6.02 |
| 10 | 0.5 | 19 | 17 | 5.91 | 6.21 |
| 11 | 0.7 | 23 | 13 | 3.75 | 4.03 |
| 12 | 0.7 | 23 | 13 | 3.70 | 4.03 |
| 13 | 1.1 | 23 | 17 | 4.04 | 5.18 |
| 14 | 0.5 | 26 | 17 | 5.22 | 4.35 |
| 15 | 0.5 | 23 | 21 | 12.45 | 11.03 |
| 16 | 0.7 | 23 | 13 | 3.71 | 4.03 |
| 17 | 0.9 | 19 | 8 | 17.79 | 16.33 |
| 18 | 0.7 | 15 | 13 | 3.73 | 4.03 |
| 19 | 0.5 | 19 | 8 | 27.47 | 25.88 |
| 20 | 0.3 | 23 | 13 | 12.05 | 13.55 |

Figure 1 – 3 shows the effect of the variables against corrosion rate. From Figure 1, it can be observed that at low volume of oil (inhibitor), and increasing the brine concentration, the corrosion rate rises. The corrosion rate slightly reduces at lower brine concentration. Figure 1 shows that the corrosion rate rises when the brine concentration was increased even when high volume of inhibitor (oil) was used. The effect of inhibitor volume (oil) and time on the corrosion rate is presented in Figure 2. It was observed that higher reaction time favors higher corrosion rate. The corrosion rate was at minimum at lower reaction time, this occur as a result of less amount of time available for the mild steel to be attacked. Figure 3 shows the effect of brine concentration and time on the rate at which corrosion occurs. It can be seen that at lower reaction time and brine concentration, the corrosion rate was slow while increasing the exposure time of metals at higher brine concentration increases the rate of corrosion attack on the metal.

The fitness of the model was analyzed by the coefficient of determination ($R^2$), this should be a minimum of 0.80 for the model validity [32]. The exactness of the model was determined by evaluating $R^2$ value. The result demonstrates that the optimization tool gave valid prediction, which gave an $R^2$ value of 97.55%. The adjusted $R^2$ (95.76%) proved that the model was highly significant. The variables considered have a reasonable conformance due to the relationship between the adjusted and predicted $R^2$ values. Figure 4 shows a linear correlation between the predicted and experimental values of corrosion rate values.
Figure 1: Contour plot showing effect of inhibitor volume and brine concentration on the corrosion rate

Figure 2: Contour plot showing effect of inhibitor volume and time on the corrosion rate

Figure 3: Contour plot showing effect of the brine concentration and time on the corrosion rate.
3.2 Inhibitor characterization using GCMS

The components present in the binary inhibitor of castor and sesame oil were analyzed to identify different components present in the inhibitor [30, 31]. 7 components were identified for the binary inhibitor. It is interesting to note from Table 2 that all the compounds identified possess oxygen and/ or π electrons present in their molecules. Figure 5 shows the fatty acids present in the binary mixture. The presence of fatty acids in the mixture help to minimize the rate of corrosion attack on the mild steel by blocking its active sites.

Figure 4: Predicted corrosion rate against experimental corrosion rate

Figure 5: GC-MS Chromatograph of the binary inhibitor.
Table 2: GC-MS analysis of the binary inhibitor.

| Peak | R.Time | Area% | Compounds          | Molecular Formula | Molar mass (g/mol) |
|------|--------|-------|--------------------|-------------------|-------------------|
| 1    | 15.021 | 2.55  | Oleic acid         | C_{18}H_{34}O_{2} | 282.47            |
| 2    | 15.552 | 21.49 | Stearic acid       | C_{18}H_{36}O_{2} | 284.48            |
| 3    | 15.908 | 1.9   | Methyl ricinoleate | C_{19}H_{36}O_{3} | 312.494           |
| 4    | 16.021 | 24.52 | Behenic acid       | C_{22}H_{44}O_{2} | 340.58            |
| 5    | 16.263 | 23.2  | Palmitic acid      | C_{16}H_{32}O_{2} | 256.43            |
| 6    | 16.571 | 12.91 | Undecylenic acid   | C_{11}H_{20}O_{2} | 184.279           |
| 7    | 17.025 | 7.19  | Nonadecyclic acid  | C_{19}H_{38}O_{2} | 298.5038          |

The electrochemical properties of the sesame oil and castor oil has been reported in literature. Swathi et al. [33] reported the inhibiting properties of castor oil against mild steel in acid and base medium. Mubofu [34] studied the functional properties of castor oil which includes foam capability and stability, water and oil absorption, bulk capacity and nitrogen solubility. High concentrations of stearic acid, behenic acid and plamitic acid observed in this study have been studied for their corrosion inhibitory properties [35 – 37]. The presence of these fatty acids leads to formation of a metal oxide passive layer over the metal surface thereby preventing corrosion attack.

4. Conclusion
This study shows that the binary mixture of castor and sesame oil serve as a good corrosion inhibition for mild steel in brine environment. The Corrosion rate was observed to reduce as volume of the binary mixture increases. The highest corrosion rate of 42.20 mm/yr was observed at 0.7 M brine solution, 19 mL volume of the binary inhibitor, over a period of 21 days. The lowest corrosion rate (3.01 mm/yr) was observed at 0.7 M brine solution, 23 ml of binary inhibitor and at 13 days. The optimization tool gave valid prediction with a high $R^2$ value of 97.55 % which was in agreement with the adjusted $R^2$ of 95.76 %. Thus proved that the model was highly significant. The GCMS confirms the presence of organic compounds that serve as a protective cover over the metal surface thereby inhibiting the corrosion rate.

5. Recommendation
Weight loss method is an essential method required for estimation of preliminary data of a metal corrosion rate. Several other methods such as potentiodynamic polarization, electrochemical impedance spectroscopy, gravimetric method, electrochemical frequency modulation etc. should be utilized to analyze the corrosion inhibition of mild steel samples by binary mixture of castor and sesame oil.

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Reference
[1] El-Sabbah, M.M.B., Mahross, A. Z. G., M. H., Khalil, H. F. Y., and Mahran, B. N. A.
(2016). Effect of Biocide on the Stability of Pomegranate Peel and Roselle as Eco-friendly Inhibitor on the Corrosion Control of Mild Steel in Acidic Medium. *Applied Chemistry*, 92: 38764-38773.

[2] Corrosion Costs and Preventive Strategies in the United States, NACE Publication NO. FHWA-RD-01-156. 08:06:2018 [cited 2018 08:06:2018]; Available from: https://www.nace.org/uploadedFiles/Publications/ccsupp.pdf.

[3] Akinyemi, O.O., Nwaokocha, C. N., Adesanya, A. O. (2012). Evaluation of corrosion cost of crude oil processing industry. *Journal of Engineering Science and Technology*, 7(4): 517–528.

[4] Jekayinfa, S.O., Okeekunle, P. O., Amole, P. I. G., Oyelade, J. A. (2015). Evaluation of corrosion cost in some selected food and agro - processing industries in Nigeria. *Anti-Corrosion Methods and Materials*, 52(4): 214-218.

[5] The Effects and Economic Impact of Corrosion, Corrosion: Understanding the Basics. 8 June 2018 [cited 2018 8 June 2018]; Available from: www.asminternational.org/documents/10192/1849770/06691g_chapter_1.pdf.

[6] Elaya, P. K. (2014). Corrosion risk analysis, risk-based inspection and a case study concerning a condensate pipeline. *Procedia Engineering*, 86: 597–605.

[7] Camila, G. D., Alexandre, F. G. (2013). Corrosion inhibitors – principles, mechanisms and applications. Developments in corrosion protection. *Intechopen*, 365–379

[8] David, A.W. (2017). Predicting the performance of organic corrosion inhibitors. *Metals*, 7(12): 553.

[9] Fouda, A. S., Diab, M. A., Fathy, S. (2017). Role of some organic compounds as corrosion inhibitors for 316L stainless steel in 1 M HCl. *International Journal of Electrochemical Science*, 12: 347–362.

[10] Loto, R. T., & Olowoyo, O. (2018). Corrosion inhibition properties of the combined admixture of essential oil extracts on mild steel in the presence of SO4 2– anions. *South African Journal of Chemical Engineering*, 26: 35–41.

[11] Rivera-Grau, L.N., Casales, M., Regla, I., Ortega-Toledo, D. M., Ascencio-Gutierrez, J. A., Porcayo-Calderon, J., Martinez-Gomez, L. (2013). Effect of organic corrosion inhibitors on the corrosion performance of 1018 carbon steel in 3% NaCl solution. *International Journal of Electrochemical Science*, 8: 2491–2503.

[12] Azhar, M.E., Mernari, M., Traisnel, M., Bentiss, F., Lagreneee, M. (2001). Corrosion inhibition of mild steel by the new class of inhibitors [2, 5-bis(n-pyridyl)- 1,3,4-thiadiazoles] in acidic media. *Corrosion Science*, 43: 2229.

[13] Elayyachy, M., El Idrissi, A., Hammouti, B. (2006) New thio-compounds as corrosion inhibitor for steel in 1 M HCl. *Corrosion Science*, 48: 2470.

[14] Emregül, K.C., Hayvalı, M. (2006). Studies on the effect of a newly synthesized Schiff base compound from phenazone and vanillin on the corrosion of steel in 2 M HCl. *Corrosion Science* 48: 797.

[15] Mernari, B., Elattari, H., Traisnel, M., Bentiss, F., Lagreneee, M. (1998) Inhibiting effects of 3,5-bis(n-pyridyl)-4-amino-1,2,4-triazoles on the corrosion of mild steel in 1 M HCl medium. *Corrosion Science*, 40: 391.

[16] Quraishi, M. A., Jamal, D. (2002). Inhibition of mild steel corrosion in the presence of fatty acid triazoles. *Journal of Applied Electrochemistry*, 32: 425.

[17] Wang, L. (2001) Evaluation of 2-mercaptobenzimidazole as corrosion inhibitor for mild steel in phosphoric acid. *Corrosion Science*, 43: 2281.
[18] Roberge, P. R. (1999). Corrosion inhibitors. Handbook of Corrosion Engineering. New York: McGraw-Hill.
[19] Amin, M.A., El-Rehim, S. S. A., El-Sherbini, E. E. F., Bayoumy, R. S. (2007). The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid: Part I. Weight loss, polarization, EIS, PZC, EDX and SEM studies. Electrochimica Acta, 52: 3588.
[20] El-Etre, A.Y. (1998). Natural honey as corrosion inhibitor for metals and alloys. I. Copper in neutral aqueous solution. Corrosion Science, 40: 1845.
[21] El-Etre, A.Y. (2003). Inhibition of aluminum corrosion using Opuntia extract. Corrosion Science, 45: 2485.
[22] El-Etre, A.Y. (2006). Khillah extract as inhibitor for acid corrosion of SX 316 steel. Applied Surface Science, 252: 8521.
[23] El-Etre, A.Y.A., M., El-Tantawy, Z. E. (2005). Corrosion inhibition of some metals using lawsonia extract. Corrosion Science, 47: 385.
[24] Oguzie, E. E. (2008). Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel. Corrosion Science, 50: 2993.
[25] de Souza, F.S., Spinelli, A. (2009). Caffeic acid as a green corrosion inhibitor for mild steel. Corrosion Science, 52: 1847.
[26] Zhang, D.Q., Cai, Q. R., Gao, L. X., Lee, K. Y. (2008). Effect of serine, threonine and glutamic acid on the corrosion of copper in aerated hydrochloric acid. Corrosion Science, 50: 3615.
[27] Bouyanzer, A., Hammouti, B., Majidi, L. (2006). Pennyroyal oil from Mentha pulegium as corrosion inhibitor for steel in 1 M HCl. Materials Letters, 60: 2840.
[28] Fallavena, T., Antonow, M., Gonçalves, R. S. (2006). Caffeine as non-toxic corrosion inhibitor for copper in aqueous solutions of potassium nitrate. Applied Surface Science, 253: 566.
[29] Gonçalves, R.S., Mello, L. D. (2001). Electrochemical investigation of ascorbic acid adsorption on low-carbon steel in 0.50 M Na2SO4 solutions. Corrosion Science, 43: 457.
[30] Oyekunle, D.T., (2017). Analysis of the Chemical Composition of the Essential Oil extracted from Thevetia peruviana seeds Using Gas Chromatography Analysis. American Journal of Engineering Research, 6(10): p. 51-55.
[31] Aprotoibi, M.S., Al-mayouf, A. M., Khan, M., & Mousa, A. A. (2014). Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. Arabian Journal of Chemistry, 7(3): 340-346.
[32] Betiku, E., Adepoju, T. F. (2013). Methanolysis optimization of sesame (Sesamum indicum) oil to biodiesel and fuel quality characterization. International Journal of Energy and Environmental Engineering, 2013. 4(9).
[33] Swathi, P. N., Rasheeda, K., Samshuddin, S., & Alva, V. D. P. (2017). Fatty acids and its derivatives as corrosion inhibitors for mild steel – an overview. Journal of Asian Scientific Research, 7(8), 301–308.
[34] Mubofu, E. B. (2016). Castor oil as a potential renewable resource for the production of functional materials. Sustainable Chemical Processes, 1–12.
[35] Chatoui, K., Echihi, S., Harhar, H., Zarrour, A., & Tabyaoui, M. (2018). An investigation of carbon steel corrosion inhibition in 1 M HCl by Lepidium sativum oil as green inhibitor. Journal of Materials and Environmental Sciences, 9(4), 1212–1222.
[36] Rodríguez-Torres, A., Valladares-Cisneros, M. G., Salinas-Bravo, V. M., & Gonzalez-
Rodriguez, J. G. (2017). Acid corrosion inhibition of 1018 carbon steel by using mentha spicata. *International Journal of Electrochemical Science, 12*(6), 5756–5771.

[37] Hmamou, D. Ben, Salghi, R., Zarrouk, A., Hammouti, B., Al-Deyab, S. S., Bazzi, L., Bammou, L. (2012). Corrosion inhibition of steel in 1 M hydrochloric acid medium by Chamomile essential oils. *International Journal of Electrochemical Science, 7*(3), 2361–2373.