

Investigation of the power between cinnamon essential oil macro and nanoemulsions as green corrosion inhibitors

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Abstract

Trying to reduce the corrosion problems as a critical menace for all industries, emphasizing the urgent need to increase responsible R&D centers, the development of high inhibition efficiency green inhibitors with new treatment strategies, and innovative interventions on a global scale is a necessary challenge. Here, a new type of cinnamon essential oil macro and nanoemulsions as green, sustainable, and low-cost corrosion inhibitors were introduced. The prepared macro and nanoemulsions were characterized with the DLS technique. The macro and nanoemulsion were used for investigating C1018 steel corrosion within acidizing media due to the implementation of corrosion inhibitors continuing to be a significant concern in chemical sectors. To our knowledge, there is no comparative study on the effect of nano and macro-emulsions of cinnamon essential oil on the corrosion resistance properties. The results obtained show that the nanoemulsion of the cinnamon essential oil due to the lower particle size of the oil nanoemulsion droplet and more effective interaction with the metal surface could act as an effective inhibitor compared to the macroemulsion sample for the corrosion protection of C1018 steel in HCl media. As can be seen from Scanning Electron Microscopy (SEM) images that were used to confirm the vital role and activity of the CNE in reducing the corrosion rate, It is clear that the CNE inhibitor can inhibit the dissolution of iron, thereby reducing the rate of corrosion and which means an affording better protection against corrosion in 0.1 M HCl.

Keywords: Cinnamon essential oil, Macroemulsion, Nanoemulsions, Corrosion, Acidic media

1. Introduction

The oil and gas production operations are on the increase and have maintained a significant contribution to the global economy for exploration. Based on the literature survey, the current global number of producing oil and gas wells peaked at 950,000 and the need for effective corrosion inhibitors during industrial processes like descaling, pickling, and acidizing for the protection of fluid transportation pipelines and storage tanks is indispensable [1]. Hitherto, chemical formulation based on aromatic amines and their salts, chromates, dichromates, phosphate, nitrates, etc. were at the forefront as anti-corrosion materials because of their high protection effectiveness [2]. Despite their high protection effectiveness, their environmental risks and high toxicity levels have relegated them to the backdoor and have intensified the call for green chemistry formulation—substances. So, to phase out hazardous chemicals, many researchers have been introduced for the fabrication of novel compositions with no or minimal negative effects on lives and the natural environment by 2030 [3]. Extracts and essential oils of different plant parts have been extensively investigated as antioxidant, anticorrosive, anthelmintic, antibacterial, and antifungal aspects. Numerous research groups developed them dedicated to exploring the basic components and properties of different essential oils as eco-friendly, green, and sustainable, as well as low-cost anti-corrosive treatment in diverse corrosive environments with good performance as a protective coating [4]. Recently, the focus of various studies has been the employing of cinnamon essential oils as green metal corrosion inhibitors.

In particular, investigations made into cinnamon essential oils by Lazrak et al. titled as "valorization of cinnamon essential oil as eco-Friendly corrosion inhibitor for solid Steel in 1.0 M hydrochloric acid solution" [5]. Cinnamon essential oil is a mixture of aldehyde, phenol, and terpene active compounds, exhibiting anti-corrosive characteristics and as a nontoxic additive can be widely applied in many inhibitor formulations [6]. Regarding the literature review, no studies have been focused on the effect of macro and nanoemulsion produced from cinnamon

essential oil for anti-corrosive investigation as a comparative study. In a comparison of previous work in microemulsion systems [7] as soft templates to engineering nanomaterials with controlled size, shape, and morphology with good monodispersity [8-12] and several applications in pre-water treatment [13], wastewater treatment [14-18], antibacterial agents [19-22], hydrophilic pattern surface [23,24], in this work, two types of macro (>400 nm) and nanoemulsion (particle size <100 nm) of cinnamon essential oil were prepared based on the surfactant based-emulsion system. Therefore, the objective of this research was to produce lecithin surfactant-based macro and nanoemulsion of cinnamon oil prepared by using homogenization and ultrasonication and then characterized by DLS and AFM techniques. As an application and to compare the effects of these two types of emulsion systems on anti-corrosive properties, corrosion inhibition on the C1018 alloy was examined and AFM-3D analysis was used to study the film forming on the surface of C1018 steel in an acidic solution.

2. Experimental

2.1. Materials

Lecithin as green surfactant to produce oil-in-water macro and nanoemulsion was purchased from Sigma-Aldrich, Cinnamon essential oil ($C_6H_5CH=CHCHO$) as green corrosion inhibitor was purchased from Noshad Iranian Co., and analyzed with GC-Mass. The analyzed cinnamon oil consists mainly Trans-cinnamaldehyde (47.18 %), δ -cadinene (10.25 %) and β -Cubebene (5.76 %) being the major constituents of cinnamon oil. Deionized water (0.055 $\mu S/cm$) which was produced in our lab with PKA (Smart two pure) instrument. C1018 alloy that the chemical compositions of the alloys are summarized in Table 1, was received.

Table 1. The chemical compositions of the exemplary alloy

Chemical composition (%) of C1018 alloy									
C	Si	Mn	P	S	Cr	Ni	Cu	Mo	V
0.14-0.20	-	0.60-0.90	≤ 0.040	≤ 0.050	-	-	-	-	-

2.2. Preparation of surfactant-based cinnamon oil macro and nanoemulsion

To obtain macro and nanoemulsions, two surfactant solution samples were made by adding an amount (0.5 g) of lecithin to 20 ml of double-distilled water, separately, followed by homogenization by Homogenizer (IRAN Nano product), for 1 min. Then, cinnamon essential oil (0.25 ml) was added to each clear surfactant solution mixed again for 2 min, and labeled as cinnamon macroemulsion (CME) [25,26]. To make cinnamon nanoemulsion (CNE), another prepared (CME) was sonicated at 30 KHz frequency, 250 W input power for 15 min by Ultrasonicator (Fanavari Iranian Pajohesh Nassir) to obtain nanoemulsion. In all experiments during the sonication process, to prevent the increase of temperature in macro and nanoemulsion systems, both systems were kept in a water bath. The total experiment steps to make CME and CNE are illustrated in Fig. 1.

2.3. Characterization

The average droplet size and PDI of both CME and CNE were measured by dynamic light scattering (DLS) in a Zetasizer (Malvern instruments) to compare the stability of both emulsion systems. The surface topography of the uninhibited and inhibited C1018 with CNE compared to the C1018 (before immersion in HCl solution) were investigated with Scanning Electron Microscopy (SEM) (TESCAN).

2.4. Corrosion study with gravimetric analysis

To study the impact of acid corrosion inhibitor, inhibitor concentration, and also the impact temperature, weight loss-based C1018 alloy surface corrosion analysis for all experiments was carried out at different temperatures from 303 K to 343 K in 0.1 M HCl in the absence of inhibitor as control sample and the presence of new green inhibitor at concentrations of 2-10 ppm that the total exposure time of 5 days was selected. The experiment conditions are as follows: 50 ml of uninhibited or control sample and working solution (inhibited corrosion solution) was employed, and the size of the metal surface C1018 samples was 8.7 cm \times 1.4 cm \times 0.1 cm. The following equation (Eq. 1) was utilized for the calculation of the corrosion rate of the prepared green inhibitor and control sample.

$$\text{Corrosion rate (\%)} = \frac{W_o - W}{W_o} \times 100 \quad (1)$$

where W_0 and W are the weight loss of C1018 alloy in the absence and the presence of the acid anti-corrosive, respectively. In corrosion study, an acid corrosion inhibitor provides sufficient corrosion inhibition so that a pitting index has definitions of the integers [27].

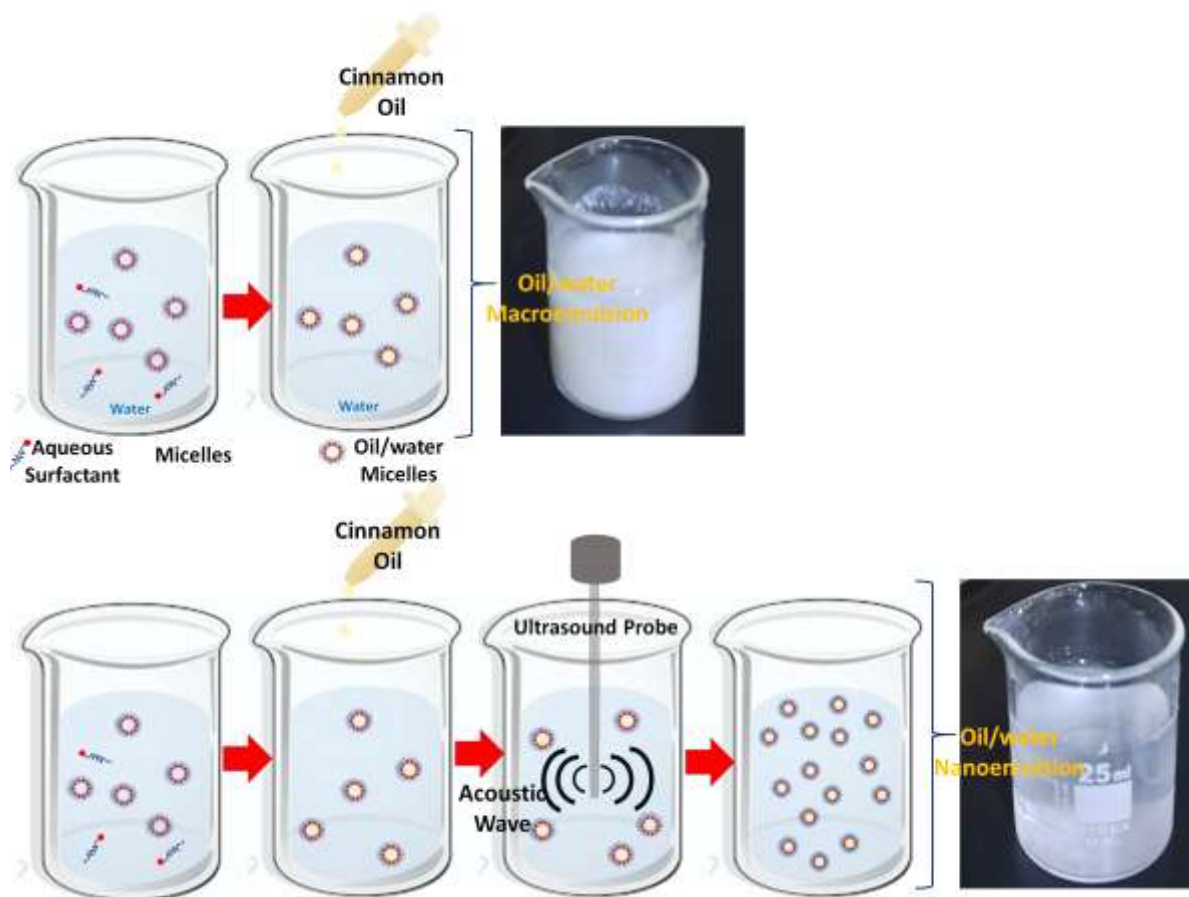


Fig. 1. Total experiment steps to made CME and CNE.

3. Results and discussion

3.1. DLS

The size distribution of the cinnamon essential oil macro and nanoemulsion droplets was measured with DLS. The intensity-weighted size average values (Z-average) and the polydispersity index (PdI) for both CME and CNE were (172.3 nm and 0.35) and (80.5 nm and 0.22). The mean size and size distribution of nanoemulsion droplets could become smaller by Ultrasonication treatment and a decrease in the mean size of 80 nm was obtained. Sonication had a significant effect on the decrease of both mean droplet size (Z-average) and size distribution (PdI) of CNE. Sonication treatment led to create an interfacial wave. The obtained interfacial wave produces microbubbles, the collapse of which resulted in the disruption of oil droplets, reducing their particle size to a less than 100 nm scale.

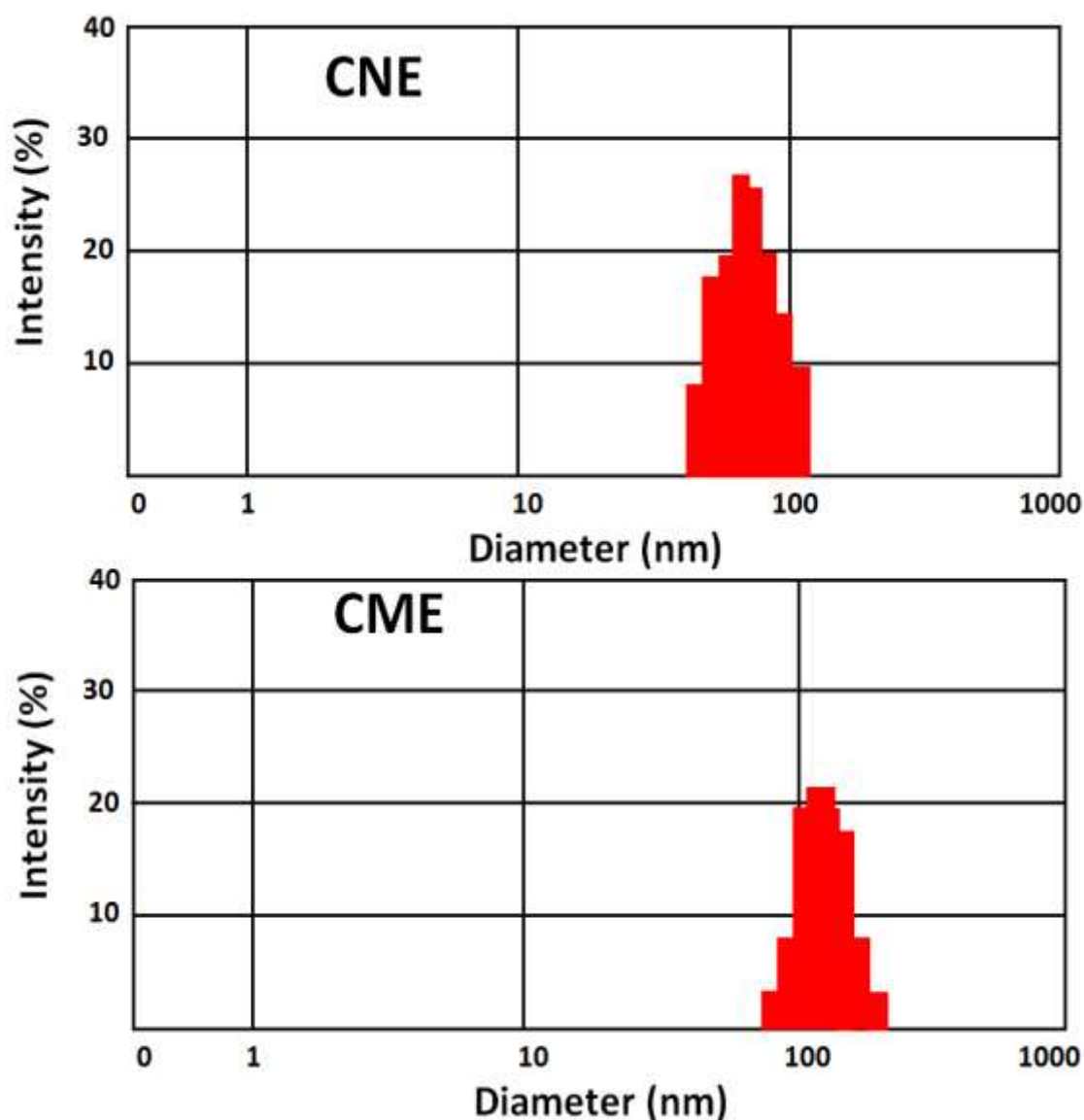


Fig. 2. DLS analysis of CME and CNE systems

3.3. Corrosion study

3.3.1. The effect of inhibitor concentration

All experiments on the effect of the inhibitor concentration to investigate the corrosion efficiency and corrosion rate were conducted at standard room temperature by using the weight loss method after 5 days of immersion in acidic solution. Fig. 4, presents the results obtained for the weight loss experiments and calculation of the corrosion rate and efficiency. The results obtained show nanoemulsion has a high efficiency compared to the macroemulsion. For the nanoemulsion inhibitor when the concentration of nanoemulsion was increased to 6 ppm, the corrosion rate decreased and the inhibitor efficiency increased and then with more increase in inhibitor concentration, the inhibitor efficiency was kept without any remarkable changes. The highest inhibition efficiency of about 93 % was achieved when a 6 ppm inhibitor was used. From the data gained, the inhibitor showed an excellent result for inhibiting the corrosion of C1018 steel in an acidic solution [28].

No corrosion protection was observed for the control sample (only acidic solution) in the absent of both inhibitors and rust on the surface of C1018 obtained.

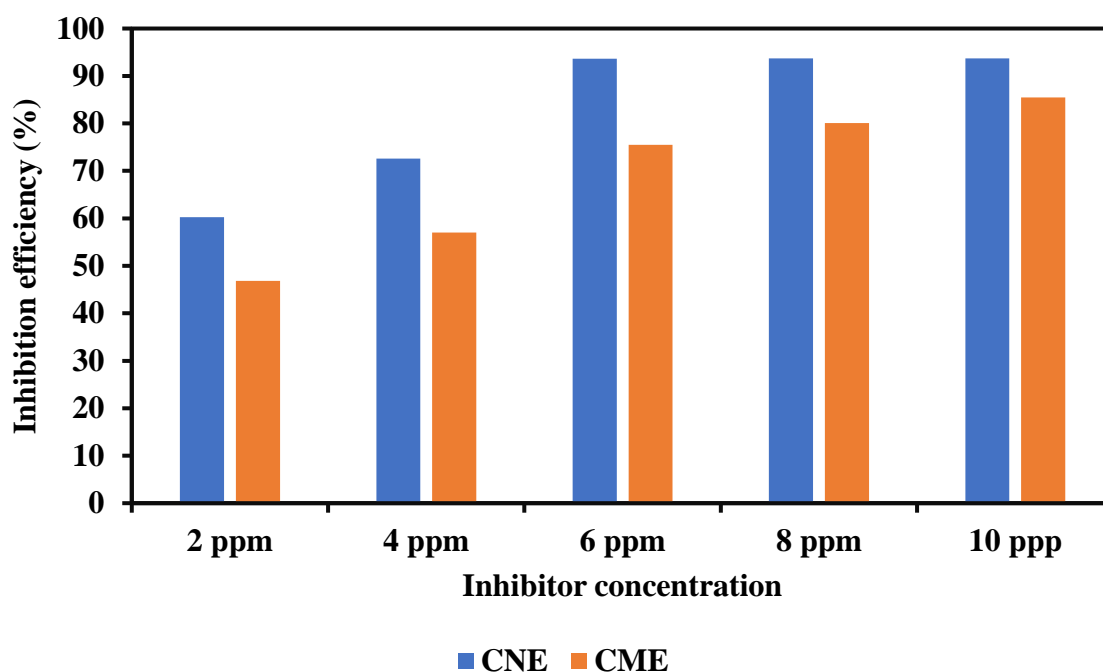


Fig. 3. The effect of inhibitor concentration for the protection of the C1018 alloy.

3.3.2. The effect of temperature on the impact of inhibition efficiency

The effect of temperature on the inhibition performances of cinnamon oil nanoemulsion was studied by using weight loss at 303 K, 323 K, and 343 K with 6 ppm concentration of corrosion inhibitor for both samples CME and CNE (Fig. 4). To further elucidate their inhibition efficiency, thermodynamic parameters such as temperature are very useful for shedding light on the adsorption behavior of corrosion inhibitors on the surface of C1018 alloy. It is shown that the corrosion of C1018 increases with temperature and the corrosion rate for CME was faster compared to the CNE. It shows a better inhibition performance at 303 K compared to the inhibitor efficiency at 323 K and 343 K with inhibitor efficiency of 93 % in the presence of CNE and 73 % in the presence of the CME.

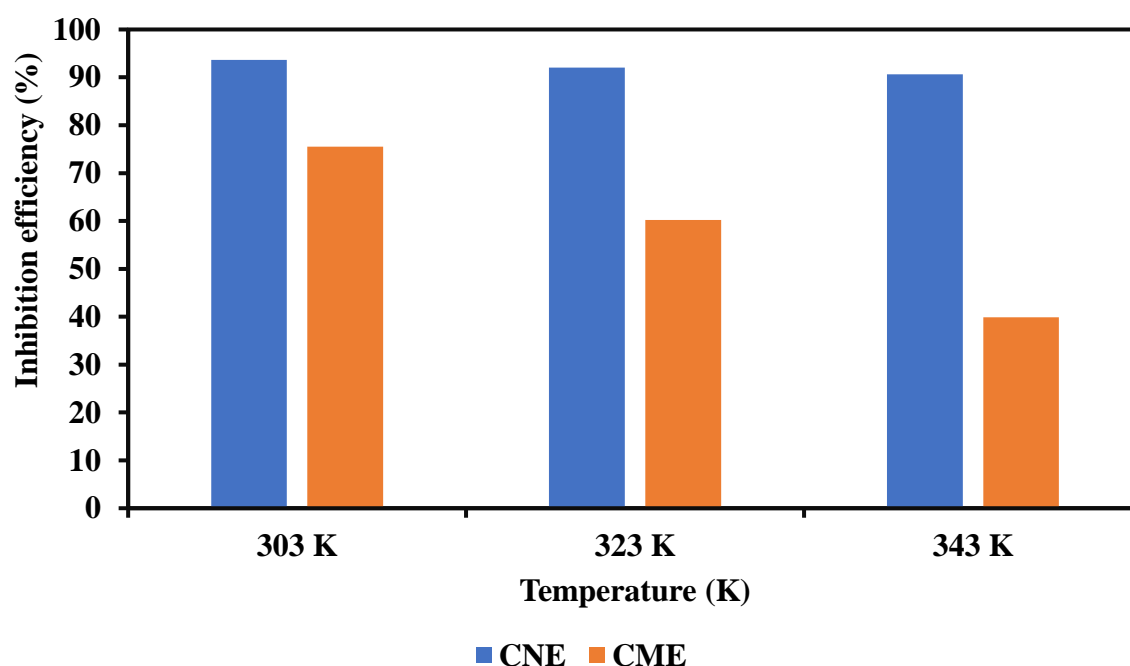


Fig. 4. The effect of temperature on the inhibition efficiency of CNE inhibitor (6 ppm) after 4 days for the protection of the C1018 alloy in acidic medium.

3.3.3. Surface analysis of C1018 with SEM study

To further elucidate the inhibition efficiency of CNE as the best corrosion inhibitor, SEM analysis is very useful for shedding light on the adsorption behavior of corrosion inhibitors on the surface of C1018 alloy after treatment compared to the uninhibited C1018 sample. Fig. 5, presents the photographs of C1018 (a) before immersion in HCl (0.1 M), (B) inhibited surface in the presence of the CNE, (and) (c) uninhibited surface (control). It can be seen from Fig. 3, that for the inhibited sample due to the protection film forming with a dark thin layer, no corrosion was observed, but for uninhibited C1018 rust on the surface was obtained. The effect of CNE inhibitors on the surface micromorphology of the tested C1018 steel was explored using SEM images of the corroded C1018 surface in the absence or presence of CNE inhibitor with a concentration of 6 ppm and also C1018 before treatment.

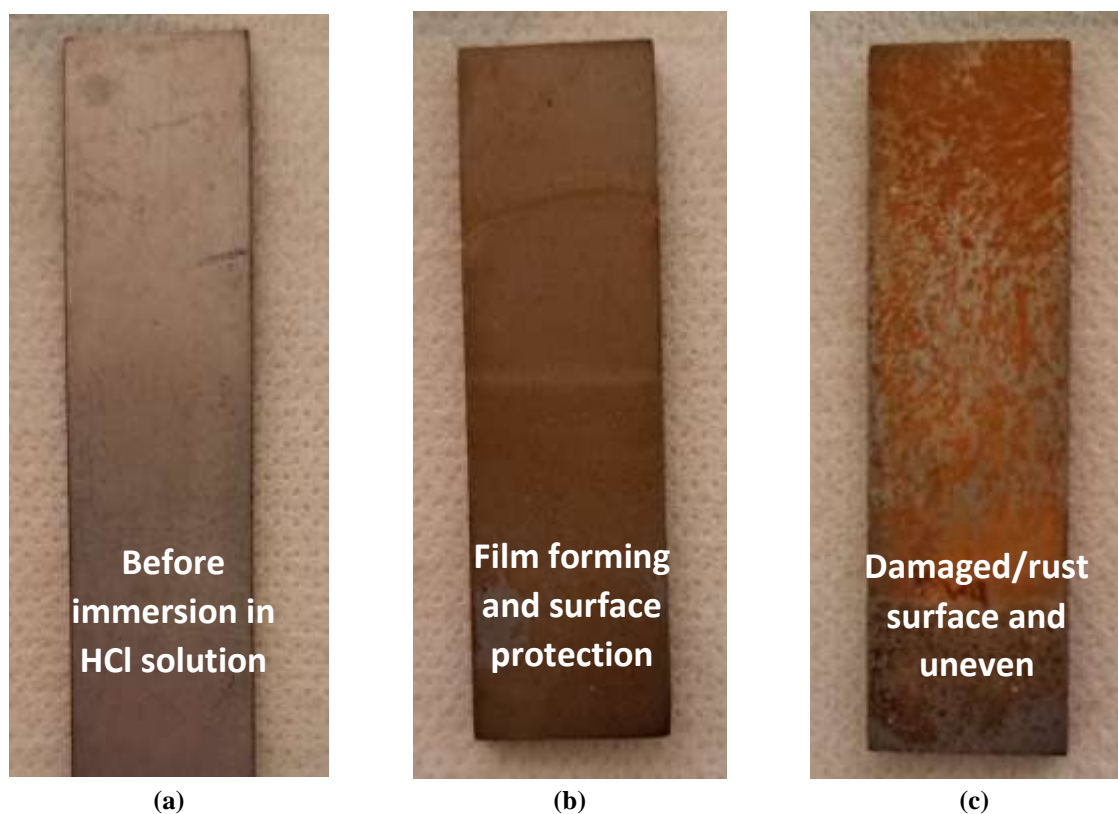


Fig. 5. Photographs of C1018 (a) before immersion in HCl (0.1 M), (B) inhibited surface in presence of the CNE, (and) (c) uninhibited surface (control).

As can be seen from Fig. 6 (before treatment and immersion in acidic solution) the C1018 steel surface shows some abrading scratch. After immersion in 0.1 M HCl at 343 K in the absence (control sample) and presence of 6 ppm CNE inhibitor for 5 days are shown in Fig. 6, respectively. Close investigation of the SEM images of inhibited and uninhibited C1018 surfaces reveals that the uninhibited specimen surface accompanied by an aggressive attack of the corroding medium, was damaged and the corrosion scale appears too uneven. Whereas the C1018 surface in the presence of CNE inhibitor displayed a smooth surface with a few small notches. The CNE inhibitor can inhibit the dissolution of iron, thereby reducing the rate of corrosion which means affording better protection against corrosion in 0.1 M HCl [29,30]. Noor Mohammad Beigi [31] prepared a novel type of cinnamaldehyde contained poly(methyl methacrylate) nanocolloid as an efficient acid anti-corrosive for steel in acidic media. He investigated the role of amine film forming on the surface of metal alloys with atomic force microscopy (AFM). This type of inhibitor has highlighted the influence of a unique combination of cinnamaldehyde-contained poly(methyl methacrylate) based on the microemulsion system on the deterioration of alloy surface in 4% HCl and 15% HCl at different temperatures 303 K-443 K.

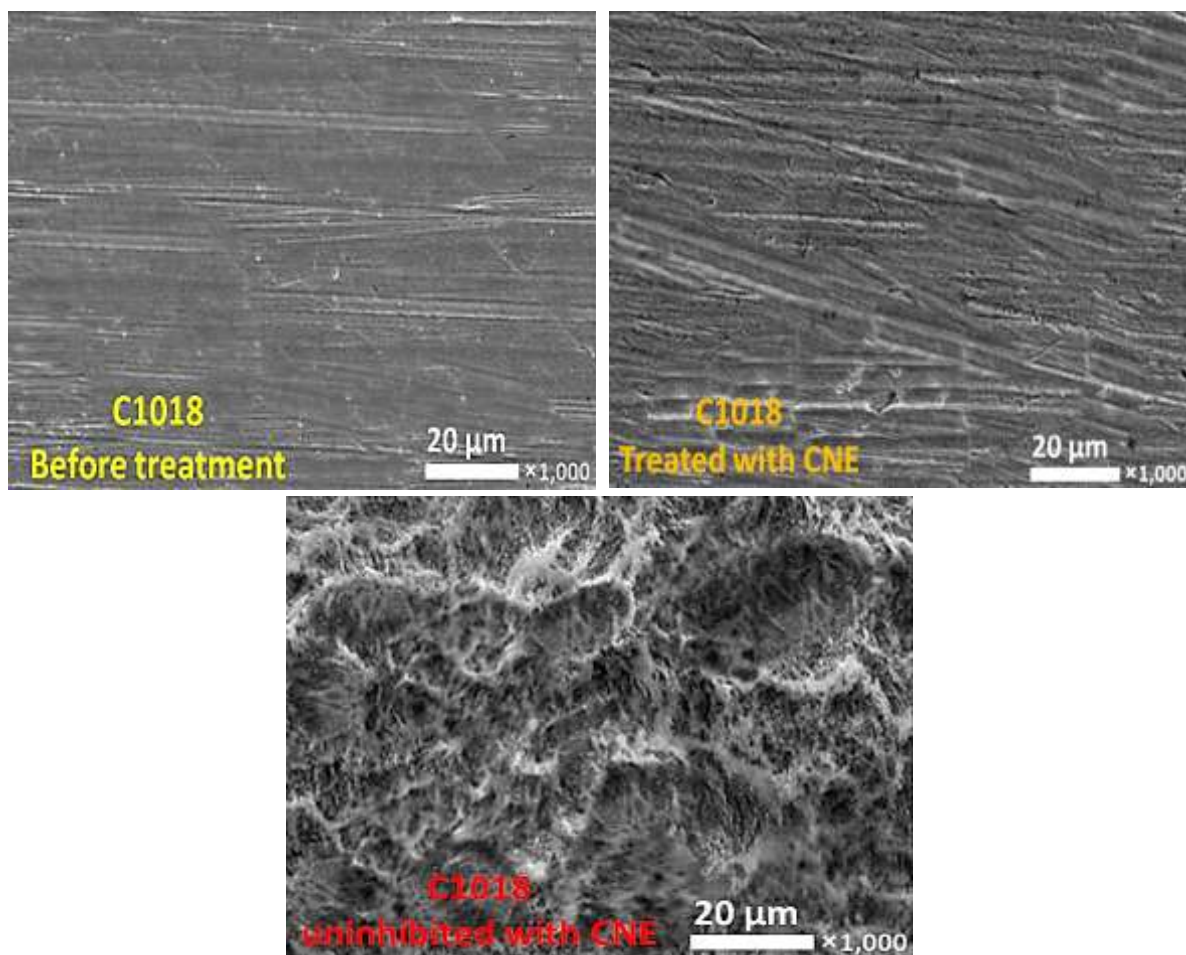


Fig. 6. SEM images of the C1018, before immersion in solution for corrosion study, after immersion in solution and study test with CNE and uninhibited with CNE (control sample).

4. Conclusion

Here, a new type of cinnamon essential oil macro and nanoemulsions as green, sustainable, and low-cost corrosion inhibitors were introduced. The prepared macro and nanoemulsions were characterized with the DLS technique. The macro and nanoemulsion were used for investigating C1018 steel corrosion within acidizing media due to the implementation of corrosion inhibitors continuing to be a significant concern in chemical sectors. The size distribution of the cinnamon essential oil macro and nanoemulsion droplets was measured with DLS. The intensity-weighted size average values (Z-average) and the polydispersity index (PdI) for both CME and CNE were (172.3 nm and 0.35) and (80.5 nm and 0.22). The results obtained show nanoemulsion has a high efficiency compared to the macroemulsion. For the nanoemulsion inhibitor when the concentration of nanoemulsion was increased to 6 ppm, the corrosion rate decreased and the inhibitor efficiency increased and then with more increase in inhibitor concentration, the inhibitor efficiency was kept without any remarkable changes. It shows a better inhibition performance at 303 K compared to the inhibitor efficiency at 323 K and 343 K with inhibitor efficiency of 93 % in the presence of CNE and 73% in the presence of the CME. The CNE inhibitor can inhibit the dissolution of iron, thereby reducing the rate of corrosion which means affording better protection against corrosion in 0.1 M HCl.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] K. Tamalmani, H. Husin, H. Review on corrosion inhibitors for oil and gas corrosion issues. *Appl. Sci.*, 10 (2020) 3389. <https://doi.org/10.3390/app10103389>
- [2] A. Marciales, T. Haile, B. Ahvazi, T.-D. Ngo, J. Wolodko, Performance of green corrosion inhibitors from biomass in acidic media. *Corrosion Rev.*, 36(3) (2018) 239–266. <https://doi.org/10.1515/correv-2017-0094>
- [3] S.A. Umoren, M.M. Solomon, I.B. Obot, R.K. Suleiman, Effect of intensifier additives on the performance of butanolic extract of date palm leaves against the corrosion of API 5L X60 carbon steel in 15 wt.% HCl solution. *Sustainability*, 13(10) (2021) 5569. <https://doi.org/10.3390/su13105569>
- [4] T. Himeur, K. Rouibah, H. Ferkous, A. Boublia, K.O. Rachedi, K. Harrouche, C. Boulechfar, A. Abdennouri, Y. Benguerba, Unlocking the power of Inula Viscosa essential oil: A green solution for corrosion inhibition in XC48 steel within acidic environments. *Process Safety and Environmental Protection: Transactions of the Institution Chem. Eng., Part B*, 187 (2024) 1422–1445. <https://doi.org/10.1016/j.psep.2024.05.061>
- [5] J. Lazrak, N. Arrousse, E. Ech-chihbi, Y. El Atki, A. Taroq, A. Abdellaoui, F. El-Hajjaji, M. Taleb, A. Nahle, A. (2021). Valorization of cinnamon essential oil as Eco-friendly corrosion inhibitor for mild steel in 1.0 M hydrochloric acid solution. *Surface Eng. Appl. Electrochem.*, 57(3) (2021) 360–373. <https://doi.org/10.3103/s1068375521030108>
- [6] A. Masyita, R. Mustika Sari, A. Dwi Astuti, B. Yasir, N. Rahma Rumata, T.B. Emran, F. Nainu, J. Simal-Gandara, Terpenes and terpenoids as main bioactive compounds of essential oils, their roles in human health and potential application as natural food preservatives. *Food Chem. X*. 13 (2022) 100217. <https://doi.org/10.1016/j.fochx.2022.100217>.
- [7] A. Salabat, B.S. Mirhoseini, F. Mirhoseini, Ionic liquid based surfactant-free microemulsion as a new protocol for preparation of visible light active poly(methyl methacrylate)/TiO₂ nanocomposite. *Sci Rep* 14, 15676 (2024). <https://doi.org/10.1038/s41598-024-66872-7>
- [8] A. Salabat, F. Mirhoseini, K. Abdoli, A microemulsion route to fabrication of mono and bimetallic Cu/Zn/γ-Al₂O₃ nanocatalysts for hydrogenation reaction. *Scientia Iranica*, 25(2018) 1364–1370. <https://doi.org/10.24200/sci.2018.5023.1048>
- [9] A. Salabat, F. Mirhoseini, Polymer-based nanocomposites fabricated by microemulsion method, *Polym. Compos.* 43 (2022) 1282–94. <https://doi.org/10.1002/pc.26504>
- [10] A. Salabat, F. Mirhoseini, Z. Masoumi, M. Mahdie, Preparation and characterization of polystyrene-silver nanocomposite using microemulsion method and its antibacterial activity, *JNS* 4 (2014) 377–382.
- [11] A. Salabat, F. Mirhoseini, F.H. Nouri, Microemulsion strategy for preparation of TiO₂-Ag/poly(methyl methacrylate) nanocomposite and its photodegradation application. *J. Iranian Chem. Soc.* 20 (2022) 599–608. <https://doi.org/10.1007/s13738-022-02693-7>.
- [12] A. Salabat, F. Mirhoseini, A novel and simple microemulsion method for synthesis of biocompatible functionalized gold nanoparticles, *J. Mol. Liq.* 268 (2018) 849–853. <https://doi.org/10.1016/j.molliq.2018.07.112>
- [13] F. Mirhoseini, A. Salabat, Polymer nanocomposite based composition and method for controlling water hardness, United States patent 11136247.
- [14] F. Mirhoseini, A. Salabat, Ionic liquid based microemulsion method for fabrication of poly(methyl methacrylate)-TiO₂ nanocomposite as highly efficient visible light photocatalyst, *RSC Adv.* 5 (2015) 12536–12545. <https://doi.org/10.1039/c4ra14612c>
- [15] F. Mirhoseini, A.S alabat, Photocatalytic filter, United States patent 10828629.
- [16] F. Mirhoseini, B.S. Mirhoseini, M. Noor Mohammad Beigi, M. Understanding the photodegradation of amoxicillin antibiotic using visible light sensitized poly(methyl methacrylate)/TiO₂ nanocomposite. *Nano Sci. Technol. J.* 1(1) (2023) 38–48. <https://doi.org/10.22034/nstj.2023.707804>

- [17] F. Mirhoseini, A. Salabat, Investigation of operational parameters on the photocatalytic activity of a new type of poly(methyl methacrylate)/ionic liquid-TiO₂ nanocomposite, *Iranian J. Chem. Chem. Eng.*, 38 (2019) 101-114. <https://doi.org/10.30492/IJCCE.2019.37613>
- [18] F. Mirhoseini, A. Salabat, Removal of methyl tert -butyl ether as a water pollutant by photodegradation over a new type of poly(methyl methacrylate)/TiO₂ nanocomposite. *Polymer Composites*, 39(4) (2018) 1248–1254. <https://doi.org/10.1002/pc.24059>
- [19] A. Salabat, F. Mirhoseini, Applications of a new type of poly(methyl methacrylate)/TiO₂ nanocomposite as an antibacterial agent and a reducing photocatalyst. *Photochem. Photobiol. Sci.*, 14(9) (2015) 1637–1643. <https://doi.org/10.1039/c5pp00065c>
- [20] F. Kamali, K. Faghihi, F. Mirhoseini, High antibacterial activity of new eco-friendly and biocompatible polyurethane nanocomposites based on Fe₃O₄/Ag and starch moieties. *Polym. Eng. Sci.*, 62(5) (2022) U1444-1462. <https://doi.org/10.1002/pen.25934>
- [21] A. Salabat, F. Mirhoseini, M. Mahdih, H. Saydi, A novel nanotube-shaped polypyrrole-Pd composite prepared using reverse microemulsion polymerization and its evaluation as an antibacterial agent, *New J. Chem.* 39 (5) (2015) 4109–4114. <https://doi.org/10.1039/c5nj00175g>
- [22] A. Salabat, F. Mirhoseini, M. Arjomandzadegan, E. Jiryaei, A novel methodology for fabrication of Agpolypyrrole core-shell nanosphere using microemulsion system and evaluation of its antibacterial application, *New J. Chem.* 41 (21) (2017) 12892–12900. <https://doi.org/10.1039/c7nj00678k>
- [23] A. Salabat, F. Mirhoseini, Photo-induced hydrophilicity study of poly(methyl methacrylate)/TiO₂ nanocomposite prepared in ionic liquid based microemulsion system. *Current Appl. Polym. Sci.*, 2(2), (2018) 112–120. <https://doi.org/10.2174/2452271602666180803141554F>
- [24] F. Mirhoseini, A. Salabat, Antibacterial activity based poly(methyl methacrylate) supported TiO₂ photocatalyst film nanocomposite, *Tech. J. Eng. Appl. Sci.* 5 (2015)115-118.
- [25] A. Salabat, F. Mirhoseini, R. Valirasti, Engineering poly(methyl methacrylate)/Fe₂O₃ hollow nanospheres composite prepared in microemulsion system as a recyclable adsorbent for removal of benzothiophene, *Ind. Eng. Chem. Research* 58 (2019) 17850-1785. <https://doi.org/10.1021/acs.iecr.9b04322>
- [26] A. Salabat, F. Mirhoseini, Applications of a new type of poly(methyl methacrylate)/TiO₂ nanocomposite as an antibacterial agent and a reducing photocatalyst. *Photochem. Photobiol. Sci.*, 14(9) (2015) 1637–1643. <https://doi.org/10.1039/c5pp00065c>
- [27] M. Chigondo, F. Chigondo, F., 2016, Recent natural corrosion inhibitors for mild steel: An overview, *J. Chem.*, 2016 (2016) 6208937.
- [28] E. Bayol, K. Kayakirilmaz, M. Erbil, The inhibitive effect of hexamethylenetetramine on the acid corrosion of steel, *Mater. Chem. Phys.*, 104 (1) (2007) 74–82.
- [29] L. Bai, L.-J. Feng, H.-Y. Wang, Y.-B. Lu, X.-W. Lei, F.-L. Bai, Comparison of the synergistic effect of counterions on the inhibition of mild steel corrosion in acid solution: electrochemical, gravimetric and thermodynamic studies. *RSC Adv.*, 5(6) (2015) 4716–4726. <https://doi.org/10.1039/c4ra12286k>
- [30] M. Noor Mohammad Beigi, The effect of amino acid type on the anti-corrosion activity of poly(methyl methacrylate) nanocolloid in boiler, 1(2) (2023) 56-67. <https://doi.org/10.22034/NSTJ.2023.2013982.1007>
- [31] M. Noor Mohammad Beigi, Boosting the impact of cinnamaldehyde-contained polymer microemulsion on the corrosion of C1018 alloy in an acidic medium, *Colloid Nanosci. J.* 2(1) (2024) 220-227.