



Original Research Article

Prospects of Nanoparticles Corrosion Inhibition in Saline Environments

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ABSTRACT

This paper presents an experimental investigation on the application of silica nanoparticles as corrosion inhibitor in saline solutions that are relevant to oil and gas production systems. The gravimetric (weight loss) method was used to analyse the corrosion loss in mild steel exposed to different salinity brines in the absence and presence of nanoparticles for a period of 360 h. The results of the study showed that the solution salinity, concentration of nanoparticles and the duration of exposure influenced the corrosion process of mild steel. The use of low concentration (1 g/L) of nanoparticles in non-saline solution was found to be more efficient in corrosion inhibition than in saline solutions of different salt concentrations. The use of high concentration (5 g/L) of nanoparticles was however more efficient in saline solutions up to 3.2 g/L but at very high salinity level (32 g/L), slight reduction in its efficiency was observed. Lower efficiency of high concentration nanoparticles was also observed in non-saline solution. The novel potential of using silica nanoparticles as corrosion inhibitor in saline environments investigated in this study has unveiled the possibility of using nanoparticles as corrosion inhibitor in hydrocarbon production system.

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1. INTRODUCTION

Corrosion is the natural way metallic materials respond to environmental influence and it is characterised by a degradation process that needs to be controlled (Udoh and Sunday, 2020). Corrosion is a major problem in the oil and gas industry due to the high use of metallic products such as flowlines and pipes in the system. This flowlines and pipelines are constantly exposed to different agents of corrosion like oxygen, carbon-dioxide, sulfur, nitrogen formation brine, injection water etc., during the oil production process.

Generally, different methods of corrosion control exist such as surface coatings and painting, use of cathodic protection and use of corrosion inhibitors (Agu, 2010). The use of corrosion inhibitors is the most common method

of corrosion control in oil production system due to the ease of applicability (Brondel et al., 1994). The cost of the conventional corrosion inhibitors is however high and most of them are non-degradable in nature thereby constituting an environmental threat (Popoola, 2019). Recent studies have explored the potential of using green corrosion inhibitors that are environmentally friendly and their results showed that they have great prospects (El-Etre, 2006, Okafor et al., 2008, AL-Mosawi et al., 2020, Udoh and Sunday, 2020). Of interest in this study is the application of nanoparticles as corrosion inhibitor. This involves the use of particles at nanoscale with dimensions of 1-100 nm (Cheraghian and Hendraningrat, 2015). Nanoparticles have found applications in different sectors of the oil and gas industry such as in drilling, production, refinery, and enhanced oil recovery operations (Agista, et al., 2018).

Explorations of the application of nanoparticles in corrosion process have previously been considered, but most of the investigations were conducted in acidic environments. For example, Al-Mosawi et al. (2020) investigated the synergistic effect of zinc oxide (ZnO) nanoparticles with organic compound (3-((3-acetylphenyl) imino) indolin-2-one) as corrosion inhibitor for hydrochloric acid medium and they found the ZnO nanoparticles highly efficient in improving corrosion inhibition of organic compound relative to their application alone. The study conducted by Sehmi et al. (2020) showed that the use of two pyrazole carboxamides 5-(4-(dimethylamino)phenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carboxamide DPC-1 and (E)-5-(4-(dimethylamino)phenyl)-3-(4-(dimethylamino)styryl)-4,5-dihydro-1H-pyrazole-1-carboxamide DPC-2 was efficient in inhibiting corrosion of mild steel in 1 mol/L HCl solution. Also, the study by Lee et al. (2019) investigated the effect of silica nanoparticles on copper corrosion inhibition process in sodium chloride solution and their results showed that silica nanoparticles can reduce corrosion rates up to four times with just 10% surface coverage. Also, the recent study by Udoh and Sunday (2020) investigated the use of biologically generated inhibitors as corrosion inhibitors of mild steel corrosion in saline environments relevant to hydrocarbon production system and their results showed that these inhibitors can reduce the corrosion rates of mild steel.

The application of nanoparticles as corrosion inhibitor is an emerging process that has not been fully explored. Most of the previous studies on the applications of nanoparticles in corrosion process were conducted in acidic solutions but corrosion problems are not limited to only acidic environments. The continuous exposure of metallic materials to saline environment can also cause corrosion problem (Lee et al., 2019). The reservoir formation water and injection water that are usually produced from and injected into the reservoirs are saline in nature and composed of salts of different compositions and salinities, and continuous exposure of pipelines or flowlines to these saline solutions may modify the corrosion process. Application of nanoparticles to corrosion control in pipelines exposed to saline environments relevant to hydrocarbon production is an area that has not been previously explored, and since nanoparticles are now being used in oil production systems for different purposes, it is needful to know their impact on the flowlines or pipelines through which they are transported. This study therefore aimed at investigating the corrosion inhibition potential of silica (SiO₂) nanoparticles in high saline brine environments that are relevant to oil production systems.

2. MATERIALS AND METHODS

2.1. Materials and Sample Preparation

The corrosion process investigations conducted in this study were carried out in deionised water and in brines of different salinities. Five saline solutions comprising of high salinity synthetic formation brine (FMB), 10D, 20D, 50D and 90D brines were used. The formation brine is an example of typical salt solution that exists in hydrocarbon reservoirs that is commonly produced alongside with oil during production process. The 10D, 20D, 50D and 90D brines are diluted formation brine prepared based on 10-, 20-, 50- and 90-times dilution factors, respectively. These brines represent different salt solutions that are usually injected into the reservoirs during water flooding process. The brines were prepared with reagent grade NaCl, CaCl₂, MgCl₂, KCl and Na₂SO₄ salts dissolved in deionised water. The compositional breakdown of the brines is presented in Table 1.

Table 1: Compositional breakdown of brines, the salt concentration is g/L.

| Components | FMB (g/L) | 10D (g/L) | 20D (g/L) | 50D (g/L) | 90D (g/L) |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|
| NaCl | 31.4240 | 3.1424 | 1.5712 | 0.6285 | 0.3492 |
| CaCl ₂ | 0.1920 | 0.0192 | 0.0096 | 0.0038 | 0.0021 |
| MgCl ₂ | 0.2560 | 0.0256 | 0.0128 | 0.0051 | 0.0028 |
| KCl | 0.0640 | 0.0064 | 0.0032 | 0.0013 | 0.0007 |
| Na ₂ SO ₄ | 0.0640 | 0.0064 | 0.0032 | 0.0013 | 0.0007 |
| Total | 32.0000 | 3.2000 | 1.6000 | 0.6400 | 0.3555 |

The corrosion inhibitor used in this study is 99.5% non-porous silica nanoparticles purchased from Skyspring Nanomaterials Inc., Houston, USA. Two solutions of nanoparticles of 1 g/L and 5 g/L concentrations were

prepared with deionised water under continuous mixing until the nanoparticles were completely dispersed in the solutions. The properties of this nanoparticles as detailed on the website of the supplier are presented in Table 2 and the TEM image is showed in Figure 1 (Skyspring Nanomaterials Inc. website).

Table 2: Properties and description of SiO₂ nanoparticles

| Properties | Quantity |
|-----------------------------------|-----------|
| Bulk density (g/cm ³) | 0.01-0.10 |
| Surface area (m ² /g) | 160.00 |
| Size (nm) | 20.00 |
| Morphology | Spherical |
| Colour | White |

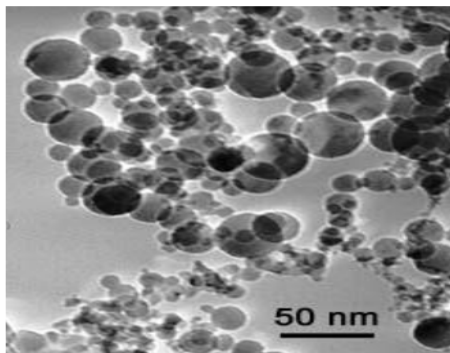


Figure 1: Image of the SiO₂ nanoparticles

In this study, mild steel was used as a representative of the flowline. The mild steel was cut into small coupons of average dimensions of 2.4 cm by 2.1 cm and thickness of 0.5 cm. Prior to the test, the surfaces of all the coupons were polished with grit size 220 emery paper. Thereafter, they were cleaned with acetone and deionised water, dried in oven at 100 °C for 2 h before their respective initial weights were measured (Lee et al., 2019).

2.2. Experimental Method

The corrosion of mild steel in different solution environments was investigated with gravimetric method that analyses corrosion loss based on the metal weight loss (Popoola, 2019). A constant volume of 50 mL of deionised water, formation brine (FMB), 10D, 20D, 50D and 90D brines were dispensed into different test bottles with and without nanoparticles. The pre-cleaned weighed mild steel coupons were immersed in relevant experimental solutions, and after every 72 hours, the coupons were brought out, cleaned and reweighed. The differences in the weights of the coupons before and after immersion in solutions were used to calculate the corrosion rates (CR) in mg/cm².h and corrosion inhibition efficiency (E) in percentage using Equations 1 and 2.

$$CR = \frac{m_0 - m}{At} \quad (1)$$

$$E = \frac{CR_0 - CR}{CR_0} \times 100 \quad (2)$$

where, m_0 and m are respectively the weights of coupons before and after immersion in relevant experimental solutions, A is area of the coupon in cm², t is the duration of contact time the coupons had with the solutions in h, CR_0 and CR are corrosion rates in the absence and presence of the inhibitor, respectively. All the experiments were conducted at 25 °C over a period of 360 h.

3. RESULTS AND DISCUSSION

Figure 2 shows the results of the rates of corrosion of the mild steel in different solution environments investigated. Different rates of corrosion of mild steel were observed depending on the type of environment it was subjected to, concentration of nanoparticles and exposure duration. When the deionised water was used as the environmental solution (Figure 2a) in the absence and presence of nanoparticles, different rates of corrosion were observed. The addition of 1 g/L nanoparticles to the deionised water reduced the corrosion rate from 0.05 mg/cm².h to 0.018 mg/cm².h over a period of 144 h, after which the corrosion rate gradually increases to 0.027 mg/cm².h with continuous exposure to the same environment for 360 h. This corresponds to 65% corrosion inhibition efficiency that progressively reduced to 45% with continuous exposure. This signifies the potential of silica nanoparticles to reduce the corrosion rate of mild steel at this low

concentration although the inhibition potential reduces with increase in exposure time. The use of higher concentration (5 mg/L) of silica nanoparticles in deionised water only reduced the corrosion rate slightly to 0.032 mg/cm² after 72 h exposure, and this progressively increased with increase in exposure time until 360 h when no effect was observed. This was characterised by low efficiency of 30% that reduced to 1.4% over the period of investigations.

In the second phase tests (Figure 2b) in which 90% diluted formation brine (90D) was used, slight reduction in corrosion rate relative to the deionised water (from 0.05 to 0.045 mg/cm².h) was observed in the absence of nanoparticles. The addition of low concentration nanoparticles to the 90D was however characterised by increased corrosion rate (~ 0.055 mg/cm².h) but the application of high concentration reduced the corrosion rate with about 60% efficiency that decreased with exposure time. From the results of the third phase tests in which 50% diluted formation (50D) brine was used (Figure 2c), a relative steady corrosion rate of 0.05 mg/cm².h was observed for over 216 h and thereafter, a 0.005 mg/cm².h increase in the corrosion rate was observed with continuous exposure till 360 h. An addition of low concentration nanoparticles to this brine solution did not reduce corrosion rate beyond 0.05 mg/cm².h that was initially observed with the brine alone, but the use of high concentration nanoparticles greatly reduced the corrosion rate to 0.01 mg/cm².h. This corresponds to corrosion inhibition efficiency of about 78% as opposed to low efficiency (1-10%) observed with the use of low concentration nanoparticles. Figure 2d presents the results of the corrosion rates of mild steel in 20% diluted formation (20D) brine. A slightly stable lower corrosion rate (0.043 mg/cm².h) relative to the deionised water was observed with the use of brine alone and addition of low concentration of nanoparticles only reduced corrosion rate by about 7% and the efficiency decreased with increase in exposure duration. On the contrary, the addition of high concentration of nanoparticles reduced the corrosion rate to 0.011 mg/cm².h within 144h exposure but slight reduction in corrosion inhibition efficiency was observed with continuous exposure thereby signifying its limits. The results of the test conducted in 10% diluted formation (10D) brine environment are presented in Figure 2e. Higher corrosion rate (0.06-0.065 mg/cm².h) was observed when only the brine was used. The addition of nanoparticles to the brine reduced the corrosion rate to 0.038-0.048 mg/cm².h and 0.015-0.028 mg/cm².h at low and high concentrations, respectively which corresponds to about 31% and 64% inhibition efficiency, respectively. Finally, Figure 2f shows the results of the corrosion test in formation brine. Interestingly, reduction in corrosion rate (0.044 mg/cm².h) was observed when the brine alone was used and further reduction in corrosion rate was observed when nanoparticles were added at low and high concentrations although their inhibition efficiencies were low but better efficiency was observed with the application of low concentration nanoparticles.

From the results of all the tests, it is obvious that the corrosion rate of mild steel in different saline solution environments is influenced by the salinity of the solution, nanoparticles concentration and exposure duration. Relating the results of corrosion rates in saline solutions to non-saline solution, an initial slight reduction in corrosion rate relative to non-saline solution was observed when very low saline solution (90D) was used but subsequently, increase in corrosion rates was observed with increase in salinity of the solutions but the lowest reduction was observed in the highest salinity solution (FMB). Comparing the corrosion rates in all the saline solutions, the lowest rate was observed in the highest saline solution i.e., formation brine. This shows that exposure of mild steel to low salinity solutions alone does not reduce its corrosion rate neither does its exposure to high salinity formation brine alone increase its corrosion. This is consistent with the previous work by Zeng et al. (2016) that observed highest and lowest corrosion rates in their lowest and highest salinities solutions, respectively. This was associated with adsorption of hydroxyl adsorption and chloride from the solutions to the metal surface. In high saline solution, increase in surface roughness exists due to adsorption competition between hydroxyl and chloride but in low saline solutions, uniform corrosion occurs due to dominant hydroxyl adsorption. The ferrous hydroxide formed as a result of the adsorption of hydroxyl enhances corrosion in the presence of chloride because more dissolved oxygen can reach the surface (Peters, 2002). The addition of nanoparticles to the saline solutions however modified the corrosion rates based on the concentration used, this is discussed further below.

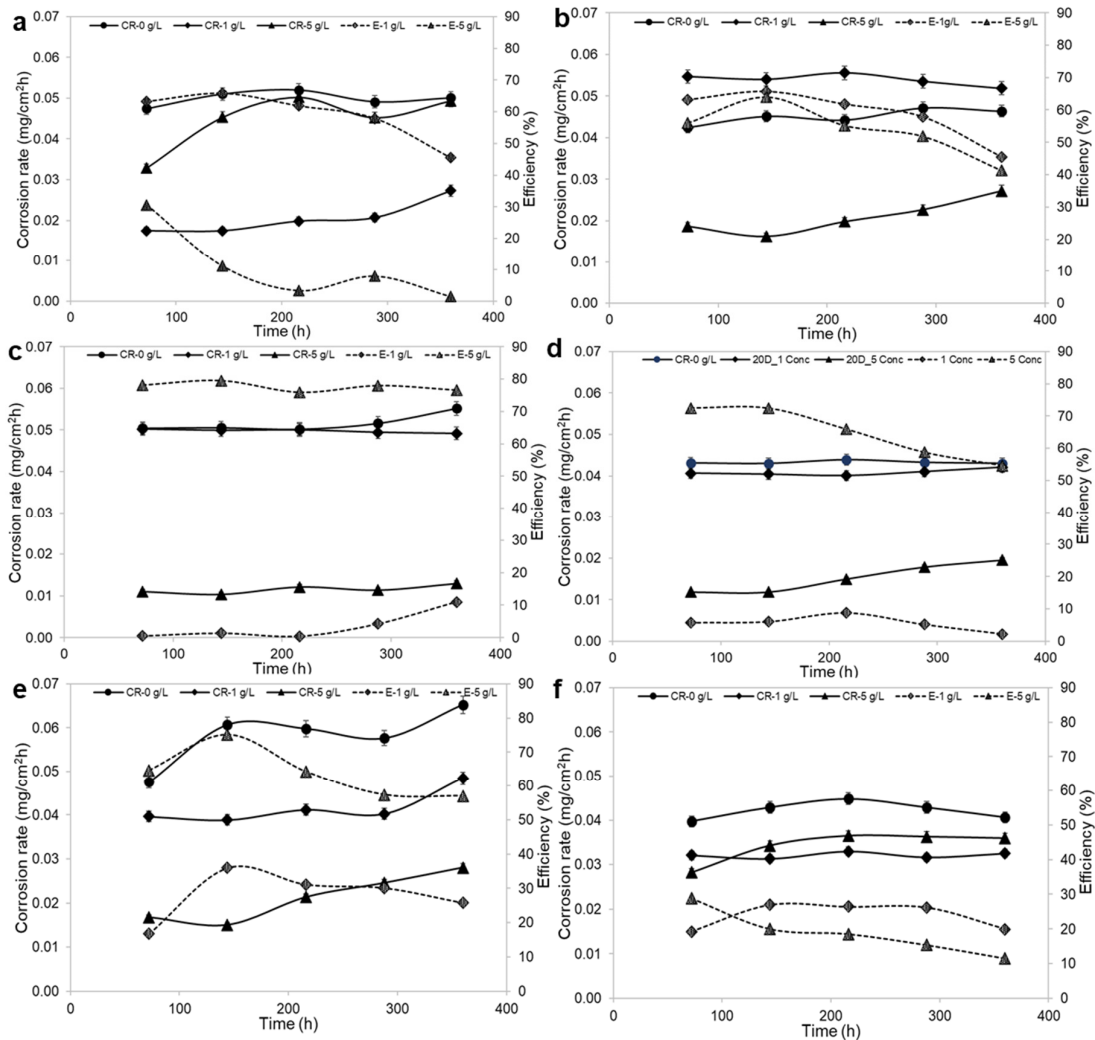


Figure 2: The rate of corrosion of mild steel and nanoparticles corrosion inhibition efficiency in different solutions for a period of 360 h. Corrosion rates of mild steel in: (a) deionised water, (b) 90D brine, (c) 50D brine, (d) 20D brine, (e) 10D brine and (f) formation brine

Relating the corrosion rates of mild steel in different solution environments investigated to the concentration of nanoparticles used for the corrosion inhibition process, the results of the tests at earlier time (72 h) and later time (360 h) are presented in Figure 3. At the earlier time (Figure 3a) when 1 g/L concentration of nanoparticles was used, the highest corrosion reduction was observed with deionised water while the lowest reduction was observed with 90D brine environment. Interestingly, lower corrosion rate was observed in the very high salinity formation brine and corrosion rate increases with reduction in brine salinity. The reverse was however observed with the use of 5 g/L concentration of nanoparticles, the lowest corrosion reduction was observed in the deionised water while highest reduction was observed in 50D and 20D brines. Similar responses were observed in the later time (Figure 3b) with slight variance in corrosion rates in diluted formation brines. Of significant importance is the observed corrosion rates in solution environments in the non-saline solution (0) and in the presence of very high salinity formation brine. The highest corrosion reduction was observed in deionised water with the use of 1 g/L concentration of nanoparticles followed by formation brine and the exact reversed was observed with the use of 5 g/L concentration. This suggests a

significant interaction between the nanoparticles and the salt molecules in the brine during the corrosion inhibition process. The evidence of the possibility of this occurrence is seen in observed corrosion rates in the diluted salt solution but further analysis will be required to justify this hypothesis.

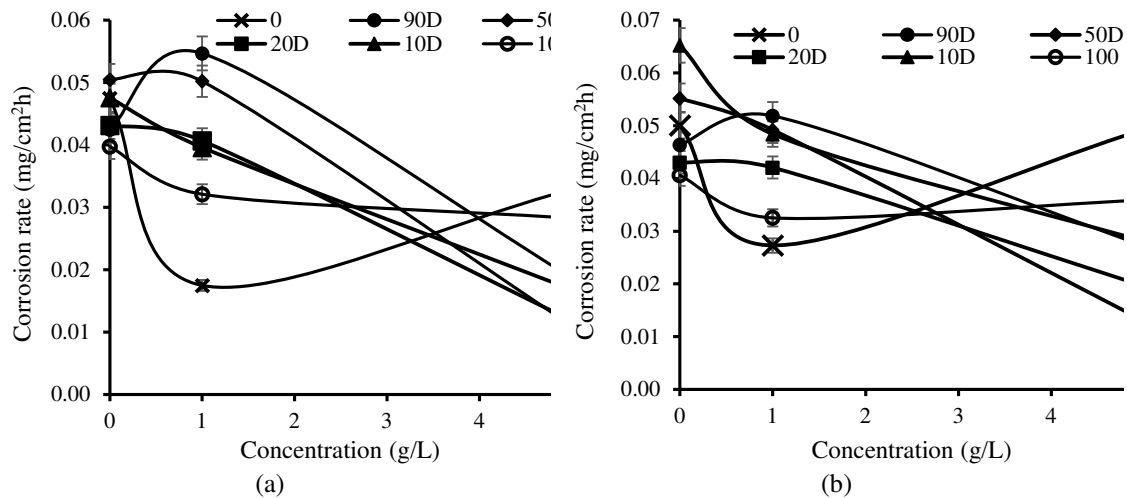


Figure 3: The effect of the concentration of nanoparticles on corrosion inhibition process in different salt solutions at: (a) early time of 72 h and (b) later time of 360 h

The results of the corrosion rates in the non-saline solutions in the presence of 1 g/L and 5 g/L nanoparticles concentrations showed pure effect of nanoparticles on the corrosion of mild steel. The observed lower corrosion rate in low concentration silica nanoparticles solution relative to the high concentration solution is consistent with the results of study by Rushing et al. (2003) that demonstrated a significant interplay between silica solution and iron corrosion. The use of high concentration of silica is said to cause more iron to be released in the water and formation of a dense scale on coupons that is more difficult to remove while low silica concentrations form a fairly uniform and easy to remove scale. Also, comparing the performances of these two concentrations of nanoparticles, similar corrosion rates were observed in high saline solutions which signified an insignificant effect of increase in nanoparticles concentration. Hence, the use of low concentration of 1 g/L suffice in reduction of corrosion rates in these solution environments.

For a better understanding of the effect of brine salinity on the corrosion rates of the mild steel in the presence of nanoparticles, the corrosion rates were related to the salinity of each of the solution at different concentration of nanoparticles used as shown in Figure 4. It is evident that the use of low concentration nanoparticles was more efficient in reducing the corrosion rate of mild steel in the non-saline solution, but the presence of salt molecules reduces its efficiency and increase in salt concentration beyond 0.36 g/L slightly improves the corrosion inhibition efficiency. On the contrary, the high concentration of nanoparticles is less efficient in the non-saline solution, but addition of salt improves its efficiency and significant reduction in corrosion rates was observed with increase in salinity up to 3.2 g/L, but its efficiency reduces slightly at very high salinity level (32 g/L). This is consistent with other studies that observed decrease in nanoparticles dispersion and adsorption on surface in saline solutions (Kanj, et al., 2009; Mcelfresh, et al., 2012; Zhang, et al., 2014).

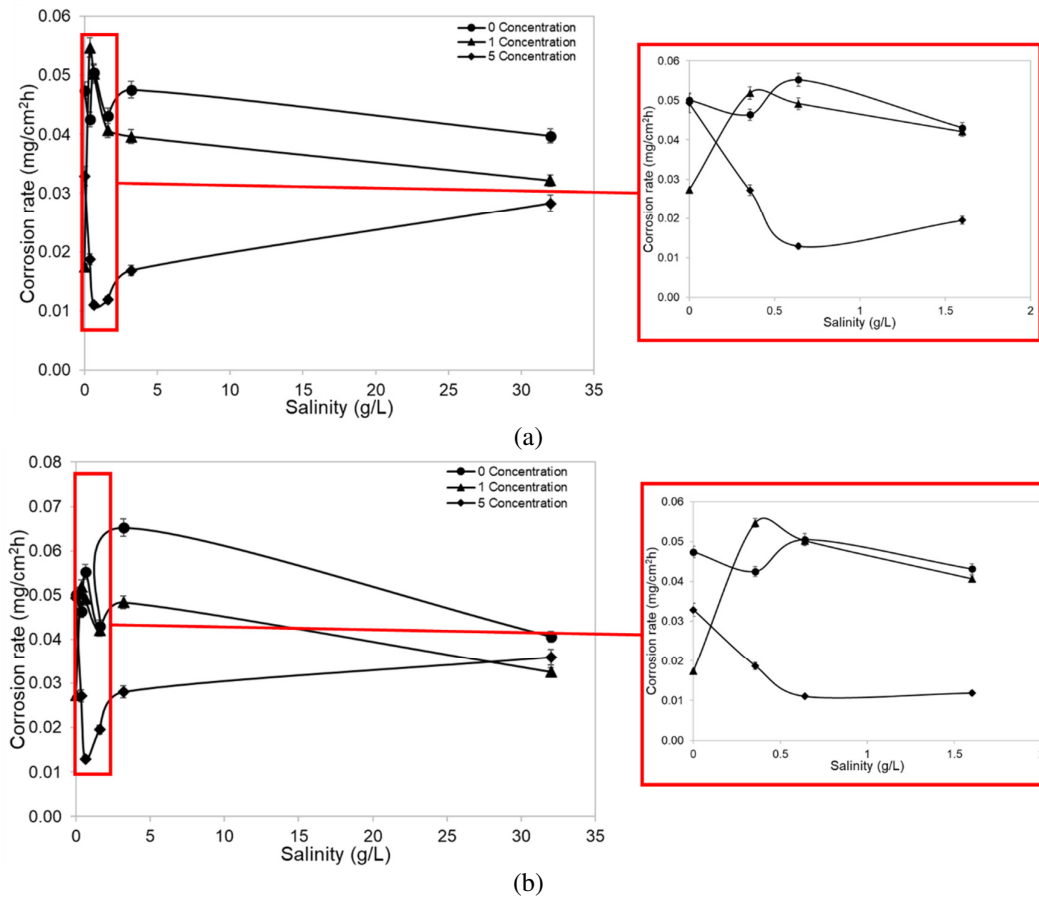


Figure 4: The effect of solutions salinity on mild steel corrosion rates in the absence and presence of nanoparticles at: (a) early time of 72 h and (b) later time of 360 h. The right plots are expansion of the compressed section of the left plots

When low concentration of nanoparticles was used in low saline solution, it seems that the salt molecules adsorb more on the metal surface than the nanoparticles due to the dominant effect of hydroxyl adsorption, thereby reducing the corrosion inhibition of the nanoparticles but as the salinity level increases, this effect was minimized and the nanoparticles efficiency was enhanced (Zeng et al., 2016, Sani et al., 2019). Also, when the high concentration of nanoparticles was used, it seems there were excess dispersed nanoparticles in the solutions relative to salt concentration in low saline solutions hence, nanoparticles could efficiently inhibit the metal corrosion. However, when the salt concentration in the solution increased relative to the concentration of nanoparticles, the corrosion rates increased with increase in salinity thereby resulting in reduction in the inhibition efficiency of nanoparticles (Zhang et al., 2014; Zeng et al., 2016). Taking a closer look at the expanded plots in Figure 4 on the right-hand side, a critical salt concentration (CSC) beyond which the nanoparticles inhibition trends were inverted was different for the low and high nanoparticles concentration. The CSC for the low concentration was 0.35 g/L while that of the high concentration was 0.64 g/L and interestingly, these two brine salinities correspond to two changes in corrosion rates trends in the non-saline solution without nanoparticles. This is consistent with previous study by Metin et al. (2011) that showed that CSC depends more on the type of salt and it is not influenced by the concentration of silica nanoparticle.

4. CONCLUSION

In this study, the corrosion inhibition potential of nanoparticles on mild steel corrosion process in saline solutions was investigated. The findings of this study showed that the application of nanoparticles can affect the corrosion rates of mild steel based on the type of solution environment, salinity level in the system, duration of the contact time and concentration of nanoparticles. All factors being equal, low concentration of nanoparticles is more efficient in inhibition process in non-saline solution while the high concentration demonstrated better efficiency in 0.64 g/L saline solution.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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