Tanzania Journal of Science 49(3): 655-663, 2023
ISSN 0856-1761, e-ISSN 2507-7961
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Evaluation of the Inhibitive Properties of Silver Nanoparticles in *Senna occidentalis* Root Extract as Corrosion Inhibitor of Mild Steel

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Received 17 Jan 2023, Revised 18 Aug 2023, Accepted 20 Aug 2023 Published Sep 2023

DOI: https://dx.doi.org/10.4314/tjs.v49i3.9

Abstract

The use of nanoparticles as corrosion inhibitors has gained popularity because of its increased corrosion efficiency due to increase surface to volume ratio. Nanoparticles which undergo physisorption/chemisorption to the corrosion metal surface and inhibit the corrosion efficiently also have low toxicity, low cost and easy production. In this research work, weight lost method was applied to study the inhibitive properties of silver nanoparticles (AgNPs) synthesized using *Senna occidentalis* root extract as environmentally benign corrosion inhibitor of mild steel in 0.5 M H_2SO_4 medium at 298 K and 308 K. It was observed that the corrosion rate of the steel sample decreases with increase in concentration of the silver nanoparticles but increased with rise in temperature. The highest inhibition efficiency of 65.59% was obtained at 308 K at the concentration of 5 gdm^{-3} and the least of 10.58% at the concentration of 1 gdm^{-3} at 308 K. The decrease in inhibition efficiency with rise in temperature is suggestive of physical adsorption mechanism. The surface coverage was observed to increase with increasing concentration of the nanoparticles and decreased with increase in temperature. This could be as a result of physical adsorption mechanism. The evaluated activation energy was found to be higher for the inhibited process than for the uninhibited process. The increase in apparent activation energy in the presence of the nanoparticles denotes physical adsorption mechanism, while the reverse is usually attributed to chemical adsorption. The negative values of heat of adsorption Q_{ads} suggest that the adsorption phenomenon is exothermic.

Keywords: Nanoparticles, Silver, Nanoparticles, *Senna occidentalis*, Corrosion.

Introduction

The use of nanoparticles as corrosion inhibitors has gained popularity because of its increased corrosion efficiency due to increase surface to volume ratio. Nanoparticles which undergo physisorption/chemisorption to the corrosion metal surface and inhibit the corrosion efficiently also have low toxicity, low cost and easy production (Suba and Anda 2016). One of the practical methods for the protection of metals against corrosion is the use of corrosion inhibitor especially in acid media (Ehbuniwe et al. 2018).

Several studies have examined the relationship between the structure of the inhibitor molecules and its efficiency but much less attention has been paid to the dependence of the protection efficiency on the size of the inhibitor molecules and the electronic distribution in the inhibitor molecules (Okhale and Imoisi 2022). However, with the rapid advancement of nanotechnology, thin films of thickness in the micro and nanometric scales are increasing their popularity in scientific and technological applications (Ayman et al. 2013a). The utilization of plant extracts as ecologically benign alternative to microbial induced corrosion treatment and the anti-corrosion potential of silver nanoparticle have gained great interest as corrosion protective film due to their high ability to form self-assembled films on the metal surfaces (Narenkumar et al. 2017). It is well known that silver nanoparticles have higher reactivity towards igneous acidic solution (Ayman et al. 2013b).

Considering the huge cost of corrosion monitoring and control, a great deal of efforts has been channeled towards developing technically efficient and cost-effective strategies for corrosion management (Adejo 2014). The use of corrosion inhibitors has been very promising particularly with the use of non-toxic materials (Ajenu et al. 2021). Such inhibitors offer a number of advantages such as biodegradability, absence of heavy metals or other toxic compounds, availability and ease of processing (Imoisi et al. 2020). It is impossible practically to stop a natural event in which corrosion is one of them, but it is feasible to design methods to reduce or alter such processes. In order to mitigate corrosion several, techniques have been developed (Adejo et al. 2013). The most common are application of coatings, anodic and cathodic protections, pH change, alloying and use of inhibitors (Adejo et al. 2010a, b).

A corrosion inhibitor is any substance, which when added to a corrosive environment in little amount reduces or minimizes the corrosion rate of the material (Liu et al. 2015). There are two main classes of inhibitors namely organic and inorganic (Okhale et al. 2021). Organic inhibitors minimize corrosion mainly by adsorption while inorganic inhibitors mitigate or arrest corrosion situations by interfering with either the anodic or cathodic regions of the corrosion process (Umoren et al. 2015). The present work was designed to enhance global sustainability, especially in the industry where corrosion is almost inevitable and as a contribution to the growing interest on environmentally benign corrosion inhibitors to study (i) corrosion inhibition of mild steel in 0.5 M H_2SO_4 solutions by silver nanoparticles of *Senna occidentalis* root extract using weight loss method at a temperature of 298 K and 306 K, (ii) to evaluate the activation energy and heat of adsorption process.

Materials and Methods

Reagents and Chemicals

Double distilled water, 98% tetraoxosulphate (VI) acid (BDH Chemicals Ltd Poole, England), 99% acetone (BDH Chemicals Ltd Poole, England), 99.9% ethanol (BDH Chemicals Ltd Poole, England), and silver nitrate ($AgNO_3$ 99.99%) (Sigma Aldrich) were used for the study. All reagents used were of analytical grade and the water used for preparation was double distilled.

Sample preparation

About 20 g each of the powdered *Senna occidentalis* root was weighed into three different 250 ml conical flasks. To each conical flask 200 ml of 99.9% ethanol was added. The flasks were properly corked and left to stand for 48 hours at ambient temperature, with occasional swirling. The extracts were filtered and the filtrates were put in a thermo-stated water bath set below the boiling point of ethanol and allowed to evaporate leaving the dried crude extract in each beaker. About 1 g of the crude extract was weighed into conical flask and dissolved in a small quantity of distilled water and then made up to 50 ml with distilled water to obtain the root extract solution. The root extract solution was kept for further use. The root extract was used as reducing and stabilizing agent for the preparation of silver nanoparticles (Ghosh et al. 2014).

Synthesis of silver nanoparticles

Silver nitrate ($AgNO_3$) solution was prepared by dissolving 0.002 moles (0.34 g) of $AgNO_3$ salt in a beaker containing 10 ml of distilled and made up to 20 ml in a volumetric flask. The solution was immediately stored in an amber coloured bottle to avoid reaction with light. The following volumes of the root extract solution 1, 2, 3, 4, and 5 ml were measured into five separate amber bottles. Then 3 ml of the silver nitrate solution was measured into each of the bottles and the mixture was gently stirred for homogenization. The mixtures were kept for 20-24 hours to observe the colored change. After 24 hours, the colour of the solution changed from light brown to dark brown which gave a clear indication of the formation of silver nanoparticles, previous works in other laboratories also reported similar hue of colour change due to silver nanoparticles formation. The mixture was centrifuged at 4,000 rpm for 60 minutes, the supernatant was taken out and the precipitate was washed thrice. Precipitate obtained from root extract solution of 1 ml and 5 ml were designated samples A and B, respectively, and used for further analysis. All bottles that were used for this experiment were amber coloured.

Characterization

The morphology of the silver nanoparticles (AgNPs) obtained was characterized using scanning electron microscopy (SEM), for samples A (Figure 1) and B (Figure 2), respectively. Fourier transform infrared spectroscopic measurement was done using Shimadzu, IR-prestige-21 spectrophotometer for the same samples A (Figure 3) and B (Figure 4).

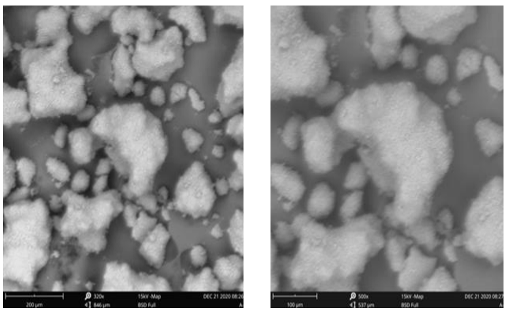

Figure 1: SEM pattern synthesized AgNPs for sample A.

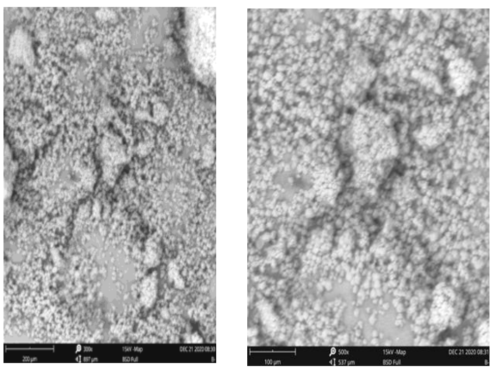

Figure 2: SEM pattern synthesized AgNPs for sample B.

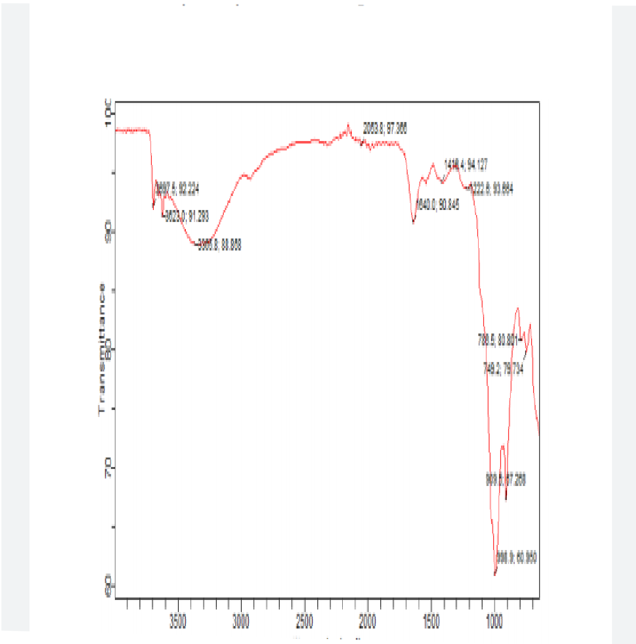

Figure 3: FT-IR spectral of AgNPs in *Senna Occidentalis* for sample A.

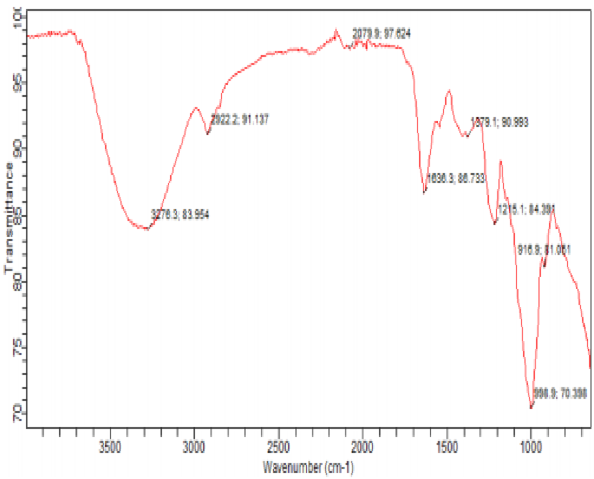

Figure 4: FT-IR spectral of AgNPs in *Senna Occidentalis* for sample B.

Preparation of the coupon

Mild steel rods were purchased and taken to the Department of Mechanical Engineering, University of Agriculture, Makurdi, Nigeria, where they were press-cut mechanically to form different coupons, each of dimensions (2 x 1.9 x 0.1) cm with a tiny hole drilled at the edge of each for the purpose of suspension in the corrodant. The surfaces of the coupons were thoroughly polished to mirror finish using sand paper, degreased in acetone and preserved in a desiccator. Subsequently, the initial weights (W_i) of the coupons were taken using analytical weighing balance and then made ready for corrosion studies (Adejo et al. 2010a, b).

Corrosion studies

A blank was prepared for the study using 0.5 MH_2SO_4 (50 ml) which acted as the corrodant. Thereafter, the coupons as prepared above were individually tied through the tiny hole bored on the coupons and firmly held by a retort stand at an equal length and uniform spacing, and placed in various concentrations of silver nanoparticles (1, 2, 3, 4, 5) gdm^{-3} in 50 ml of 0.5 M H_2SO_4. The corrodant and the inhibitor with the coupons as prepared above were put into the thermo-stated water bath set at 298 k for a period of 6 hours at the constant temperature.

After the time interval the coupons were removed quenched in ammonium acetate, washed in distilled water and dried in acetone, kept in a desiccator and then the final weight (W_f) was taken. The process was repeated at 308 K. The experiment was performed in triplicate.

Weight loss measurement

The method of Adejo et al. (2010a, b) was adopted and weight loss was represented by equation (1),

$W = Wi - Wf$ (1)

Where, W is the weight loss of the coupon, Wi the initial weight and Wf the weight after retrieval. Each reading reported is an average of three experimental readings recorded to the nearest 0.001 g. The inhibition efficiency (IE) was calculated using the formula as represented by equation (2).

% IE = [1 - $W1/W2$] x 100 (2)

Where $W1$ *and* $W2$ are the weight losses (in grams) of mild steel coupon in the presence and absence of the inhibitor in the acid solution at the same temperature. The degree of surface coverage, θ, was evaluated by the equation (3).

$\theta = 1 - W1/W2$ (3)

The corrosion rate of the mild steel coupons was determined for the immersion period from weight loss using equation (4).

Corrosion rate (mg/cm^2h^{-1}) = WL/At (4)

Where, WL is the weight loss in milligrams (mg), A the coupon surface area in cm^2 and t the immersion time in hours using an equation similar to the Arrhenius equation (equation 5), values of activation energy, E_a, was obtained.

$lnCR = \ln A - E_a RT$ (5)

The heat of adsorption $\mathbf{Q_{ads}}$ was evaluated using equation (6).

Log $(\theta/1-\theta) = logA + logK - Q_{ads}2.303(1/T)$ (6)

Where, θ is the degree of surface coverage, R is the molar gas constant, T is the absolute temperature, and A is a temperature independent factor. Values of heat of adsorption were obtained from the slope ($-Q_{ads}2.303R$) of a plot of log $(\theta/1-\theta)$ against $1/T$.

Results and Discussion

Table 1 shows the results of corrosion rate of mild steel in absence and presence of silver nanoparticles in *Senna occidentalis* roots extract in 0.5 M of H_2SO_4 at 298 K and 308 K for 6 hours of immersion and in various concentrations of silver nanoparticles (1, 2, 3, 4, 5) gdm^{-3}. The inhibition efficiency (% IE) and surface coverage (θ) are presented; activation energy and heat of adsorption are presented in Tables 2, 3 and 4.

Table 1: Corrosion rate of mild steel corrosion using the silver nanoparticles of *Senna occidentalis* root extract as inhibitor at two temperatures

Concentration (gdm^{-3}) in mL Ag nanoparticles	Corrosion rate/$mgcm^{-2}h^{-1}$	
	298 K	308 K
Blank	23.6404	36.4912
1	15.5702	32.6316
2	14.9561	30.6579
3	14.5614	28.8158
4	14.0789	21.7544
5	13.2018	12.5877

Table 2: Evaluated values of inhibition efficiency (%IE) of the silver nanoparticles of *Senna occidentalis* root extract at two temperatures

Concentration (gdm^{-3})	Inhibition efficiency (%IE)	
	298 K	308 K
1	34.14	10.58
2	36.7	15.99
3	38.39	21.03
4	40.45	40.38
5	44.16	65.59

Table 3: Values of surface coverage (θ) of the silver nanoparticles of *Senna occidentalis* root extract at two temperatures

Concentration (gdm^{-3})	Surface coverage (θ)	
	298 K	308 K
1	0.3414	0.1058
2	0.3673	0.1599
3	0.3839	0.2103
4	0.4416	0.4038
5	0.4416	0.6559

Table 4: Evaluated values of activation energy (E_a) and heat of adsorption (Q_{ads})

Concentration (gdm^{-3})	Activation energy (E_a) $kJmol^{-1}$, 298 K	Heat of adsorption (Q_{ads}) $kJmol^{-1}$, 308 K
Blank	33.1264	-
1	56.5706	-112.772
2	54.7781	-85.1283
3	52.0893	-64.8831
4	33. 2148	-0.0879
5	-3.6378	67.1326

The effects of concentration and temperature on corrosion of mild steel in 0.5 M sulphuric acid using silver nanoparticle derived from *Senna occidentalis* root extract as inhibitor were investigated at two temperatures and the results are presented in Table 1. The rate of corrosion that was observed to be high in the blank (corrodant) came down with the introduction of the silver nanoparticle inhibitor into the corroding medium, which shows that silver nanoparticles in *Senna occidentalis* root extract inhibited corrosion of the metal sample in the acid medium (Ozoh et al. 2023). It was observed that the corrosion rate of the steel sample decreased with increase in concentrations of the silver nanoparticles in *Senna occidentalis* root extract and increase with increasing temperature (Imoisi et al. 2021).

Generally, it has been established that the rate of corrosion of mild steel was affected by temperature and concentrations of inhibitors (Odewunmi et al. 2015). Table 2 shows the values of inhibition efficiency (% IE) of the silver nanoparticles in *Senna occidentalis* root extract as an inhibitor of corrosion of the metal sample in acid solution (Okhale et al. 2022). The (%IE) was observed to increase with increase in the concentration of the inhibitor and decreased as temperature increases. The highest inhibition efficiency of 65.59% was obtained at 308 K at the concentration of 5 gdm^{-3} and the least of 10.58% at the concentration of 1 gdm^{-3} at 308 K. The decrease in inhibition efficiency with rise in temperature is actually suggestive of physical adsorption mechanism (Alaneme et al. 2015).

Table 3, shows the values of surface coverage of the silver nanoparticles on the mild steel which increases with increasing concentrations of the nanoparticles and decrease as temperature increases. This could be as a result of physical adsorption mechanism (Oguzie 2006). The activation energy (E_a) evaluated at different concentrations of silver nanoparticles is presented in Table 4, and showed that the activation energy is higher for the inhibited process than for the uninhibited process (Imoisi and Michael 2020). The increase in apparent activation energy in the presence of the silver nanoparticles denotes physical adsorption mechanism, while the reverse is usually attributed to chemical adsorption (Imoisi et al. 2023).

The higher values of E_a in the presence of an inhibitor were due to the increased energy barrier. This result suggests that the corrosion inhibition by silver nanoparticles obtained from *Senna occidentalis* is feasible because of the increase in energy barrier for the metal dissolution (Josiah et al. 2023). The formation of thin film on the metal surface serves as a barrier to both energy and mass transfer, which increase the activation. Therefore, the result shows that the adsorption of silver nanoparticles is by physical adsorption (Eddy and Ebenso 2008).

The reduction in activation energy at high inhibitor concentration is consistent with the trend of inhibition efficiency with temperature in this medium and may suggest that a chemisorbed film is gradually formed on the metal surface at high concentration (Oguzie 2006). The values of E_a<80 $KJmol^{-1}$ indicate physical adsorption while E_a > 80 $Kjmol^{-1}$ indicates chemical adsorption (Eddy and Ebenso, 2008). The negative values of heat of adsorption Q_{ads} suggest that the adsorption phenomenon is exothermic (Ating et al. 2010).

Conclusion

From the above results, it has been shown that silver nanoparticles derived from *Senna occidentalis* root extract inhibited the corrosion of mild steel in 0.5 M sulphuric acid. The corrosion rate of the steel sample decreased with increase in concentrations of the silver nanoparticles, and increase with increasing temperature. The inhibition efficiency (%IE) was observed to increase with increase in the concentration of the inhibitor and decreased as temperature increases. The increase in the value of percentage inhibition efficiency and activation energy is suggestive of physical adsorption mechanism. The reduction in activation energy at high inhibitor concentration is consistent with the trend of inhibition efficiency with temperature in this medium and may suggest that a chemisorbed film is gradually formed on the metal surface at high concentrations. The negative values of heat of adsorption Q_{ads} suggest that the adsorption phenomenon is exothermic.

Acknowledgement

The authors wish to thank the Department of Medicinal Plant Research and Traditional Medicine, National Institute for Pharmaceutical Research and Development, Idu Industrial Area, Abuja, Nigeria, for providing technical support for this study.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

All authors made substantial contributions to conception and design, acquisition of data, or analysis and interpretation of data; took part in drafting the article or revising it critically for important intellectual content; agreed to submit to the current journal; gave final approval of the version to be published; and agree to be accountable for all aspects of the work. All the authors are eligible to be authors as per the International Committee of Medical Journal Editors (ICMJE) requirements/guidelines.

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