Evaluation of the Inhibitive Properties of silver Nanoparticles in *Senna ocidentalis* Root Extract as Corrosion Inhibitor of Mild Steel

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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 0.5M H_2SO_4 medium at 298K and 308K. 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 308K at the concentration of 5gdm^{-3} and the least of 10.58% at the concentration of 1 gdm^{-3} at 308K. 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.

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1. 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. 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*., 2013). 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*., 2013).

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. Such inhibitors offer a number of advantages such as biodegradability, absence of heavy metals or other toxic compounds, availability and ease of processing. 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*., 2010).

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). We have two main classes of inhibitors namely organic and inorganic. 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 0.5M H_2SO_4 solutions by silver nanoparticles of *Senna occidentalis* root extract using weight loss method at a temperature of 298K and 306K, (ii) to evaluate the activation energy and heat of adsorption process.

2. Materials and Method

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 20g each of the powdered *Senna occidentalis* root was weighed into three different 250ml conical flasks. To each conical flask 200ml 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 filtrate 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 1g of the crude extract was weighed into conical flask and dissolved in a small quantity of distilled water and then

made up to 50ml 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 (0.34g) of $AgNO_3$ salt in a beaker containing 10ml of distilled and made up to 20ml in a volumetric flash. The solution was immediately stored in an amber colored bottle to avoid reaction with light. The following volumes of the root extract solution 1, 2, 3, 4, and 5ml were measured into five separate amber bottles. Then 3ml 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 24hours, the color 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 color change due to silver nanoparticles formation (Erna *et al*., 2019). The mixture was centrifuged at 4,000rpm for 60minutes, the supernatant was taken out and the precipitate was washed thrice. Precipitate obtained from root extract solution of 1ml and 5ml were designated sample A and sample B respectively, and used for further analysis. All bottles that were used for this experiment were amber colored.

Characterization

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

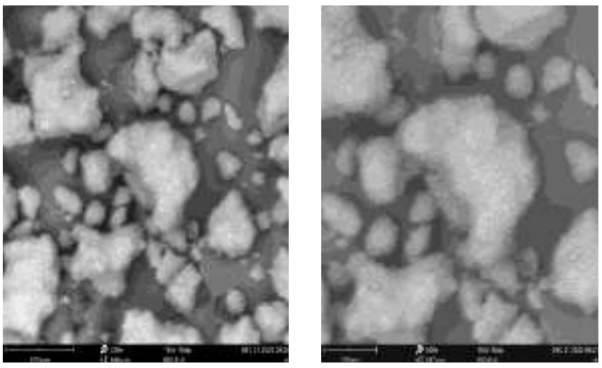

Fig 1: SEM pattern of synthesized AgNPs for sample A.

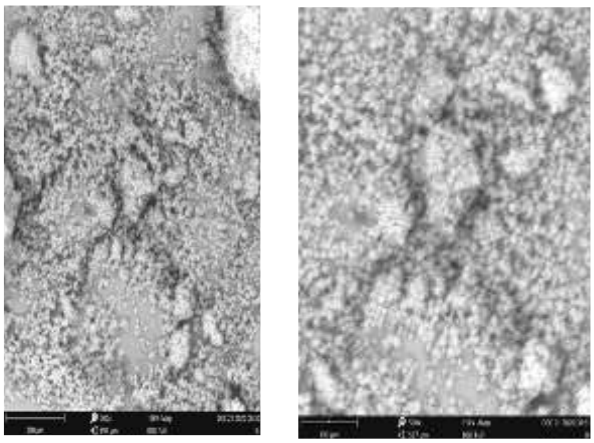

Fig 2: SEM pattern of synthesized AgNPs for sample B.

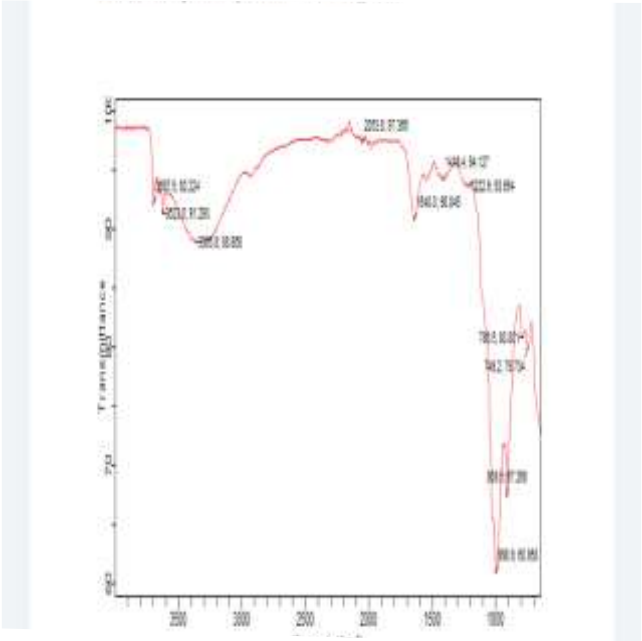

Fig 3: FT-IR spectral of AgNPs in Senna occidentalis for sample A

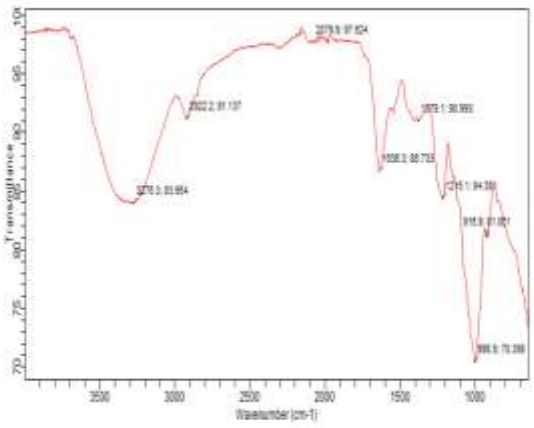

Fig 4: FT-IR spectral of AgNPs in Senna occidentalis for sample B

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*., 2010).

Corrosion studies

A blank was prepared for the study using $0.5MH_2SO_4$ (50ml) 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 298k 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.* (2010) was adopted and weight loss was represented by equation (1) below,

$$W = Wi - Wf \quad (1)$$

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 0.001g. The inhibition efficiency (IE) was calculated using the formula as represented by equation (2).

$$\% IE = [1 - W1/W2] \times 100 \quad (2)$$

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).

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

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

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

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 6), values of activation energy, E_a, was obtained.

$$lnCR = \ln A - E_aRT \quad (5)$$

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

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

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 $1/T$.

3. 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 0.5M of H_2SO_4 at 298K and 308K for 6hours 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 respectively.

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/$mgcm^{-2}h^{-1}$ 298K	308K
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	308K
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) 298K	308K
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 $kJmol^{-1}$ 298K	Heat of Adsorption Q_{ads} $kJmol^{-1}$ 308K
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

4. Discussion

The effect 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 was 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. It was observed that the corrosion rate of the steel sample decreased with increase in concentration of the silver nanoparticles in *senna occidentalis* root extract and increase with increasing temperature.

Generally, it has been established that the rate of corrosion of mild steel was affected by temperature and concentration 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. 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 308K at the concentration of $5gdm^{-3}$ and the least of 10.58 % at the concentration of 1 gdm^{-3} at 308K. 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 concentration of the nanoparticles and decrease as temperature increases. This could be as a result of physical adsorption mechanism (Oguzie, 2006). The activation energy Ea 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. 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.

The higher values of Ea 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. 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 Ea<80 $KJmol^{-1}$ indicate physical adsorption while Ea> 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 0.5M sulphuric acid. The corrosion rate of the steel sample decreased with increase in concentration 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 concentration. The negative values of heat of adsorption Q_{ads} suggest that the adsorption phenomenon is exothermic.

Conflict of Interest

The authors declare no conflict of interest.

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