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Investigation of the Corrosion Inhibition Properties of Nanoparticle on Milled Steel Synthesized Using Green Method by Gravimetric Analysis

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Abstract

In the present study, Zinc oxide nanoparticles were synthesized by green method using zinc acetate, Zinc nitrate, Zinc Chloride and Zinc Sulphate as Salt Precursors while Guava, Jatropha and Cassia leaves extracts serve as stabilizing and capping agents. 1M sodium hydroxide was added in drop to adjust the PH to 11.6 with distilled (DW) water as solvent. The structure and morphology of prepared zinc oxide nanoparticles was studied using X-ray diffraction (XRD) Spectroscopy and Scanning Electron Microscopy (SEM). UV visible spectrum shows the transparency of nanoparticles over entire visible range. In the UV visible spectrometer (UV–Vis) absorption peaks were observed between 372 to 400 nm, and energy band gap between 3.11 – 3.34 eV. The average sizes of the nanoparticles were estimated to range from 15.40 nm to 24.22 nm, while compositions of oxides of different element in the nanoparticles, shows 78.32% and 12.78% for Zinc and Oxygen, respectively. Scanning Electron Microscope (SEM) reveals the presence of Zinc oxide nanoparticles in its agglomerated form. Twelve (12) nanoparticles were selected for the corrosion inhibition to cover all the sizes obtained via the XRD analysis. When the nanoparticles are applied for corrosion inhibition of milled steel in acidic medium the smallest size have the highest relative inhibition efficiency while the largest size have the lowest relative inhibition efficiency compared to the milled steel exposed to bare acids.

1.0. Introduction

In [1]'s study on the corrosion inhibition properties of metal oxides such as ZnO, NiO, and Eu_2O_3 for carbon steel in 1 N HCl acid, it was found that the corrosion rate of mild steel is inversely proportional to the inhibitor concentration. With an increase in inhibitor concentration, the effectiveness of the inhibition increased in the following order: ZnO > NiO > Eu2O3. Examination and comparison of the corrosion rates on A-36 steel using red oxide primer, oil paint, primer plus oil paint, paint combined with TiO2, and ZnO based coatings conducted by [2] found that the zinc oxide nanoparticle-based coatings have the lowest corrosion rates (0.302 mpy). They came to the conclusion that zinc oxide nanoparticles coating made by mixing with paint shows the maximum resistance against corrosion in a base environment, acidic medium gives the largest corrosion rate in bare samples as well as in all coatings, and zinc oxide based coating gives the maximum cathodic protection among all coatings, based on the analogous drop in corrosion rate observed in the experiment. [3] investigated the effect of zinc oxide as a corrosion inhibitor of mild steel embedded in concrete by electrochemical and gravimetric methods and reported that, Zinc oxide demonstrate appreciable inhibition to the corrosion of the embedded steel bar in concrete at 100% and 75% concentrations in 3.5 percent NaCl medium, the corrosion inhibition performance was comparably better with the higher concentrations of ZnO, particularly at the 100% concentration. By using 3-((3-acetylphenyl)imino)indolin-2-one and zinc oxide (ZnO) nanoparticles (NPs), [4] investigated the synergistic effect of the two on inhibiting mild steel corrosion in 1 M HCl. They found that the addition of ZnO NPs to the corrosive solution increases the inhibition efficiency from 83 percent (without ZnO NPs) to 92% (with ZnO NPs), thus, when added to corrosive solution, ZnO NPs have synergistic effects, as was seen in the case of 3-((3-acetylphenyl) imino) indolin-2-one. In their study of Zinc Oxide Nanocomposites of Selected Polymers: Synthesis, Characterization, and Corrosion Inhibition on Mild Steel in HCl Solution, [5] found that the anticorrosion performance improved with an increase in the concentration of the inhibitors. They also found that the nanocomposites effectively repressed the dissolution of mild steel in 5 percent HCl solution. The order of the effectiveness of inhibition utilizing the nanocomposites ZnO/PVP, ZnO/PEG, and ZnO/PAN is ZnO/PVP > ZnO/PAN > ZnO/PEG. This concurs with the findings of [6] show that corrosion inhibition was most effective at 303.15 K for a Nanocomposite of biodegradable amino acid surfactant and ZnO, as demonstrated by weight loss and electrochemical tests. [7]'s investigation into the corrosion-inhibition properties of epoxy-zinc oxide nanocomposites coating on stainless steel (SS) 316L used a series of epoxy coating solutions containing varying weight percentages of ZnO nanoparticles. They found that the epoxy coating incorporated with 3 wt percent of ZnO nanoparticles provided the best corrosion protection on SS 316L, indicating that epoxy-ZnO nanocomposites coating has corrosion resistance properties on SS 316L compared to bare substrate. In order to examine the effect of ZnO NPs as an environmentally friendly corrosion inhibitor of mild steel in 1.0 M hydrochloric acid (HCl) solution, [8] biologically synthesized ZnO NPs from Pandanus amaryllifolius leaves extract. Their findings demonstrate that the size of ZnO NPs nanoparticles significantly influences their corrosion prevention property, which is dependent on the temperature of synthesis. As a result, this corrosion inhibitor provides a potential, easy option to reduce corrosion rates. [9], using outdated zinc chloride, created zinc oxide nanoparticles using Convolvulus arvensis leaf extract, and investigated their effectiveness as a corrosion inhibitor in carbon steel through weight loss and electrochemical measurements. He reported that ZnO NPs present in the extract are an effective inhibitor of corrosion in carbon steel in 1 M, though inhibition efficiency increases with increasing ZnO-NPs concentration and decreases at higher concentrations. Stearic acid was used by [10] to modify zinc oxide nanoparticles so they might function as corrosion-resistant materials. The life of coated steel in a 3.5 percent NaCl solution is increased by three times thanks to the weight gain/loss method and the static water contact angle of 140 degrees that can be seen from the modified ZnO NPs.

In their 2020 study, [11] explore the use of environmentally friendly zinc oxide nanoparticles as an eco-friendly inhibitor for steel in acidic solution. Green ZnO NPs may be employed as an eco-friendly corrosion inhibitor for steel in a 1.0 M HCl acid solution with inhibitory efficiencies dependent on concentration when cheap, nontoxic, natural Myrrh gum was used as the capping agent, according to polarization and EIS studies. From the finding above it is clear that, there was no sufficient work on the effect of the size of the nanoparticles synthesis via green method, which directly control its electrical and optical properties. On the other hand most of the nanoparticles considered in the literatures are Nanocomposite material and plant extract are not local plant found in remote areas. Thus, this study would look at the effect of sizes of nanoparticles freshly synthesis from local leaves extract from the environment on their corrosion inhibition properties on mild steel in 1 M HCl medium

2. Materials and Method

2.1: Materials

For the synthesis of nanoparticles from Guava, Jatropha and Cassia leaves, four Zinc precursors, Zinc acetate dehydrate $\mathrm{Zn(C_4H_6O_4).2H_2O}$ (219 g), Zinc Nitrate hexahydrate$\mathrm{Zn(NO_3).6H_2O}$ Zinc Chloride $ZnCl_2$ (126 g) and Zinc Sulphate heptahydrate $ZnSO_4\,.7H_2O$ (291 g) and triple distilled water were used. All important materials are cleaned by using nitric acid and additionally by deionized water, and then dehydrated by keeping it in hot air oven before the preparation of nanoparticles. The leaves of the cassia plant were gathered from Shaffa Village in Hawul Borno state, Nigeria. All the synthesis process were carried out in SHESTCO Chemistry Advanced Research Lab. Sheda Abuja Nigeria

2.2: Leaves Extract Preparations

The fresh leaves from three different plats (Guava, Jatropha and Cassia) obtained from Hawul local Government area of Borno State were obtained and washed with running tap water in order to remove the impurities adhering on their surface. The leave samples were dried away from direct sunlight for five days and ground into fine powder. 20 g each of powdered samples was added to 200 ml distilled water in 250 ml beaker and kept at 60 ^{o}C on a temperature controlled hot plate until the color of the water changed completely to their different respective colors. Then the extracts were cooled to room temperature, filtered with Whitman number 1 filter paper, and then kept at temperature of 7^{o}C for further experimental analysis. The three sample extracts were label as Sample A (Guava leaves), Sample B (Jatropha leaves) and Sample C (Cassia Leaves).

2.3: Preparation of Zinc precursors

30 g, 40 g and 50 g of zinc acetate dehydrate (Zn $(C_2H_3O_2)_2.2H_2O$) salts each were dissolved in 1000 ml distilled/deionized water. Next 30 g, 40 g and 50 g of zinc nitrate hexahydrate $(Zn(NO_3)_2.6H_2O)$ were dissolved in 1000 ml distilled water. Similarly 30 g, 40 g and 50 g of zinc chloride $(ZnCl_2)$ and sulfate heptahydrate $(ZnSO_4.7H_2O)$ solution were also prepared by dissolving the measured amount in 1000 ml distilled water which served as the precursor solution used in the synthesis of zinc oxides nanoparticles used at Sheda Science and Technology Complex (SHESTCO) Abuja, Nigeria.

2.4: Green Synthesis of Zinc Oxide Nanoparticles Using the Four Precursors

i. Zinc Acetate Dehydrate Precursor

20 ml of the extract A (guava leave extract) was added to 200ml of zinc acetate dehydrate $(Zn(NO_3)_2.2H_2O)$ solution of concentration 30 g/dm^3, the PH of the mixture was adjusted to 11.6 by dropwise addition of 1M solution of sodium hydroxide (NaOH) then placed on electric heater with magnetic stirrer at 60 °C for 2 hours. When the reaction was completed, the mixture was cooled down to 25 °C and then allowed to settle down for three hours. The clear solution above the settled nanoparticles was discarded, the remaining filtered and washed thrice with distilled water, poured into a clean Petri plate, and oven-dried at 100 °C for one hour. The dried material was then ground into fine powder in a pestle and mortar and calcined for 2 h at 550 °C to remove any impurities. The annealed powder was stored in an airtight glass vial for further characterizations. This procedure was repeated for the other samples 40 g and 50 g of zinc acetate dehydrate precursors. The same procedures were repeated for the extract B (Jatropha Leave) and likewise Extract C (Cassia Leave). At the end, nine different nanoparticles were synthesized from Zinc Acetate precursor labeled as A1, B1, C1, AA1, BB1, CC1, AAA1, BBB1 and CCC1 respectively.

(a). Guava leaves Guava leaves powder Guava leaves solution

(b) Jatropha leaves Jatropha leaves powder Jatropha leaves solution

(c). Cassia Leaves Cassia Leaves Powder Cassia Leaves solution

Figures 1 (a) Guava extract sample, (b) Jatropha Extract sample And (c) Cassis Extract Sample

(a) (b) (c) (d)

Figure 2: Stages in nanoparticles synthesis: (a). Plant extract and precursor (b).Mixture in a heated with constant stirring for two hours (c). Mixture cooled and overnight to settle (d). After filtering the residue was dried in oven then calcined at 550 °C for two hours.

ii. Zinc Nitrate Hexahydrate Precursor

The procedure described for zinc acetate dehydrate precursor were repeated for Zinc Nitrate Hexahydrate precursor which also produced nine Zinc Oxides Nanoparticles labeled A2, B2, C2, AA2, BB2, CC2, AAA2, BBB2 and CCC2 respectively.

iii. Zinc Chloride Precursor

Similarly, from Zinc Chloride precursor, nine Zinc Oxides Nanoparticles were also synthesized and labeled A3, B3, C3, AA3, BB3, CC3, AAA3, BBB3 and CCC3.

iv. Zinc Sulphate Heptahydrate Precursor

Finally the nanoparticles A4, B4, C4, AA4, BB4, CC4, AAA4, BBB4 and CCC4 were also produced using Zinc Sulphate Heptahydrate precursor.

2.5: Corrosion Inhibition Studies

The elemental compositions (in percentage by weight) of the mild steel used for corrosion studies are Fe (99.10), C (0.17), Mn (0.46), Si (0.26), S (0.017), and P (0.019). The mild steel coupons were cuts into 4 cm × 4 cm dimension, and the filling machine was used for the mechanical abrasion of the metal coupons to get rid rust on the surface of the mild steel. Then, the polishing of the mild steel specimens was done to near mirror image with emery sand papers of different grit sizes. Thereafter, the surface was washed under running water and degreased in acetone. All electrochemical experiments were conducted using mild steel coupons with a freshly pretreated surface. The gravimetric analysis was carried out in a thermostat water bath for duration of 8 h as per ASTM designation G1-90 at chemistry advance research laboratory, university of Maiduguri. The mild steel of dimension 4 cm^2 and thickness 2 mm was cut from the metal sheet. The surface of the mild steel coupons were scrubs with sand paper to removed painting and other greasy oil on the steel coupon then wash with ethanol and rinsed in distilled water. 250 ml beakers containing 150 ml of test solutions 1M HCl made by dissolving 1.3 g/dm^3 of each ZnO nanoparticles of different sizes at 303 K and for the ZnO NPs. From the same experimental conditions, the experiment was conducted in two different phases, Using digital balance the masses of the coupons measured, then first sets were immersed into the and suspended in the solution for six hours at once, the other sets were suspended for and removed for measurement on an hourly basis until after eight hours. In each case, the coupons were removed, using tissue paper, the liquids on the coupons were removed before taking any measurement. The immersion was done in duplicate and average corrosion rates in mgh were calculated using equation suggested by [9]. Using Origin lab 2022 the value of lost in weight of metal coupons were plotted against time to show the decay of mild steel with time in hours.

Figure 3: Set up for corrosion Inhibition

$$C_{rate} = \frac{w}{at} \tag{1}$$

$$\text{or } C_{rate} = \frac{534W}{\rho AT} \tag{2}$$

where W is weight loss in mg; "ρ" is the density of carbon steel in g/cm^3 "A" is the initial area of specimen in centimeter squares and "t" is exposure time in hrs. The degree of surface coverage (θ) and percentage corrosion inhibition efficiency (η) of the HCL and HCL-ZnO NP would be evaluated using the following equation [12]

$$(\Theta) = \frac{CR_o - CR_i}{CR_o} \tag{3}$$

$$(\eta) = \frac{CR_o - CR_i}{CR_o} x\ 100 \tag{4}$$

$$RWA = {}^{\Delta M_s}/_{\Delta M_w}\ x\ 100 \tag{5}$$

Where $CR_o$the corrosion rate of carbon steel in its bare 1 M HCl solution or absence of ZnO NPs and $CR_i$is the corrosion rate of carbon steel in presence of 1 M HCl and ZnO nanoparticle.

In order to elucidate the inhibitive properties of the ZnO NPs and the temperature dependence on the corrosion rates, the apparent activation energy (E_a) for the corrosion process in the absence and presence of ZnO NPs could be evaluated according to [6] using Arrhenius equation given by relation:

$$\log CR = logA - \frac{E_a}{2.303RT} \tag{6}$$

where CR is the corrosion rate of the green synthesized surfactant, A is Arrhenius constant, R is the molar gas constant and T is the absolute temperature. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature ($\frac{1}{T}$) was plotted for 1 M HCl alone and with additive (ZnO NPs) and values of activation energy obtained from the slope of the linear portion,

The supplementary kinetic parameters like enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) for the corrosion of stainless steel in 1 M HCl in presence of ZnO NPs) were calculated using the equation: [6]

$$CR = \frac{RT}{Nh} exp\frac{\Delta S}{R} exp\frac{\Delta H}{RT} \tag{7}$$

where "N" is the Avogadro's number, "h" is the Planck's constant, "R" is the molar gas constant and "T" is the absolute temperature. Linear plots of log($\frac{CR}{T}$) versus($\frac{1}{T}$) for 1 M HCl and (ZnO NPs) additive were plotted from which the slope S and intercept C were calculated using the equation [6]

$$S = \left(-\frac{\Delta H}{2.303RT}\right) \tag{8}$$

$$C = log\left\{\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303R}\right)\right\} \tag{9}$$

3. Results

Corrosion Inhibition Studies

Table 1: Mass loss of milled steel in 1M HCl with and without NPs after one hour interval

S/N	NPs	Size	Mo	1hour	2 hours	3hours	4hours	5hours	6 hours	7 hours	8 hours
1	CC (1)	15.4	23.625	23.5392	23.4677	23.411	23.368	23.339	23.3247	23.3153	23.3104
2	BB (1)	16.62	23.6	23.4692	23.3602	23.273	23.208	23.164	23.1422	23.1278	23.1204
3	BBB(3)	17.54	23.625	23.49	23.3775	23.288	23.22	23.175	23.1525	23.1376	23.1299
4	CCC(4)	18.31	23.62	23.4795	23.3625	23.269	23.199	23.152	23.1285	23.113	23.105
5	B (2)	18.64	23.61	23.5009	23.41	23.337	23.283	23.246	23.2283	23.2163	23.2101
6	AA (3)	19.08	23.625	23.5059	23.4125	23.335	23.283	23.245	23.2253	23.2125	23.2059
7	CCC(3)	19.27	23.64	23.5228	23.4251	23.347	23.288	23.249	23.2298	23.2169	23.2103
8	A (3)	20.55	23.62	23.4755	23.355	23.259	23.186	23.138	23.114	23.0981	23.0899
9	BBB(1)	21.22	23.6	23.5032	23.4225	23.358	23.31	23.277	23.2612	23.2505	23.245
10	A (4)	22.42	23.565	23.4709	23.3925	23.33	23.283	23.251	23.2357	23.2253	23.22
11	BBB(2)	23.47	23.43	23.2992	23.1902	23.103	23.038	22.994	22.9722	22.9578	22.9504
12	CCC(1)	24.22	23.52	23.37	23.245	23.145	23.07	23.02	22.995	22.9785	22.97
13	Control	C. G	23.61	23.4232	23.2675	23.143	23.05	22.987	22.9562	22.9356	22.925

Table 1 show the nanoparticles selected for the corrosion study which includes: as CC (1), BB (1), BBB (3), CCC (4), B (2), AA (3), CCC (3), A (3), BBB (1), A (4), BBB (2), and CCC (1) which covers the available sizes from the twenty four nan0particle that underwent XRD analysis. AA (3), A (3) and A (4) are particles from Guava plants extract, BB (1), B (2), BBB (1) and BBB (2) are from Jatropha plant extract while CC (1), CCC (4), CCC (3) and CCC (1) are from Cassia plants Extract respectively

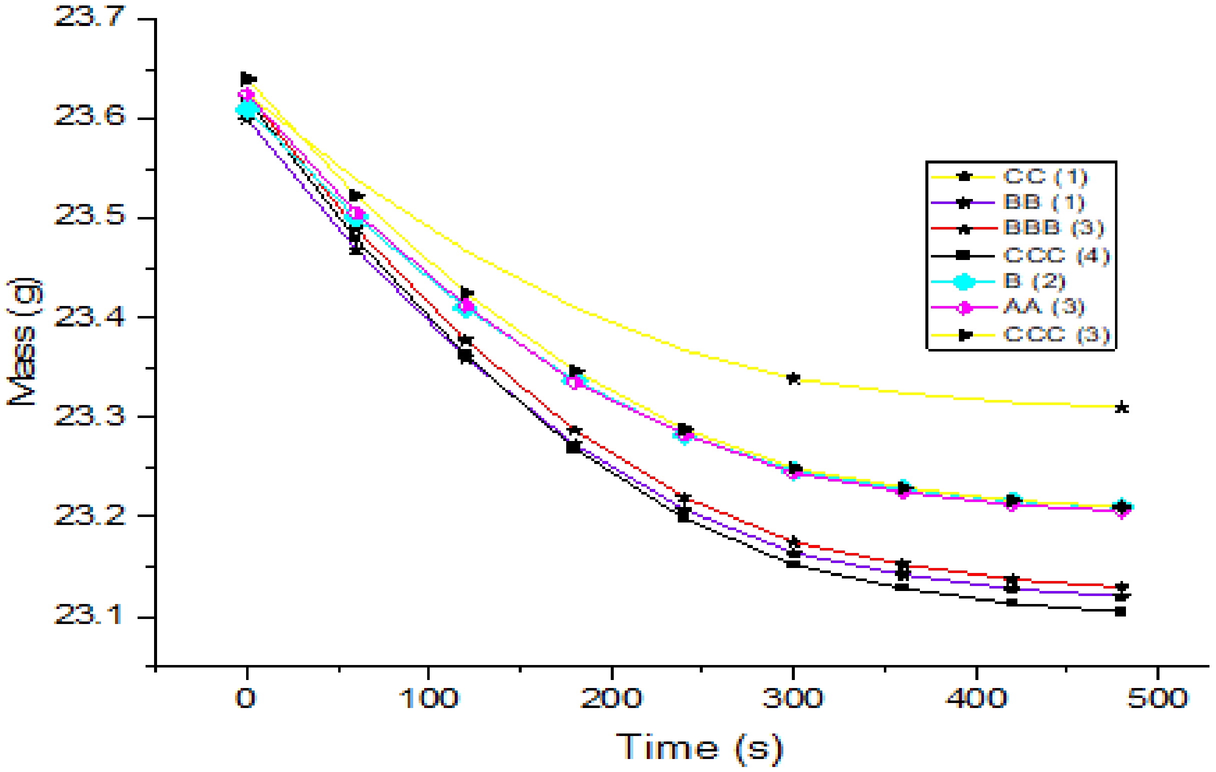

Figure: 4a: Rate of Decay of milled still in 1M HCl and Different sizes ZnO NPs with time

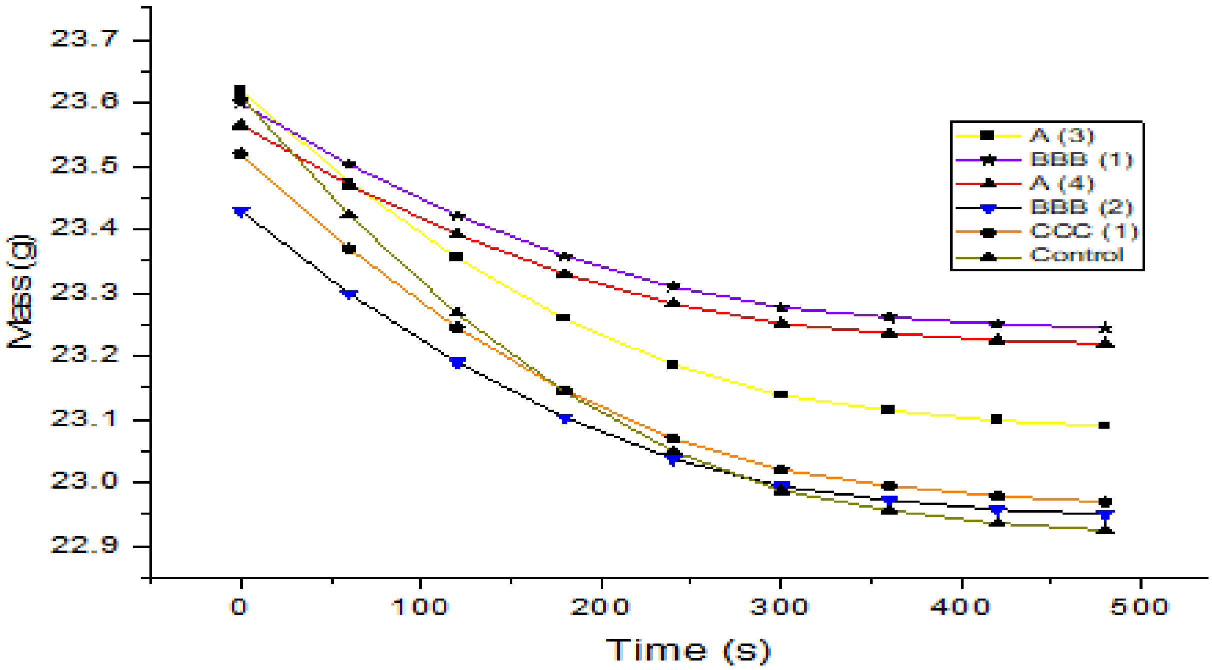

Figure: 4b: Rate of Decay of milled still in 1M HCl and Different sizes ZnO NPs with time

Figures 4a and 4b present the rate of mass loss of milled steel I M HCl with and without ZnO NPs. From the plots it show that, CC (1) which is the nanoparticle with size 15.40 nm has the least decay over the period of 480 minutes (8hours) monitored. The control group where no any nanoparticle was added demonstrates the highest rate of decay or mass lost compared to the remaining. These rates of decayed show that ZnO nanoparticles function as a corrosion inhibitor of milled steel.

Table 2. Weight loss of corrosion of mild steel in 1 M HCl after 6 hour immersion

S/N	NPs	NPs Size	$M_o\,(g)$	$M_I\,(g)$	$M_0 - M_I\,(g)$	$Mean\,(g)$	$W_I\,(g)$
1	A	15.40	23.63 23.62	23.31 23.31	0.32 0.31	0.315	0.0315
2	B	16.62	23.60 23.60	23.11 23.13	0.49 0.47	0.480	0.0480
3	C	17.54	23.63 23.62	23.13 23.13	0.50 0.49	0.495	0.0495
4	D	18.31	23.62 23.62	23.11 23.10	0.51 0.52	0.515	0.0515
5	E	18.64	23.62 23.60	23.22 23.20	0.40 0.40	0.400	0.0400
6	F	19.08	23.63 23.62	23.19 23.10	0.44 0.41	0.425	0.0425
7	G	19.27	23.66 23.62	23.23 23.19	0.43 0.43	0.430	0.0430
8	H	20.55	23.62 23.62	23.07 23.10	0.55 0.51	0.530	0.0530
9	I	21.22	23.60 23.60	23.25 23.24	0.35 0.36	0.355	0.0355

10	J	22.42	23.56	23.22	0.34	0.345	0.0345
			23.57	23.22	0.35		
11	K	23.47	23.41	22.92	0.49	0.480	0.0480
			23.45	22.98	0.47		
12	L	24.22	23.44	22.94	0.50	0.550	0.0550
			23.60	23.09	0.51		
13	Control		23.60	22.92	0.68	0.685	0.0685
			23.62	22.93	0.69		

Table 2. shows the results of corrosion rate of mild steel in absence and presence of Zinc Oxide nanoparticles in 1 M of HCl at 303 K for 6 hours of immersion and the same concentrations of ZnO nanoparticles of different grain size (15.40, 16.62, 17.54, 18.31, 18.64, 19.08, 19.27 20.55, 22.42, 21.22, 23.47, 24.22 nm) label as CC (1), BB (1), BBB (3), CCC (4), B (2), AA (3), CCC (3), A (3), BBB (1), A (4), BBB (2), and CCC (1) respectively. The average mass lost and weight lost by each coupon is presented in Table 4.8. The result show the control group which has no nanoparticle has greater weight loss of about 0.0685 N while NPs CC (1) of particle size of 15.40 nm has the lowest weight loss of about 0.0315 N. The largest nanoparticle CCC (1) having size 24.22 nm has the highest weight loss next to the control group.

Table 3: Rate of corrosion per year (CR)(mpy), degree (θ) of coverage and inhibition efficiency (ɳ %) of mild steel in 1 M HCl after 6 hour immersion

S/N	Nanoparticle	CR $(mpy$	(θ)	(ɳ)
1	CC (1	0.010145845	0.540142075	54.01420751
2	BB (1)	0.015460336	0.299264114	29.92641145
3	BBB (3)	0.015943471	0.277366118	27.7366118
4	CCC (4)	0.016587652	0.248168789	24.81687895
5	B (2)	0.012883613	0.416053429	41.60534287
6	AA (3)	0.013688839	0.379556768	37.9556768
7	CCC (3)	0.013849884	0.372257436	37.22574359
8	A (3)	0.017070787	0.226270793	22.62707931
9	BBB (1)	0.011434207	0.481747418	48.1747418
10	A (4)	0.011112116	0.496346082	49.63460823
11	BBB (2)	0.015460336	0.299264114	29.92641145
12	CCC (1)	0.017714968	0.197073464	19.70734645
13	Control	0.022063188		

Table 3 present the rate of corrosion per year (CR) (mpy), degree (θ) of coverage and efficiency (ɳ %) of the nanoparticles of the mild steel coupon. It is clearly observed that, the smallest size from the nanoparticle gives the highest degree of coverage as well as the highest inhibition efficiency of 54 % thereby, having the least rate of corrosion per year which is 0.010145845 / cm^2 . On the other hand the nanoparticle CCC (1) with the largest size of 24.22 nm gives the lowest degree of coverage of the surface of the mild steel and the lowest corrosion inhibition efficiency of 19.7 %. Table 4.9 clearly shows that, the nanoparticles next to nanoparticle CC (1) with good inhibition efficiencies and degree of surface coverage are particles A (1) and BBB (1) with size 22.42 nm and 21.22 nm having inhibition efficiencies of 49.6% and 48.2% respectively. Alternatively, three particles with the lowest performance efficiency are CCC 94) (24.8%) with size 18.31 nm, particle A (3) (22.6%) with size 20.55 nm and particle CCC (1) (19.7%) with size 24.22 nm. Previous works on corrosion rate of mild have been performed using different types of nanoparticles and show similar results. Thus, the corrosion protection efficiency on the mild steel surface in an acidic environment can be exhibited based on the size of the inhibitor molecular chemical structure, the interaction modes with the iron atoms of the metal surface include the nature of the bonds and the number of adsorption sites [13]. For example, [14] reported that, magnetite-RK/amidoxime nanoparticles act as good corrosion inhibitor for mild steel and inhibition efficiency increased with inhibitor concentration. The inhibition efficiency of the inhibitor by polarization technique exhibited the maximum inhibition efficiency 96.6% for the highest concentration 150 ppm.

In another separate study, the corrosion protection effect of epoxy-ZnO nano-composite coating was demonstrated by decline in corrosion rate (CR) value when optimum ZnO nanoparticles were incorporation by [7] in Corrosion Inhibition Properties of Epoxy-Zinc Oxide Nanocomposite Coating on Stainless Steel 316L. This is also in agreement with the study by [15] as the protecting ability of epoxy coating against corrosion increased particularly at the initial stage [16]. Low percentage of ZnO nanoparticles (1%) wt was not sufficient to impart corrosion inhibition effect on epoxy coating while excessive addition of ZnO nanoparticles (< 3 wt %) altered the amorphous state of polymer coating, thus weakened the barrier properties of overall coating [17].

In a study by [18] they reported iron oxide nanoparticles (IONPs) to be highly active as corrosion inhibitor of mild steel. Its corrosion inhibition efficiency was measured using Weight Loss Method. It was found that, olive oil stabilized IONPs can be applied as anticorrosive additive for epoxy paint coated on mild steel with corrosion inhibition efficiency 80.88 %. In accessing the immersion time for various coupons in HCl medium, mild steel, stainless-steel and aluminum lost 2.24 g, 1.71 g and 1.45 g, respectively after 2000 h of exposure when no inhibitor was added to the HCl solution. These lost masses were reduced to 1.34 g, 1.24 g and 0.77 g, respectively when 5 µg/ml of AgNPs solution was added. At the highest concentration of AgNPs (20 µg/ml), the total dissolved masses were 1.09 g, 0.51 g and 0.58 g, respectively. This indicates that the weight loss decrease sharply with concentration and exposure time. Inhibition efficiency increased with increased exposure time and concentration of AgNPs solution. The increase in (η) may be due to the formation of a protective film attributed to the transition of the metal/solution interface from an active dissolution state to a passive state [19] This implies that the concentration of the nanoparticle solution reduces dissolution of metallic ions but not sufficient enough to fully inhibit the reactive surface of the different metal alloys from the aggressive environment of the acidic medium. They could serve as a viable inhibitor for metal alloys in HCl solution. However, once adherent film (barrier) was formed on the surface, the effect of the exposure time became less significant because of the difficulty experienced by the corrosion agents in passing through the formed barrier [20]

When we look at the report of study by [21], where the outline says, corrosion inhibition mechanism of mild steel in acidic solution by ZnO NPs, can be explained using molecular adsorption when they study polyacrylamide, and ZnO/PAA nanocomposites as corrosion inhibitors. They point out that, n an acidic solution, polyacrylamide emerges as protonated species that adsorb on the surface of mild steel cathodically and reduce the hydrogen evolution process. Adsorption on anodic sites occurs via pi-electrons of the carbon chain and lone pairs of electrons from nitrogen and oxygen atoms, resulting in mild steel surface being coated with complex from the nanoparticles which is similar to what was reported by [22] where creation of a complex of ferric (Fe^{+2}) and zinc oxide nanoparticles (ZnONPs)and the functional group slow down corrosion rate when they study Zinc oxide nanomaterials as good inhibitors of steel corrosion in chloride solution. They further reported that, inhibitor molecules were spontaneously absorbed on surface of the steel surface through chemical adsorption mechanism due hetero atoms with a free electron pair and the decomposition mechanism by electrostatic interaction between the electrons which were adsorbed on the surface of carbon steel. This show that, the sizes of nanoparticles or inhibitors sizes is important by giving fine coverage for smaller sizes while larger sizes will result in larger pore which can lead to penetration of corroding to the mild steel surface.

[9] Considered an appropriate technique for testing immersion time. He observes the response of mild steel to corrosion in 1M HCl in the presence of 0.06 mg/ml of the ZnO-NPs at different immersion durations at the temperature of 298 K. He later found out that, the increase in immersion time does not affect the corrosion process mechanism jus as reported by [23]. He observed in his Nyquist plots that, the diameter of the semicircle increases with an increase in immersion time. The important EIS parameters when observed show that resistance current (Rct) increases with an increased immersion time, indicating the decreased corrosion rate. Thus, suggesting that, prolonged immersion time increases the adsorption of ZnO-NPs molecules on the carbon steel surface, ensuring its stability. It was at the same time observed that the surface coverage became stable after approximately 6 hours.

Table 4.10 shows some comparisons of different nanoparticles on mild steel in Acidic medium and their corresponding inhibition efficiencies attained under variable condition such as concentration of the acid medium, temperature, times of immersion and or co-inhibitors used and their effects. According to [24] The inhibition efficiency of ZnO NPs and their nanocomposite increased with the inhibitor concentration (100–400 ppm) and decreased with the rise in temperature (308–338 K) for all their studied, they further point out that, adsorption of inhibitor molecules on the surface of carbon steel follows step by step procedures which involves: physical adsorption where inhibitor molecules adsorbed on surface of the carbon steel by electrostatic interaction of electrons deposited on surface of the carbon steel. The next step is Chemical adsorption is when surface of carbon steel becomes increasingly negative as electrons accumulate on it due to presence of heteroatoms with a free electron pair. Thus, electrons from the Fe orbitals were transfer to the non-bonding orbitals of the inhibitor molecules, which leads to better adsorption of the inhibitor on the carbon steel surface hence inhibition. This is similar to reports by [24] where they outline the steps of inhibitions to includes: (i) electrostatic attraction between charged molecules and the charged metal coupon, (ii) interaction of lone pair electron from molecule with coupon, (iii) interaction of p-electrons with the coupon, these process above lead to formation of protective film on mild steel surface that reduces the corrosion rate by preventing the corroding species from reaching the metallic surface [26] and their result shows good agreement with the experimental results result in this study.

4. Conclusion

When the nanoparticles are applied for corrosion inhibition of milled steel in acidic medium the smallest size have the highest relative inhibition efficiency (54 %) while the largest size have the lowest relative inhibition efficiency compared to the milled steel exposed to bare acids in absent of nanoparticles, therefore, the inhibition property of Nanoparticles to a great extend depend on the sizes of particles because the efficiency of inhibition is a function of degree of coverage of the surface of the metal (ϴ) which in turn determine efficiency of inhibition. From this study, it shows that, the smaller the sizes of the nanoparticles, the greater the degree of surface coverage, thus, the higher the inhibition efficiency.

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