Nano-Parctials as corrosion inhibitors for Aluminum alloys in acidic solution at different Temperatures

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Abstract

Synthesis of sulfur nanopartical (SNPs) from mixture theosulphate sodium with Alhagi extra plant. When the change of the color after mixture theosulphate sodium with Alhagi extra plant from yellow to brown indicated the synthesis sulfur nanopartical. Atomic forces microscope (AFM) was used to study the surface topology of the formulated sulfur nanopartical was size 82.39nm. The sulfur nanopartical was used protection aluminum from corrosion in acid media, the study corrosion in different temperature, the inhibition efficiency (%IE) of sulfur nanopartical was high in low temperature, therefore the sulfur nanopartical was active inhibition for aluminum in low temperature in acid media. The values of the thermodynamic parameters at different temperatures for Aluminum in presence sulfur nanopartical are higher than in the absence sulfur nanopartical, also the negative value of $\Delta H^*$ for corrosion processes in absence and presence sulfur nanopartical reveal the exothermic nature of Aluminum.

Key words: Alhagi extra plant, Aluminum alloys, corrosion Thermodynamic parameters, Thiosulfate sodium, Hydrochloric acid, sulfur nanopartical.

Introduction

The Alhagi maurorum have secondary metabolites triterpenes, tannins, carbohydrate, vitamins, glycosides, fatty acids and sterols. It was used antioxidant ,analgesic, antibacterial ,anti-inflammatory ,diuretic and dematological [1]. In medicine Alhagi was used to treatment liver disorders, general tonic, anthelmintic ,jaundice and rheumatic pains, also used antimicrobial, hemorrhoids , upper respiratory system problems, curing kidney stones and oil of Aalhagi for curing rheumatism [2]. The applications of sulfur in agriculture area therefore used fungicide for vegetables, strawberry. Sulfur very good
persticide was used in griculture (black spot and powdery mildew). The properties of sulfur nanopartical was high surface areas and over micro sulfur for quantum size [3]. The used sulfur nanopartical in synthesis of nanocomposites for lithium batteries and agrochemical industries. Hybrid materials were compound from reaction sulfur nanowires with carbon, hybrid materials used catalytic applications and gas sensor[4]. The morphological characteristics of green synthesized sulfur nanopartical exhibits enhanced for example surface area, spatial confinement, reduced size and energy[5]. The nanopartical was used corrosion inhibitors but in air unstable after synthesis therefor the coatings of surface nanopartical [6]. Aluminum alloys was used in structural components due low cost, high wear resistance and high power to weight ratio. The used casting and mixing methods were preparations aluminum alloys by mixing graphite, powder compounds and silicon carbide [7]. The more efficient and environmentally methods product was used raw materials by application of nanotechnology. In chemical moieties localization mixing with topographic by nanoscale modification of surfaces. Corrosion protection of epoxy and zeolite by add nanoparticals, Synthesis nanopartical was provide corrosion inhibitor self healing effects and encapsulated agents [8]. The surface of metal or alloy was exposed change chemical and corrosion when metal or alloy have cracks on surface, the estimated corrosion on surface 3.4% of the global therefore most[9].

Experimental

1-Materials
Aluminum alloy from( England), the composition of aluminum alloy in given in Table 1[10], (0.05N)HCl Hydrochloric acid, sodium thiosulfate, distill water and Alhagi extra plant.

Table 1: The composition of aluminum alloy

|   | Al   | Cu   | Cr   | Fe   | Mu   | Mg   | Si   | Zn   | Ti   |
|---|------|------|------|------|------|------|------|------|------|
|Bal.| 3.8-4.9 | <0.1 | <0.5 | 0.3-0.9 | 1.2-1.5 | <0.5 | <0.25 | <0.15 |

2-Synthesis of sulfur nanopartical
The prepare the sulfur nanopartical from mixing 5ml sodium thiosulfate solution with 50ml Alhagi extra plant solution, cold water as solvent. The solution yellow color than mix Cher cooking for 30 min., the change of the color after mixture to brown indicated the synthesis sulfur nanopartical. Than separation by centrifuge for 15 min. at 3500 rpm at room temperature, the resulted in the formation of sulfur nanopartical was size 82.39nm, the size distribution diagnosed by Atomic Force Microscopy (AFM)[11].

3-Test Sampl
The aluminum was treatment by polished with (100,200,600 and 1400)mm Sic, than the specimen was treatment chemical cleaning by 5%NaOH solution, washing by die zoned water and keep in desiccator for used.

4-Corrosion Testing
The corrosion protection of the sulfur nanopartical was study in different temperature by using polarization measurements, used (0.05 N) HCl solution in presence and absence of sulfur nanopartical, the used corrosion cell and three electrodes. The polarization curve can calculated by Tafel technique. In cell corrosion, the area of the working electrode
was 2cm², the sample aluminum was located in working electrode in contact with reference electrode injection by hydrochloric acid, the solution of test was hydrochloric[12] Figure (1) set up the corrosion cell and three electrodes.

![Corrosion cell setup](image)

**Figure (1) set up the corrosion cell and three electrodes**

**Results and Discussion**

1-Characterization of Sulfate Nanopartical

**Atomic Force Microscopy (AFM)**

The distribution of particles size and surface morphology for nanoparticle can detected by AFM. The AFM morphologies have two and three dimensional. Figs.(2) show 2D and 3D views of AFM image of sulfur nanoparticals, the explain surface topography of sulfur nanopartical and roughness images for cross sectional. Figs.(3) show Granularity Cumulation Distribution Report. The average size of the particle size 82.39nm [13].

2-Weight loss measurements

**Effect of inhibitor concentration**

The inhibition efficiency (%IE) was decreased in high temperature, due the greater area aluminum was exposed to the hydrochloric acid therefore the adsorbed molecules sulfate nanopartical on surface aluminum was instable at higher temperature [14]. The percentage efficiency (%IE) was calculated by equation:

\[
\%IE = \frac{i(corr) - i(corr^\theta)}{i(corr)} \times 100 \quad (1)
\]

Where \(i(corr)\) the corrosion current in absence sulfur nanopartical, \(i(corr^\theta)\) the corrosion current in presence sulfur nanopartical, respectively and can calculated the degree of surface coverage (\(\theta\))by used equation:

\[
\theta = \frac{i(corr) - i(corr^\theta)}{i(corr)} \quad (2)
\]
In Table (2) surface coverage (θ), corrosion rate, (%IE) the inhibition efficiency for aluminum in presence sulfur nanopartical [15]. Corrosion rate can be calculated from equation (3)
\[ CR=0.13* i_{corr}* e/\rho \] (3)
Where e: Chemical equivalent, ρ: density of aluminum

| T(K) | Corrosion rate (g/d.m²) | %IE | θ   |
|------|-------------------------|-----|-----|
| 293  | 1.5970                  | 87.15 | 0.8715 |
3-Polarizaton Curve
The reaction of corrosion was control on extrapolation of anodic and cathodic tafel lines can calculated current density (I corr), and corrosion potential (E corr). The process of corrosion was developed by Traud and Wagner and this experimental was based electrochemical. The polarization curve can be estimated from plotted (Ecorr) ingest (I corr) for aluminum alloys with different temperature presence and absence sulfur nanopartical in( 0.05N )HCl . Table (2,3) shows the corrosion protection (I corr), and corrosion potential(E corr), The percentage efficiency (%IE), calculated the degree of surface coverage (θ),catholic Tafel slope and (ba) anodic Tafel slope [16] . 

|   |   |   |   |
|---|---|---|---|
| 303 | 1.9359 | 85.6  | 0.856 |
| 313 | 2.6945 | 80.01 | 0.8001 |
| 323 | 2.9145 | 79.64 | 0.7964 |

Fig. (4) Potentidynamic Polarization curve for aluminum alloys with different temperature in absence sulfur nanopartical in (0.05N) HCl
Fig. (5) Potentiodynamic Polarization curve for aluminum alloys with different temperature and presence sulfur nanoparticle in (0.05N) HCl.

Table (3) Potentiodynamic Polarization date for aluminum alloys with different temperature in absence sulfur nanoparticle in (0.05N) HCl.

| T (K) | Icorr (µA/cm²) | -Ecorr (mv) | -ba (mv/Dec) | bc (mv/Dec) | W.L (g/m².d) | P.L (mm/a) | %IE | θ | Rp/Ω.cm² |
|-------|----------------|-------------|--------------|-------------|--------------|-------------|------|---|----------|
| 293   | 287.07         | 390.2       | 220.7        | 267.1       | 2.31 E+001   | 3.12 E+000 | -    | - | 182.790  |
| 303   | 310.93         | 341.3       | 309.1        | 236.9       | 2.50 E+001   | 3.38 E+000 | -    | - | 187.290  |
| 313   | 313.33         | 346.7       | 290.7        | 277.9       | 2.52 E+001   | 3.4 E+000  | -    | - | 196.893  |
| 323   | 330.71         | 386.7       | 260.4        | 270.3       | 2.66 E+001   | 3.60 E+000 | -    | - | 174.139  |
Table (4) Potentiodynamic Polarization date for aluminum alloys with different temperature in presence sulfur nanopartical in (0.05N) HCl.

| T (K) | Icorr (µA/cm²) | -Ecorr (mv) | -ba (mv/Dec) | bc (mv/Dec) | W.L (g/m².d) | P.L (mm/a) | %IE | θ | Rp/Ω.cm² |
|-------|----------------|-------------|--------------|-------------|--------------|-------------|------|---|---------|
| 293   | 36.88          | 107.8       | 97.6         | 69.8        | 2.97E+000    | 4.01E-001  | 87.15| 0.8715  | 479.142 |
| 303   | 44.71          | 68.4        | 104.2        | 78.7        | 3.60E+000    | 4.86E-001  | 85.6 | 0.856   | 435.441 |
| 313   | 62.23          | 129.7       | 138.9        | 90.3        | 5.02E+000    | 6.78E-001  | 80.01| 0.8001  | 381.840 |
| 323   | 67.31          | 154.6       | 133.4        | 86.3        | 5.42E+000    | 7.32E-001  | 79.64| 0.7964  | 338.086 |

Table (4) explain (Icorr) in presence the sulfur nanopartical was less than (Icorr) in absence sulfur nanopartical in Table (3) with increasing temperature ,the best (%IE) for sulfur nanopartical to protection aluminum from corrosion in 293K , the aluminum alloys was active due the corrosion potential (Icorr ) in cathodic direction .The negative value of corrosion potential was increassin in presence of sulfur nanopartical while in absence sulfur nanopartical is decrease ,due the sulfur nanopartical made of the aluminum alloy in all temperature is more active toward corrosion aluminum [17]. The values of polarization resistance(Rp) in presence sulfur nanopartical was increased compared with absence sulfur nanopartical. The polarization resistance can be determination by equation(4) [18]:

\[ Rp = \frac{ba \cdot bc}{2.303 \cdot (ba + bc) \cdot i_{corr}} \]

4-Kinetic and Thermodynamic Studies
The activation energy (Ea) and Arrhenius factor (A) were calculated from equation (5):

\[ \log i_{corr} = \frac{-Ea}{2.303RT} + \log A \]

Where R:the gas constant , A : Arrhenius factor was determine from intercept for plots of Log icorr against T, the slope give The activation energy (Ea). The values of ∆H*and ∆S* can calculated from equation (6):

\[ \log \left( \frac{i_{corr}}{T} \right) = \log \left( \frac{R}{Nh} \right) + \frac{\Delta S^*}{2.303} - \frac{\Delta H^*}{2.303} R \]

Where T is temperature in (K),h is the planks constant,i_corr is the corrosion current density ,N is the Avogadro number , ∆S*is the entropy of activation and-∆H*is the enthalpy. When the plots of Log icorr /T against 1/T, give slop equal (-∆H*/2.303 R), and intercept of Log(R/Nh)+ ∆S*/ 2.303R [19] .In Table (5).The values of the thermodynamic parameters at different temperatures for Aluminum in presence sulfur nanopartical are higher than in the absence sulfur nanopartical, also the negative value of ∆H* for corrosion processes in absence and presence sulfur nanopartical reveal the exothermic nature of Aluminum[20].
Fig. (6) Plot of 1/T against log $i_{corr}$ for aluminum in 0.05N HCl with different temperature.

Fig. (7) Plot of 1/T against log $i_{corr}$ for aluminum with sulfate nanoparticle in 0.05N HCl with different temperature.

Fig. (8) Plot of 1/T against log ($i_{corr}/T$) for aluminum in 0.05N HCl with different temperature.
Fig. (9) Plot of 1/T against log (icorr/T) for aluminum with sulfur nanoparticle in 0.05N HCl with different temperature.

Table (5) The values of the thermodynamic parameters at different temperatures for Aluminum in 0.05N HCl in the absence and presence sulfur nanoparticle.

|               | T(K) | \( \text{E}_a / \text{KJ/mol} \) | \( \text{A} \) \( \text{Molecules. cm}^{-2} \text{S} \) | \( -\Delta \text{H}^* / \text{KJ/mol} \) | \( \Delta \text{S}^* / \text{J/mol} \) | \( \Delta \text{G}^* / \text{KJ/mol} \) |
|---------------|------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Aluminum      | 293  | 2.4508                          | 1.8100*10^{19}                 | 0.8364                          | 194.8631                        | 44.269*10^{23}                 |
|               | 303  |                                 |                                 |                                 |                                 |                                 |
|               | 313  |                                 |                                 |                                 |                                 |                                 |
|               | 323  |                                 |                                 |                                 |                                 |                                 |
| Aluminum with Inhibitor | 293  | 12.7711                         | 2.399*10^{19}                  | 10.8759                         | 177.6651                        | 230.76*10^{23}                |
|               | 303  |                                 |                                 |                                 |                                 |                                 |
|               | 313  |                                 |                                 |                                 |                                 |                                 |
|               | 323  |                                 |                                 |                                 |                                 |                                 |

5-Mechanism of inhibition

The explained mechanism of inhibition to protection metal (aluminum) from corrosion by basis of adsorption of sulfur nanoparticle on the aluminum surface in hydrochloric acid by interaction metal with electrons also interaction between charged metal with charged molecules and interaction the metal with the molecule by unshared pair of electrons. The charged of inhibitor sulfur nanoparticle and charged of surface aluminum were requires physical adoption to protection aluminum from corrosion. The electrostatic interaction between sulfur nanoparticle and Cl- ions gives protection for aluminum from corrosion. Therefore %IE was decrease with increase temperature [21].
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