Green synthesis of zinc sulfide nanoparticles-organic heterocyclic polyol system as eco-friendly anti corrosion and anti-bacterial corrosion inhibitor for steel in acidic environment

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ABSTRACT
Green synthesis, characterization and evaluation of nanoscale zinc sulfide (ZnS) by precipitation chemical method. The zinc sulfide nanoparticles were prepared by chemical precipitation method using heterocyclic polyvinyl alcohol, PVA as a sensitizer. The prepared heterocyclic compounds system ZnS nanoparticles, PVA, EG were used as anti-bacterial corrosion towards sulfate-reducing bacteria (SRB) and anti-corrosion for carbon steel substrate in sulfuric acid and hydrogen sulfide bacterial corrosive environment using chemical, analytical, and electrochemical techniques. Effect of adding PVA, and ethylene glycol, EG to ZnS nanoparticles were studied. Effect of ZnS nanoparticles concentrations and the reaction temperature on the corrosion inhibition efficiency were studied. The inhibition due to adsorption of nanoparticles on steel surface, the adsorption agree well with Langmuir isotherm with suggested chemical adsorption mechanism. Potentiodynamic polarization (PD) and Electrochemical impedance spectroscopy (EIS) data explain that the used inhibitor is mixed-type and improves polarization resistance and inhibition performance by adhering to metal/electrolyte interface. The cathodic and anodic reactions are delayed when inhibitor molecules are added to an aggressive medium, which results in a negative shift in the open circuit potential. Addition of both PVA, and EG as organic polyol materials enhance the adsorption and inhibition properties of zinc sulfide nanoparticles on steel surface.

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1. Introduction
Nanoscale zinc sulfide(ZnS) is one of the nanomaterials with unique properties and applications. Zinc sulfide nanoparticles are (II–VI) group of wide band gap semiconductor material, that has unique optoelectronic and adsorption properties (1–3). ZnS of high potential...
applications including solar cells, light-emitting diodes, electroluminescent devices, and corrosion inhibitors. Nanocrystalline zinc sulfide (ZnS) has a large surface-to-volume ratio (1–8). Nanoparticles of broad application spectrum are used in the industrial field as corrosion inhibitors (9, 10). The use of nanomaterials as a corrosion inhibitor is of great industrial, economical, and environmental impact. Nanomaterials have higher corrosion inhibition properties because their surface-to-volume ratio has increased. Many processes have been used for the preparation of nanoparticles (1–10). Various researchers have successfully demonstrated the applicability of nanomaterials as corrosion inhibitors (9–13). The most important application of nanoparticles in the industrial field is having a great specific characteristic to protect the metal from corrosion in different environments (9). Nanocomposites stop the reaction of the surface, control the corrosion rate by blocking active sites of metal surfaces, and provide hardness, straightness, durability, optical qualities, and thermal stability (9–13). These types of compounds are eco-friendly and degradable to the environment. The prominent option is to use inhibitors to protect the metal from corrosion. These inhibitors make a protective film on the metal surface and help to control the corrosion rate. Many organic and inorganic inhibitors were used to reduce corrosion in metal industries (14–21). The traditional corrosion inhibitors are undesirable as it is toxic, expensive, difficult to prepare, and hazardous. Scientific efforts concentrated on the use of eco-friendly corrosion inhibitors (14–51), such as natural products, expired drugs, plastic waste, and nanomaterials (14–51). Surfactants or surface-active materials are widely used as corrosion inhibitors for many acidic, alkaline, marine, and aqueous salts with corrosive materials (14–21). Surfactants act as inhibitors through adsorption on the metal substrate. The most effective inhibitors are nanomaterials but the addition of the surfactant molecules into the nanomaterials not only improves and manages its particle size but also enhances the adsorption and inhibition properties of the nanomaterials. Nanomaterials have higher corrosion inhibition properties because their surface-to-volume ratio has increased. Because the surface-to-volume ratio of nanomaterials has increased, their corrosion inhibition properties have improved. Nanoparticles have been prepared using a variety of methods. Several researchers have demonstrated the effectiveness of nanomaterials as corrosion inhibitors. Metals and their oxide nanoparticles are excellent corrosion inhibitors. It is simple to use as a corrosion inhibitor on metallic surfaces (13). It is simple to use as a corrosion inhibitor on metallic surfaces. Many studies have demonstrated corrosion inhibition by the adsorption of metal nanoparticles and their oxides on metal surfaces. Recent nanoparticle studies have used metal and oxide nanoparticles to improve corrosion resistance, such as TiO2 (52, 53), Cu2O (10, 54), ZnO (55), ZrO2 (56), SiO2 (57), and Ag nanoparticles (58). Atta et al. (10, 21) reported that silver nanoparticles inhibited the corrosion of carbon steel in an acidic solution. By forming oxide film, nanocrystal alloys provide hardness, wear resistance, electrical resistivity, and high-temperature corrosion resistance (49–52).

Numerous techniques have been used to study and evaluate the corrosion behavior of nanocrystal alloys in various environments (59–61). Another excellent method for reducing corrosion costs is nanocomposite (13, 62–69). Nanocomposite preparation involves the use of polymers and nanomaterials. In general, organic and inorganic constituents combine to form a composite (13). The inorganic components of nanocomposite provide super adhesive- ness, high ductility, and good mechanical strength, while the organic components allow for flexibility, compatibility improvement, porosity reduction, and defect reduction. Epoxy (13), polyurethane (13), polyethylene glycol (PEG) (65), polyaniline (PANI) (13), polystyrene, polyacrylic, polyvinyl alcohol (PVA), polypyrrole, polyamide, and other organic polymers are commonly used for the preparation of nanocomposite coatings (13). Metal nanoparticles and their oxides, carbides, and phosphates (13) are commonly used in inorganic constituents. Some articles (13, 62–69) report preliminary research on the corrosion resistance performance of nanocomposite. In the previous work, silver nanomaterials were prepared by the green method using some plant extract and characterized as green corrosion inhibitors for steel alloys used in the manufacturer of petroleum pipelines in an acidic environment, chemical, analytical, and electrochemical techniques were applied to evaluate the inhibition action of the prepared nanomaterials (70, 71). In the present work nanoscale zinc sulfide was prepared by the participation chemical method with PVA as surface active materials as a sensitizer and promotion for both particle size and inhibition properties of the ZnS nanomaterials on the carbon steel surface in an H2SO4 corrosive environment. The prepared heterocyclic compounds system ZnS nanoparticles, PVA, EG were used as anti-bacterial corrosion towards sulfate-reducing bacteria (SRB) and anti-corrosion for carbon steel substrate in sulfuric acid and hydrogen sulfide bacterial corrosive environment using chemical, analytical, and electrochemical techniques. The effect of the addition of surface-active materials PV5 and EG on the corrosion inhibition efficiency of zinc sulfide, ZnS and nanoparticles were studied. The effect of concentration, temperature, and surfactant addition is studied. Inhibition mechanism and adsorption isotherm are the third goal of the present study.
2. Experimental and methods

2.1. Materials used in the present study

Hydrated zinc chloride (ZnCl₂·2H₂O), sodium sulfide (Na₂S) polyvinyl alcohol (PVA), sulfuric acid, sodium carbonate Na₂CO₃, and ethylene glycol (EG). All chemicals used of analytical grade were from Sigma Aldrich. The corrosive solution prepared in this study is aggressive 1.0 M sulfuric acid that was prepared from analytical grade 98% H₂SO₄ (Sigma Aldrich). Distilled water was used as a solvent for all experiments. 1.0 M Na₂CO₃ was used for titration and standardization of 1.0 M sulfuric acid corrosive solution. Each experiment was performed in aerated stagnant solutions and was repeated at least three times under the same conditions to check the reproducibility and the average of the three replicated values was used for further processing of the data. The gravimetric composition of steel materials employed in this study is given in Table 1. It is similar to the composition of the carbon steel used in the manufacturer of petroleum pipelines.

2.2. Preparation nanoparticle zinc sulfide (ZnS) nanoparticles (chemical method)

The chemical precipitation method as mentioned elsewhere (2) was used for the preparation of zinc sulfide nanoparticles (ZnS) (2). In this method, ZnS nanoparticles Capped by PVA were prepared in the solution by chemical precipitation method: A simple chemical co-precipitation method (2, 3) was used to synthesize ZnS nanoparticles in colloidal solution using aqueous solutions of hydrated ZnCl₂·2H₂O and Na₂S in equal molar ratios as source materials and PVA as the capping material. In this procedure, ZnCl₂ (0.1 M) and Na₂S (0.1 M) were dissolved in 500 and 720 ml of distilled water, respectively.

The two solutions were stirred continuously for 30 min. After that, A 5 wt. % (for the total weight of the reactants) solution of PVA was stirred to achieve complete dissolution at room temperature. For the synthesized nanoparticles samples ZnS of molar ratio of zinc chloride and sodium sulfide, 50 ml of sodium sulfide solution was added drop by drop to zinc chloride (ZnCl₂) 100 ml, with continuous magnetic stirring (addition about 30 min) PVA (70 ml) as surfactant solution was then added to the reaction mixture with constant stirring. The white color zinc sulfide (ZnS) nanoparticles grew slowly in the solution, in accordance with the following reaction:

\[ \text{ZnCl}_2(aq) + \text{Na}_2\text{S}(aq) \rightarrow 2 \text{NaCl}(aq) + \text{ZnS(S)} \]  

(1)

The precipitate was isolated by filtration and dried at 40° C for 36 h to remove any organic residue, water, and other byproducts formed during the reaction process. After drying, the precipitate was used for the synthesis of the inhibitor colloidal solution. The synthesized ZnS, nanoparticles were synthesized and characterized by methods discussed and mentioned elsewhere (2, 3) and was used in the present study as corrosion inhibitor for carbon steel alloy in an 1.0 M sulfuric acid corrosive environment with and without both PVA and EG.

2.3. Inhibitor solution preparation

Five inhibitors materials formulated for the present study, three of which are individual materials with are zinc sulfide nanoparticles (symbolized as (ZnS, Nano)), polyvinyl alcohol (symbolized as (PVAI)), ethylene glycol (symbolized as EG). In addition, two mixtures from zinc sulfide nanoparticles – PVA and or EG (symbolized as (ZnS Nano – PVA)), zinc sulfide nanoparticle – ethylene glycol system (symbolized as (ZnS Nano-EG)). All the inhibitors materials used in the solution at concentration ranges of 50,100, 150, and 200 ppm. All selected materials were used as an inhibitor for carbon steel alloy in an acidic 1.0 M H₂SO₄ corrosive environment.

2.4. Evaluation of the prepared mixture as a corrosion inhibitor

2.4.1. Gravimetric studies (weight loss measurement)

The gravimetric measurements were carried out in a stagnant (but not in dynamic) solution so that the metal sample and inhibitor could have sufficient time to interact with the corrosive medium. Low carbon steel coupons, which cut into dimensions 4.0 × 2.0 × 0.2, were scraped away using emery sheets of different grades. This was put in an acetone bath for 10 min for further cleaning. After that, it was cleaned using a soft cloth and dried. Measurements for weights with the help of a four-digit analytical balance were taken. These carbon steel coupons were hung into the different solutions of inhibitor materials (50,100, 150, and 200 ppm)) in 1.0 M H₂SO₄ from 303 K to 333 K for 7 h. The experiments were done thrice to check for

Table 1. Gravimetric composition of the used steel materials.

| Element | Mn      | Si      | Zn      | S       | P       | C       | Fe       |
|---------|---------|---------|---------|---------|---------|---------|----------|
| Composition weight (%) | 0.517   | 0.201   | 0.215   | 0.009   | 0.007   | 0.157   | About 99 |
uniformity in results and the calculations performed. From these, the average value of the weight loss was noted. For each new reading, a freshly prepared inhibitor solution was used. The following are the calculations used to study the inhibition parameters.

Corrosion inhibition efficiencies (% I.E.) were calculated based on the weight/mass loss (mg) with (M) and without (M₀) the corrosion inhibitor using the following equation (39–47):

\[
\%\text{I.E.} = \left(\frac{M₀ - M}{M₀}\right) \times 100
\] (2)

For calculating the corrosion rate, the following equation was used:

\[
CR = 87.6 \times \left[\frac{\Delta M}{A \times t \times \rho}\right]
\] (3)

where CR represents corrosion rate in mm/year; weight/mass loss of low carbon steel (mg) as \(\Delta M\), \(A\) represents the exposed surface area of the coupon in cm², \(t\) is the exposure time (h), and \(\rho\), the density of the mild steel in g/cm³.

The fraction of surface coverage was calculated as \(\theta\) from the following equation (39–47):

\[
\theta = \left(\frac{M₀ - M}{M₀}\right)
\] (4)

The surface coverage values obtained from the weight loss method were fitted graphically into various isotherms and the best fit was concluded from the highest regression coefficient value.

2.4.2. Gasometrical measurements (analytical studies)

The progress of the corrosion reaction was determined by volumetric measurement of the evolved hydrogen. The metal sample was put in a Büchner flask containing the test solution. The flask is sealed with a rubber bung, and from its hose barb protruding from its neck, rubber tubing is connected to the bottom of an inverted measuring cylinder which is fitted above a basin. The cylinder and the basin are filled with distilled water. The evolved hydrogen gradually displaces the distilled water and is collected at the top inside the cylinder, and its volume is measured directly with time (34–37)

The experiment is done with and without different concentrations of the tested inhibitor.

2.5. Electrochemical measurements

Electrochemical measurements are made in stagnant solutions, without agitation. Because the agitation can affect the corrosion potential and the current density. The protective film on the metal surface can be affected by agitation, thus reducing the inhibiting power of the used inhibitor (15).

Electrochemical measurements as accurate and high-performance techniques were applied to evaluate the inhibition performance of the prepared nanoparticles, ZnS-Nano – EG nanoparticles mixture 2 which evaluated as a corrosion inhibitor for steel in 1.0 M H₂SO₄ at 303 K. Electrochemical measurements with a Versa STAT 4 potentiostat were carried out using the Versa Studio software. For the electrochemical testing, a glass cell with three electrodes was used, with platinum as the auxiliary electrode, Ag/AgCl as the reference electrode, and steel samples as the working electrode. The surface area of the steel electrode used in the electrochemical studies was 1.00 cm², and the glass cell held 100 mL of solution. To have a stable open circuit voltage, the working electrode’s potential was maintained for 30 min before each test. The polarization curves were performed at a scan rate of 1 mV S⁻¹ with a potential range of about 250 mV based on the open circuit potential (OCP). The inhibition efficiency (I.E.%) was calculated from the corrosion current density readings using Equation (4) (15–20):

\[
\text{I.E.\%} = \frac{(i_{corr}^0 - i_{corr})}{i_{corr}^0} \times 100
\] (5)

\(i_{corr}^0\): the corrosion current density value with an inhibitor.

\(i_{corr}\): the corrosion current density value without an inhibitor.

In the frequency range of 100 kHz the EIS approach was used with 10 points per decade. To plot and analyze Nyquist curves, a suitable comparable circuit was used. The inhibitory efficiency was calculated using Equation (5) (15–20):

\[
\text{I.E.\%} = \frac{(R_p' - R_p)}{R_p'} \times 100
\] (6)

\(R_p\): the polarization resistance of the steel electrode without an inhibitor.

\(R_p'\): the polarization resistance of the steel electrode with an inhibitor.

2.6. Anti-Bacterial corrosion measurement
(Sulfate Reducing Bacteria Test)

Sulfate-reducing bacteria (SRB) are easily capable of producing hydrogen sulfide (H₂S). The fatigue damage brought on by corrosion is increased by H₂S liberation. SRB (SRB-BART™ – DBI) vials were chosen because of their short testing time (maximum of 11 days) and high approximate population results. The test is finished when the vial turns black, at which point the SRB population may be identified. The findings can be obtained in a maximum of eleven days, which is the test time. The test is finished when the first black sign appears on the test vial, and each day corresponds to
3. Results and discussion

3.1. Synthesis of zinc sulfide nanoparticles (ZnS − nano)

Zinc sulfide nanoparticles (ZnS) were prepared from the aqueous solution of zinc chloride and sodium sulfide with PVA as a sensitizer by the chemical precipitation method. The net ionic reaction is represented in Equation (5):

\[ \text{Zn}^{2+} + \text{S}^{2-} \xrightarrow{\text{PVA}} \text{ZnS}_{(s)} \]  (7)

PVA as a sensitizer helps the formation of zinc sulfide in the nanoscale particle in the formed precipitate as methods mentioned elsewhere (1−3). In the present work, the same experimental conditions mentioned in the references (1) were applied to ensure the formation of zinc sulfide particles in the nanoscale to be more effective as corrosion inhibitors for steel in a sulfuric acid corrosive environment. As mentioned in the introduction part in general, the unique characteristic of nanolattices is reported from the previous studies (1−10).

3.2. Evaluation of zinc sulfide nanomaterials as a corrosion inhibitor

In the present part the prepared zinc sulfide nanoparticles were evaluated as a corrosion inhibitor for carbon steel in a 1.0 M sulfuric acid corrosive environment using a chemical technique (weight loss method). Different concentrations of the prepared zinc sulfide nanoparticles were used such as 25, 50, 75, and 100 ppm. The data obtained are listed in Table 2. It was found that the zinc sulfide nanoparticles act as good inhibitors and the inhibition efficiency was increased with increasing concentrations of zinc sulfide nanoparticles. The value of the corrosion rate is decreased with the addition of zinc sulfide nanoparticles and it is affected also by concentrations. The inhibition due to the adsorption and adhesion of zinc sulfide nanoparticles on the steel surface affects both the anodic and cathodic active sites (14−19). Figure 1 shows the relation between the weight loss of carbon steel and time with and without different concentrations of the used zinc sulfide nanoparticles. From the figure, it is clear that the addition of zinc sulfide controlled the weight loss of the steel in an acidic environment, and the weight loss of steel was increased with time of immersion in an acidic medium but decreased with increasing the concentrations of zinc sulfide.

3.3. Evaluation of PVA and EG as a corrosion inhibitor

The data in Table 2 also show the corrosion rate, surface coverage \( \theta \), and corrosion inhibition efficiency % I.E. for both polyvinyl alcohol (PVA) and ethylene glycol (EG) which evaluated as inhibitors for carbon steel alloy with a 1.0 M \( \text{H}_2\text{SO}_4 \) corrosive solution. Table 2 shows that the inhibition efficiency increases by increasing inhibitor concentrations and inhibition of ethylene glycol more than that of polyvinyl alcohol. The inhibition efficiency as compared to the inhibition of zinc sulfide nanoparticles is less than by more than 10% for all used concentrations. The same concentrations were taken which are 25, 50, 75, and 100 ppm to make a comparison between the three individual inhibitors. The order of inhibition is ZnS, Nano > EG > PVA, where the maximum inhibition efficiency for corrosion of steel was 90, 81, 78 using 100 ppm from the three inhibitors, respectively.

3.4. Effect of temperature on the % I.E. of the studied individual inhibitors

To understand the mechanism of corrosion and inhibition for the three used individual inhibitors the inhibition efficiency was calculated at different temperatures. A temperature range of 303 K–333 K was taken for investigation for the three samples, ZnS, Nano, EG, and PVA. The highest concentration used from the three used inhibitors materials, which shows the higher inhibition efficiency in all cases is 100 ppm. The relation between temperature and corrosion inhibition efficiency is shown in Figure 2.
inhibition efficiency increased by increasing temperature. This may be attributed to the chemical bond formed between inhibitor molecules and the steel surface; this reveals that the adsorption is chemical in nature.

### 3.5. Adsorption studies

The process of adsorption is affected mainly by the charge, metal surface nature, electronic characteristic of the metal surface, the temperature of the reaction, the presence of the electrorepelling or electro-donating groups in the derivatives, the electrochemical potential at the solution interface, solvent adsorption, and other ionic species. Weight loss data were used to find out the values of surface coverage ($\theta$) at different inhibitor concentrations to explain the best-fit isotherm for the adsorption process. The results are best fitted by the Langmuir adsorption isotherm according to the following equation (14–19):

$$\frac{C_i}{\theta} = \frac{1}{K_{ads}} + C_i$$  (8)

where $K_{ads}$ and $C_i$ are the equilibrium constants of the adsorption process and the drug concentration, respectively (14–19).

Plotting $C_i/\theta$ versus $C_i$ gave a straight line, as shown in Figure 3. The straight line with approximately a unit slope value has an intercept of $1/K$. The standard free energy of adsorption $\Delta G^\circ_{ads}$ is calculated using the equation (14–19):

$$K_{ads} = \frac{1}{55.5} \exp \left( \frac{-\Delta G}{RT} \right)$$  (9)

where $K_{ads}$ is the adsorption equilibrium constant, 55.5 is the dose of water in the bulk of solution in mole/liter, $T$ is the absolute temperature, and $R$ is the gas constant.
The calculated values of $\Delta G_{\text{ads}}$ are $-38.7$ kJ/mol, $-37.6$, and $-36.4$ for the three used inhibitors ($\text{ZnS}$, $\text{Nano}$, $\text{EG}$, and $\text{PVA}$), respectively. The negative value of $\Delta G^\circ_{\text{ads}}$ indicates that the adsorption process of drug molecules on the metal surface is spontaneous (14–20). On the other hand, all the obtained values are nearly equal to the threshold value of $-40$ kJ/mol required for chemical adsorption, which indicates that the mechanism of adsorption is chemical adsorption (14–20). The studied inhibitor compounds inhibit the corrosion process by adsorbing their constituent molecules at the metal/solution interface. In addition, it is believed that the formation of solid complex molecules with the metal atom has received considerable attention (14–20).

3.6. Studies of the corrosion inhibition efficiency of the mixed inhibitors system

Zinc sulfide nanoparticles ($\text{ZnS-Nano}$) mixed with polyvinyl alcohol and ethylene glycol were used as a mixed inhibitor system. The effect of adding 100 ppm from both $\text{PVA}$ and $\text{EG}$ to zinc sulfide nanoparticles was studied at 303 K. Two different mixtures were formulated by mixing zinc sulfide nanoparticles with $\text{PVA}$ and $\text{EG}$ and evaluated as corrosion inhibitors mixture for carbon steel in a 10 M $\text{H}_2\text{SO}_4$ corrosive environment. The corrosion inhibition efficiency of zinc sulfide nanoparticles ($\text{ZnS-Nano}$) with $\text{PVA}$ and $\text{EG}$ as additives are listed in Table 3. This shows that the inhibition efficiency in the case of mixture 2 ($\text{ZnS-Nano – EG}$) is more than the inhibition efficiency in the case of mixture 1 ($\text{ZnS-Nano – PVA}$). Comparing the corrosion inhibition efficiency of the individual inhibitors Table 2 with the inhibition efficiency of the mixed inhibitor system Table 3 it was found that the inhibition increased by about 10% in the case of the mixed inhibitor system. This difference means that the inhibitors system acts as a promoter of the inhibition efficiency, the order of the corrosion inhibition efficiency for all studied materials s as follows: ($\text{ZnS-Nano – EG}$) > ($\text{ZnS-Nano – PVA}$) > ($\text{ZnS-Nano}$) > ($\text{EG}$) > ($\text{PVA}$). Figure 4 shows the inhibition efficiency of the five studied materials, and the inhibition efficiency increased by increasing inhibitor concentrations. For all concentrations the inhibition efficiency

![Langmuir adsorption isotherm model for the three-used inhibitors ZnS, Nano, EG, and PVA, on the carbon steel in a 1.0 M H$_2$SO$_4$ solution at 303 K of, weight loss data.](image)

Table 3. Effect of concentration of the mixed inhibitor system, ($\text{ZnS-Nano – EG}$), ($\text{ZnS-Nano – PVA}$), on the inhibition efficiency of steel corrosion in 1.0 M $\text{H}_2\text{SO}_4$, at 303 K, WL data.

| Mixed inhibitor system | Mixture No. | ZnS-Nano concentration ppm | (PVA / EG) concentration ppm | The total concentration of mixture ppm | Inhibition efficiency % I.E. |
|-----------------------|------------|-----------------------------|-----------------------------|--------------------------------------|---------------------------|
| Blank Free Free Free Free Free | Blank Free Free Free Free Free | Blank Free Free Free Free Free | Blank Free Free Free Free Free | Blank Free Free Free Free Free | Blank Free Free Free Free Free |
| (Zinc sulfide nanoparticles – PVA) | Mixture 1 | 12.5 | 12.5 | 25 | 90 |
| (ZnS-Nano – PVA) | | 25 | 25 | 50 | 92.5 |
| | | 37.5 | 37.5 | 75 | 94.5 |
| | | 50 | 50 | 100 | 96 |
| (Zinc sulfide nanoparticles – EG) | Mixture 2 | 12.5 | 12.5 | 25 | 93 |
| (ZnS-Nano – EG) | | 25 | 25 | 50 | 94 |
| | | 37.5 | 37.5 | 75 | 97 |
| | | 50 | 50 | 100 | 98 |
for mixed inhibitors systems is more than the inhibition efficiency for individual inhibitors. This summarized the results recorded in both Tables 2 and 3.

3.7. Gasometrical measurement hydrogen evolution method (analytical studies)

Analytical techniques were used to compare the inhibition effect of both individual materials and mixed nanomaterial systems. Gasometrical or hydrogen evolution technique was based on the measurements of the volume of the evolved hydrogen during the corrosion reaction at different time intervals. When carbon steel or any active metals placed in the acidic environment upon the electrochemical reactivity series more active metal like iron replace hydrogen of the acid and the hydrogen was evolved in the form of hydrogen gas. The evolved hydrogen was measured using a gasometric system and used for the calculation of corrosion inhibition efficiency % I.E. in the present study the gasometrical technique was used for evaluation and comparison of the five prepared nanomaterials’ polyol system which was used as an inhibitor for steel in the 1.0 M H₂SO₄ acidic environment.

The volume of hydrogen evolved during the corrosion reaction of iron acidic 1.0 M H₂SO₄ medium with and without four different concentrations of nanomaterials as an inhibitor, 25, 50, 75, and 100 ppm were measured with time at room temperature (30°C). The inhibition efficiency was calculated using the following equation (34–37):

\[
\% I.E. = \left[1 - \frac{V_{inh}}{V_{free}}\right] \times 100
\]

where \( V_{inh} \) is the volume of hydrogen gas evolved for the inhibited solution and \( V_{free} \) for the uninhibited solution. The values of evolved hydrogen volumes and inhibition efficiencies at different concentrations of the used nanomaterials inhibitor are shown in Table 4. The inhibition efficiency increase with increasing the inhibitor concentration. This indicates that the applied inhibitor materials act as a good inhibitor for carbon steel in the 1.0 M H₂SO₄ acidic environment (34–37). Table 4 and Figure 5 show that the inhibition efficiency increase by about 15% in the case of the mixed inhibitor system, the mixed inhibitor system acts as a promoter for the corrosion inhibition efficiency, and the order of the corrosion inhibition efficiency for the five studied inhibitors materials is as follows: \((ZnS-Nano – EG)\) >

### Table 4. Gasometrical comparison of the mixed Nano-system and individual inhibitor materials, corrosion inhibition efficiencies of steel in 1.0 M H₂SO₄, the effect of different concentrations of zinc sulfide nanomaterials (ZnS-Nano) at 303 K.

| Types of inhibitor materials | Inhibitor name | Sample     | Corrosion inhibition efficiency % I.E % (Equation 10) |
|-----------------------------|----------------|------------|------------------------------------------------------|
| Free                        | Blank          | Free       | Concentrations ppm                                    |
| Mixed inhibitor systems     | (Zinc sulfide nanoparticles – EG) | (ZnS-Nano – EG) | 25 | 92 | 94 | 96 | 97 |
|                             | (Zinc sulfide nanoparticles – PVA) | (ZnS-Nano – PVA) | 50 | 91 | 92 | 94 | 95 |
| Individual inhibitor material | (Zinc sulfide nanoparticles) | (ZnS-Nano) | 75 | 82 | 85 | 78 | 89 |
|                             | (Ethylene glycol) | EG        | 100 | 74 | 76 | 79 | 80 |
|                             | Polyvinyl alcohol | PVA     |                                                        |

The volume of hydrogen evolved during the corrosion reaction of iron acidic 1.0 M H₂SO₄ medium with and without four different concentrations of nanomaterials as an inhibitor, 25, 50, 75, and 100 ppm were measured with time at room temperature (30°C). The inhibition efficiency was calculated using the following equation (34–37):

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|                             | (Zinc sulfide nanoparticles – PVA) | (ZnS-Nano – PVA) | 50 | 91 | 92 | 94 | 95 |
| Individual inhibitor material | (Zinc sulfide nanoparticles) | (ZnS-Nano) | 75 | 82 | 85 | 78 | 89 |
|                             | (Ethylene glycol) | EG        | 100 | 74 | 76 | 79 | 80 |
|                             | Polyvinyl alcohol | PVA     |                                                        |

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The data in Table 4, calculated from the analytical gasometrical technique, agree well with those obtained from the chemical technique (weight loss method) with small acceptable experimental differences.

Table 5. The polarization parameters with and without various inhibitor mixture doses (ZnS-Nano – EG).

| Solution type | Inhibitor mixture (ZnS-Nano – EG) ppm | $i_{corr}$ mA cm$^{-2}$ | $-\xi_{corr}$ mV (SCE) | $\beta_a$ mVdec$^{-1}$ | $\beta_c$ mVdec$^{-1}$ | $\theta$ | % I.E. |
|---------------|--------------------------------------|----------------------|----------------------|-------------------|-------------------|--------|-------|
| Inhibitor mixture (ZnS-Nano – EG) | Free | 1.5 | 498 | 118 | 127 | – | – |
| | 50 | 0.11 | 573 | 158 | 172 | 0.926 | 92.6 |
| | 100 | 0.08 | 582 | 169 | 184 | 0.947 | 94.7 |
| | 150 | 0.06 | 594 | 172 | 193 | 0.96 | 96.0 |
| | 200 | 0.05 | 602 | 176 | 199 | 0.967 | 96.7 |

Figure 5. The gasometrical data for the relation between concentration and inhibition efficiency for both individual and mixed inhibitor systems.

Figure 6. Steel polarization curve measured in 1.0 M sulfuric acid with and without various concentrations of mixed inhibitor systems (ZnS-Nano – EG).
3.8. Potentiodynamic polarization study  
(electrochemical studies)

Table 5 lists Tafel parameters such as corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slope ($\beta_c$), and inhibition efficiency (I.E.%). Figure 6 depicts typical potentiodynamic polarization curves for steel in 1.0 M H$_2$SO$_4$ with and without various concentrations of the mixed inhibitor system (ZnS-Nano – EG). As seen, the addition of the inhibitor mixture (ZnS-Nano – EG) results in a decrease in current, owing to the steel being protected from corrosion. With and without an inhibitor, the cathodic branch has distinct Tafel lines, demonstrating that activation regulates the hydrogen evolution reaction. The addition of the inhibitor combination to the corrosive media reduced the cathodic Tafel slope ($\beta_c$). Furthermore, a decrease in hydrogen evolution that does not affect the reaction process can account for the decrease in cathodic surface area. When the $E_{corr}$ shift exceeds 85 mV, which corresponds to the uninhibited solution, it is used to determine whether an inhibitor is cathodic or anodic. When the displacement is less than 85 mV, the inhibitor is classified as a mixed-type inhibitor (15–20). In the current study, the inhibitor mixture (ZnS-Nano – EG) acts as a mixed-type inhibitor.

3.9. Electrochemical impedance spectroscopy  
(electrochemical studies)

The Nyquist diagram for the steel solution in 1.0 M H$_2$SO$_4$ with and without various inhibitor combination concentrations is shown in Figure 7 (ZnS-Nano – EG). The characteristics related to the impedance of the schematic, such as charge transfer resistance $R_{ct}$, double layer capacitance $C_{dl}$, and inhibitory efficiency, are provided in Table 6 after a thorough simulation by the EC-Lab V10.02 program. A charge transfer process governs the corrosion reaction primarily. Figure 7 shows that all fitted Nyquist plots show a single capacitive loop and that the size of these plots increases with an increasing inhibitor concentration (15–20). Table 6 shows that the $R_p$ values increased as the inhibitor concentration increased and that the inhibition efficiency reached 97% at 100 ppm. In contrast, the $C_{dl}$ and $Q$ values decreased, indicating adsorption on the steel surface.

3.10. Kinetics and thermodynamic parameters

For the determination of the kinetic parameters of the corrosion process, and to elucidate the mechanism of inhibition, weight loss measurements were performed at different temperatures: 303, 313, 323, and 333 K. for the inhibitor mixture 2 (ZnS-Nano – EG) as the best inhibitor of higher inhibition efficiency than another used inhibitor in the present study. The

| Solution type | Inhibitor mixture (ZnS-Nano – EG) ppm | $R_1$ (Ohm/ cm$^2$) | $R_\infty$ (Ohm/ cm$^2$) | $C_{dl}$ µF cm$^{-2}$ | $\Theta$ | % I.E. |
|---------------|--------------------------------------|---------------------|----------------------|-------------------|--------|--------|
| Blank solution | Free | 1.84 | 19.8 | 1.73 | – | – |
| Inhibitor mixture | 50 | 11.7 | 289 | 11.7 | 0.903 | 93.1 |
| | 100 | 12.4 | 354 | 12.4 | 0.931 | 94.4 |
| | 150 | 16.9 | 498 | 13.9 | 0.944 | 96.1 |
| | 200 | 18.3 | 613 | 18.5 | 0.968 | 96.8 |

Figure 7. Nyquist diagram for steel in 1.0 M sulfuric acid with and without different concentrations of the mixed inhibitor system (ZnS-Nano – EG).
corrosion inhibition efficiency of inhibitor mixture 2 was found to increase by increasing temperature proving that the protective film formed from this mixture on the steel surface is more bonded and more stable at higher temperatures (15). The Arrhenius equation and the transition state equation (15–21) can be used to express the relationship between corrosion rate and temperature:

$$\ln R_{corr} = \exp \left( -\frac{E_a}{RT} \right) + A$$  \hspace{1cm} (11)

where $E_a$ is the apparent activation energy, $R$ is the universal gas constant, $A$ is the Arrhenius pre-exponential factor, and $T$ is the absolute temperature.

Figure 8 shows an Arrhenius curve for carbon steel submerged in 1.0 M sulfuric acid with and without different concentrations of the mixture 2 inhibitor ($ZnS-Nano – EG$). The plots obtained are straight lines, with the slope of each straight line corresponding to the apparent activation energy, as given in Table 7. The higher value of $E_a$ for carbon steel with the inhibitor mixture ($ZnS-Nano – EG$) compared to that without the

| Inhibitor                  | Inhibitor concentrations (ppm) | $E_a$ (kJmol$^{-1}$) | $\Delta H_a$ (kJmol$^{-1}$) | $-\Delta S_a$ (Jmol$^{-1}$) |
|----------------------------|--------------------------------|----------------------|-----------------------------|-----------------------------|
| Blank Free acid (1.0 M H$_2$SO$_4$) | 56.5                           | 48                   | 158                         |
| Mixture 2 inhibitor (ZnS-Nano – EG) | 25                             | 63.6                 | 56                          | 149                         |
|                            | 50                             | 67.5                 | 58                          | 141                         |
|                            | 75                             | 69.7                 | 62                          | 137                         |
|                            | 100                            | 73.2                 | 69                          | 129                         |
|                            | 500                            | 78.6                 | 74                          | 121                         |

Table 7. Values of activation parameters for carbon steel in 1.0 M H$_2$SO$_4$ with and without different concentrations of the expired drug inhibitor.

Figure 8. Arrhenius plot for carbon steel in an 1.0 M H$_2$SO$_4$ solution with and without varying concentrations of the inhibitor mixture 2 ($ZnS-Nano – EG$).

Figure 9. Transition state plot for carbon steel in 1.0 M H$_2$SO$_4$ with various inhibitor mixture 2 ($ZnS-Nano – EG$) doses.
inhibitor mixture (ZnS-Nano – EG) could be attributed to its chemical adsorption in the current investigation.

The inhibition efficiency increases with an increase in temperature, leading to the conclusion that the protective film of these compounds formed on the carbon steel surface is stable at higher temperatures; this indicates that the inhibitor system (ZnS-Nano – EG) produces chemical adsorption (15).

The higher value of activation energy (Ea) with an inhibitor is higher than without it, which is attributed to its chemical adsorption (15, 16).

In the present study, the higher value of Ea for carbon steel, with the inhibitor system, compared to that without it, is attributed to its chemical adsorption (15).

An alternative form of the Arrhenius equation is the transition state equation (45–51):

$$CR = \left( \frac{RT}{Nh} \right) \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( -\frac{\Delta H_a}{RT} \right)$$

(12)

where h is Plank’s constant, N is Avogadro’s number, $\Delta S_a$ is the entropy of activation, and $\Delta H_a$ is the enthalpy of activation. A plot of log (CR/T) vs. 1/T, as shown in Figure 9 gave a straight line, with a slope of $(-\Delta H_a/2.303R)$ and an intercept of $[\log(R/Nh) + (\Delta S_a/R)]$, from which the values of $\Delta H_a$ and $\Delta S_a$ were calculated and listed in Table 7.

The endothermic nature of the metal dissolving process is reflected by the positive values of $\Delta H_a$ for corrosion of carbon steel with and without the inhibitor. The decrease in carbon steel corrosion rate is primarily regulated by kinetic parameters of activation, as seen by the increase in $\Delta H_a$ with increasing inhibitor system concentrations (15–21). The entropy of activation values for inhibited solutions is less negative than for uninhibited solutions. This shows that as the reactants progressed to the active complex, the unpredictability increased (40–51). This suggests that an increase in randomness occurred while moving from reactants to the activated complex (15).

3.11. Corrosion inhibition mechanism

The mechanism of corrosion inhibition in an acidic solution is the adsorption of inhibitor onto the metal surface. In acidic conditions, inhibitor adsorption at the metal/solution interface is the initial stage of the inhibitory mechanism. Four different types of adsorption may take place during inhibition involving organic molecules at the metal/solution contact (15–21):

1. The electrostatic attraction of charged metals and molecules.
2. The metal’s interaction with the molecules’ unshared electron pairs.
3. Pi-electrons’ interactions with metal, and
4. A synthesis of the three options above.

The number of adsorption sites and their charge density, molecule size, the heat of hydrogenation, the mechanism of contact with the metal surface, and the creation of metallic complexes are some of the variables that determine an inhibitor’s ability to inhibit (14–21). Physical adsorption requires the presence of a metal with a vacant low-energy electron orbital, an inhibitor with molecules that are very loosely coupled to electrons or a heteroatom with lone pair electrons, and charged species in the bulk of the solution. However, in an acidic media, the described chemical can be protonated. They consequently transform into cations and coexist with the equivalent molecular form:

$$[\text{INHIBITOR}] + x^+ H^+ [\text{INHIBITOR}]^{x+}$$

(13)

where $H^+$ stands for the hydrogen proton from the acidic, corrosive environment, and [INHIBITOR] for the tramadol molecule. The protonated $[\text{INHIBITOR}]^{x+}$ could be linked to the carbon steel surface by the electrostatic interaction between $SO_4^{2-}$ and protonated $[\text{INHIBITOR}]^{x+}$ (15–21) since the steel surface has a positive charge in the H$_2$SO$_4$ medium. This might be further explained by the idea that when $SO_4^{2-}$ is present, negatively charged $SO_4^{2-}$ binds to positively charged surfaces, causing protonated INHIBITOR to adsorb to the metal surface. Chemical interaction exists in addition to electrical interaction. Chemical contact was brought about by non-bonding oxygen, nitrogen, and benzene ring electrons (15–21). In the present work, the suggested mechanism for the inhibition process is due to the adsorption and adhesion of the inhibitor molecules on the steel surface with the formation of the complex between the metallic surface and inhibitor molecules. This suggestion was proved by obeying the adsorption process to the Langmuir adsorption isotherm model which suggests the monolayer adsorption of the inhibitor molecules on the metallic surface. In addition, the positive values of enthalpy of the adsorption process are shown. The observed increment of the inhibition efficiency with the rising temperature is because of the absorbed energy needed for the formation of the chemical bond (chemisorption mechanism) between the metallic surface and adsorbed inhibitor nanoparticles. All the mentioned points prove the complex formation between steel and inhibitor molecules.

3.12. Anti-Bacterial Activity (SRB biological resistivity)

The sulfate-reducing bacteria (SRB) is a kind of pathogenic bacteria that can grow in water tanks and petroleum tanks causing the reduction of sulfate ions into hydrogen sulfide gas (H2S) which is dangerous [70].
The production of corrosive hydrogen sulfide (H2S) causes severe problems for tanks and pipelines. Heterocyclic compounds containing sulfur, oxygen, and nitrogen are efficient compounds against sulfate-reducing bacteria. In the present work, the prepared heterocyclic mixture from polyol and zinc sulfide (ZnS) nanoparticles were tested as anti-sulfate-reducing bacteria. Individual inhibitor compounds were also tested against the same kind of bacteria the antibacterial efficiency of both mixture inhibitors and individual inhibitors were compared. The water sample that included the sulfate-reducing bacteria (SRB) came from an Egyptian gas field. The water analysis, SRB population, and monitoring techniques used with SRB (BART) vials have all been covered previously (capacity of 15 ml). In ultra-pure water, a tiny concentration of each inhibitor was created (1 ppm mol-1), and only 1 ml of this solution was introduced to the SRB test vial along with the water sample (15 ml) containing the SRB source [70]. As a blank, a different vial was created with only 15 ml of SRB water supply and no other inhibitors. All vials were cultured in an incubator at 35°C. The maximum SRB test duration is just 11 days, although it may be shorter if it is realized that the first black sign has shown on the test vials. The test for the blank was finished in just 4 days with an aggressive population value of roughly 27000 (cfu ml-1). For PVA and EG, the test was finished after 7 days, yielding a population value of 325 (cfu ml-1), with the severity of SRB being changed from aggressive to moderate in the case of the blank sample. As shown in Table 8, the observed results for all inhibitor mixture systems (ZnS-Nano - EG), (ZnS-Nano - PVA), and (ZnS-Nano) were achieved after 8 days with good efficiency against SRB bacteria, giving 75 cfu ml-1 population (not aggressive). The findings unmistakably offer a useful signal of a decrease in SRB reactivity. Additionally, the corrosion brought on by the presence of sulfate-reducing bacteria (SRB) can be reduced thanks to the biological activity of the inhibitors (ZnS-Nano - EG), (ZnS-Nano - PVA), and (ZnS-Nano). This means that, the antibacterial efficiency against the sulfate-reducing bacteria (SRB) for the heterocyclic polyol compounds is higher in the case of an inhibitor mixture than in the case of individual inhibitors.

4. Conclusions

From the experimental data and calculation results, the following important points can be concluded:

- The addition of PVA during the preparation of zinc sulfide nanoparticles improves the size of nanoparticles and their efficiency toward corrosion inhibition of steel.
- All the studied materials act as good corrosion inhibitors for steel in a 1.0 M H2SO4 acidic environment.
- The inhibition efficiency of the studied inhibitors was found to increase by nanoparticle concentration, Polyol concentrations, and reaction temperature.
- The inhibition is due to the adsorption and adhesion of zinc sulfide nanomaterial molecules on the steel surface, and the adsorption obeys the Langmuir adsorption isotherm model, the suggested inhibition mechanism is chemical adsorption.
- The inhibition efficiency of the mixed – nanomaterials-drug system is higher by 15% than the inhibition efficiency of the individual nanomaterials or polyol.
- The order of the inhibition efficiency of the five studied nanomaterials drugs is (ZnS-Nano – EG) > (ZnS-Nano – PVA) > (ZnS-Nano) > (EG) > (PVA).
- The antibacterial efficiency against the sulfate-reducing bacteria (SRB) for the heterocyclic polyol compounds is higher in the case of an inhibitor mixture than in the case of individual inhibitors.

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