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Protection of Carbon Steel from Corrosion by Sulfur Nanoparticles Mixed with Meloxicam Drug

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Abstract

Inhibition performance of sulfur nanoparticles mixed with meloxicam drugs as corrosion inhibitor by potentiostat technique with metal in 3.5% NaCl Sodium chloride solution based on different temperature. The sulfur nanoparticles were prepared by using Alhagi extra plant with thiosulphate sodium. The surface morphology was studied using the Atomic Force Microscope (AFM) with a size of 100.32 nm. The inhibition efficiency increased with increasing temperature, around 81.94% in 50 ºC. With the absence of an inhibitor, the polarization resistance decreased with increasing temperature, Although the resistance to polarization increased in the presence of the inhibitor. Compared to the absence of the inhibitor, the activation energy (Ea) and activation enthalpy Δ H * values for carbon steel increased in the presence of the inhibitor. The values of ΔG were positive, this indicated the non-spontaneousness and increase in the presence of inhibitor.

Key word: Atomic Force microscope (AFM); carbon steel; mixture of nanoparticles sulfur- meloxicam drug; three electrodes potentionstat; 3.5% NaCl Sodium chloride;

1.Introduction

Corrosion is the reaction of metals and element in environment such as oxygen, carbon dioxide, chlorine , etc. , for that, the metal deteriorates .The corrosion damages involves equipment of damage ,materials loss, efficiency is lower, also the corrosion effects on social life such as fire, toxic of products and pollution [1].The substantial difference of corrosion rate between cathode and anode ,the increase corrosion because the oxygen concentration difference for example tanks of steel water was filled in water [2]. The importance of nanomaterial is due to having properties and structure different than atoms , molecules with respect to their bulk materials and size of particles equal 100nm, there are different methods used to produce nanoparticles such as chemical, biological and physical [3]. Nanoparticles are developing quickly because they have new properties dependent on morphology, distribution and size [4].The adsorption of inhibitor is influenced by many factors such as the factor of steric, in donor site of electron density, structure of inhibitor ,the functional group for example –N=N,R-OH,-CHO and molecular weight of inhibitor [5].The plants are free from toxic chemicals, therefore plants provide synthesis of nanoparticles ,the cost of microorganisms is reduced by using extra plant. The science of material that has nano biotechnology is active research [6]. There are various applications for nonmetal sulfur nanoparticles and microparticles in industrial activities for example production of Sulfuric acid, industries pulp and paper, gun powder and plastics. It is also used in agriculture such as apple scab disease, vegetables and spot black disease [7]. The methods use inhibitor for protecting metal from corrosion. The corrosion rate of metal and alloys exposed to the corrosive environments is low in the presence of inhibitor [8].

2.Materials and methods

2.1.Materials

2.1.1.Chemicals

As mentioned in Table 1, carbon steel metal was used as a metallic material with a chemical composition.

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Table (1) Chemical composition for carbon steel metal.

Grade	C45
%C	0.42-0.50
%Si	<0.40
% Mn	0.50-0.80
%S	<0.045
% P	<0.045
%Ni	0.40
%Cr	<0.40
%Mo, Cr+Ni	<0.10
% Fe	97.31-97.69

2.2.Metal Preparation

The carbon steel metal were cut with thickness of 0.5mm and dimensions of 2.5cm diameter. The carbon steel metal were polished with emery paper in different grade (100,200,1000 and 2400) than cleaned by immersion with 5%HCl solution for 15min. then washed with acetone and finally rinsed with distilled water and kept in a desiccator for further use.

2.3 Preparation of Solution

Seawater preparation (3.5% NaCl): the solution was prepared by adding 35 grams of NaCl to one liter of distilled water.

2.4. Preparation of sulfur nanoparticle

Sulfur nanoparticle has been prepared in a micro emulsion technique. Sulfur nanoparticle was synthesized by the chemical reaction between extra of Alhagi plant with sodium thiosulfate pent hydrate. The extra Alhagi plant was prepared from mixing 10gram leave plant powder with (20%H_2O+80%Ethanol), the solution was heated for 1hr at 80ºC using magnetic stirrer, the solution was filtered using filter paper. After that, 10ml of filtrate was mixed with 50 ml of sodium thiosulfate pentahydrate, stirred for 10min. then 25ml of 20% citric acid was added with stirring for 30 min. The solution color changed from yellow to brown [9].

2.5.Electrochemical Measurement

The working electrode potential (carbon steel) is used to create polarization, varying the polarized potential of corrosion (Ecorr) from its equilibrium value, first in the negative and then in the positive direction, and recording the current response to the potential applied. The polarization provided the voltage / current density data pairs.

2.6.The Cell of Corrosion

The Pyrex corrosion cell with (1L) power is composed of two vessels, internal and external. To make the water temperature that flows through the external vessel constant at (20, 30, 40, and 50) 0C, chiller equipment was used. The corrosion cell and the three electrodes are shown in Figure (1), and reference electrodes are used to determine the working electrode potential according to the reference electrode potential. The reference electrode potential is well understood and specific, and two tubes are combined; the inner tube contains Ag, AgCl, KCl. The outer tube is filled with the solution being prepared, but it should be noted that the Ag / AgCl electrode converts to the calomel electrode in a potentiostat unit. The reference electrode is at the distance 2 mm from the working electrode. The auxiliary electrode consists of platinum metal of high purity; its length is (10 cm) and the working electrode is the target studied and tested whose potential is to be measured; this electrode is made from metallic wire of 20 cm length and linked to the mounted specimen. Sea water solution was used as corrosive media (3.5 percent sodium chloride) and the solutions were applied to the corrosion cell.

Figure (1) Corrosion Cell and Three Electrode

3.Results and Discussion

The surface morphology of protective sulfur nanoparticles plays a great role in enhancing the corrosion protection efficiency. More uniform grains may lead to more inhibition results, 2D and 3D views of AFM image for sulfur nanoparticles were estimated in addition to the statistical determination of the particles size distribution [10].

3.1.Surface Morphology of sulfur nanoparticle

Figure (2) shows the topographic structures in 2D and 3D views for sulfur nanoparticle. The result seems to be very smooth surfaces with grains equal to (100.32 nm) [11]. The particle size distribution is shown in Figure (3).

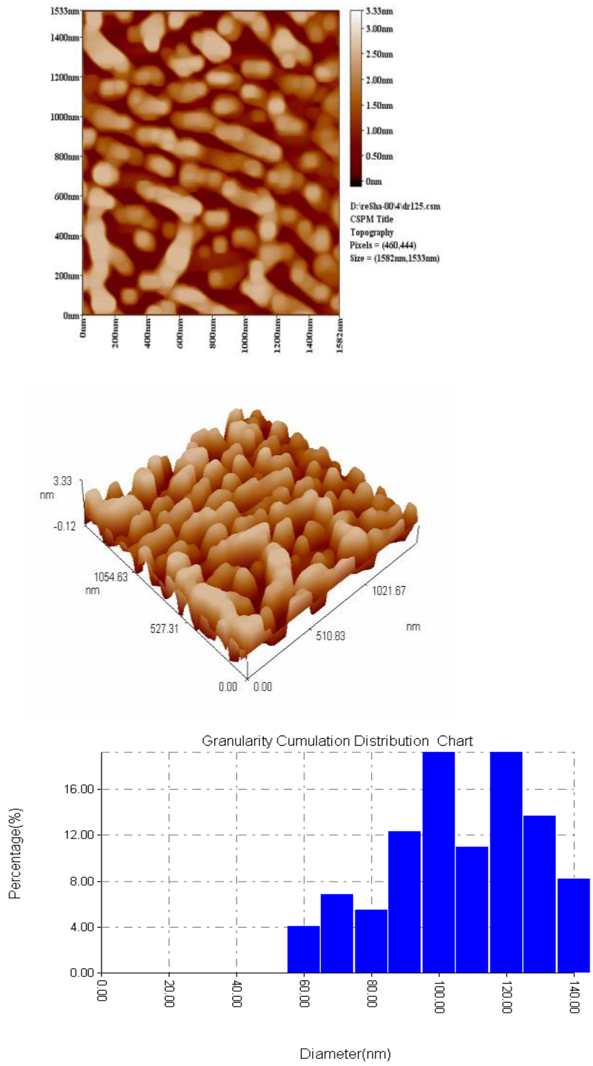

Figure (3) the reprint of AFM reports for statistical measuring particle size and their distributions of sulfur nanoparticles applied on carbon steel.

3.2. Corrosion Measurements Evaluation

Corrosion measurements were calculated by using Tafel plots produced from potentiostatic scan ±200 mv around the open circuit potential of the carbon steel specimenses with and without sulfur nanoparticles mixed with meloxicam drug in (3.5% NaCl) sodium chloric over a range of temperature (20-50)^{0}C.

3.3.Potentiostatic Polarization Measurement

Tafel plots offered the measurements of: corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), weight loss (W.L), penetrations rates (PR), and Protection efficiencies (PE) are shown in Table (2).

3.4.Corrosion Protectiveness of Carbon Steel Specimens

As predicted, as shown in Figure 4 and Table 2, the corrosion rates of the carbon steel sample in the absence of an inhibitor increased with an increasing electrolyte temperature of up to 50 ^{o}C.

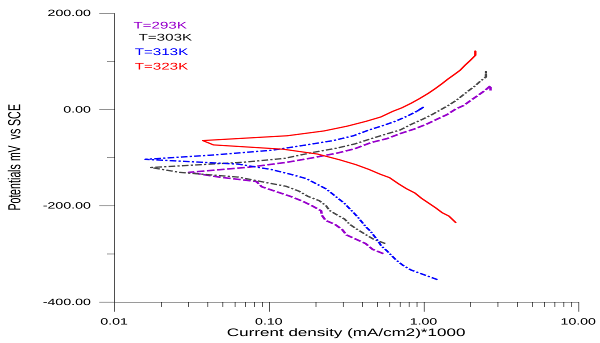

Figure (4) Tafel plots of carbon steel at various temperatures in (3.5 percent sodium chloride).

Table(2)Tafel parameters of the carbon steel at various temperatures in (3.5% sodium chloride)

T(K)	Icorr (μA/ cm^2)	-Ecorr (mV)	ba mV/Dec	-bc mV/ Dec	W.L (g/m^2.d)	P.L (mm/a)	Rp Ω.cm2
293	83.11	144	207.3	86.6	2.08E+001	9.65 E-001	319.13
303	106.40	128.6	219.5	108.3	2.66E+001	1.23E+000	295.95
313	137.80	108.6	253.4	126	3.44E+001	1.60E+000	265.17
323	282.07	71.6	212.2	183	7.05E+001	3.27E+000	151.261

The data listed in Table 3 will be used as a reference to evaluate the corrosion protection effectiveness of carbon steel by sulfur nanoparticles mixed with meloxicam drug. Table 3 shows that the (Icorr) for carbon steel sample with inhibitor sulfur nanoparticles mixed with meloxicam drug decreased as compared with carbon steel without inhibitor. (Icorr) for carbon steel is (83.11-282.07 **μA/ cm$^{2)}$** while (Icorr) for carbon steel with inhibitor is 25.62-50.93 **μA/ cm^2** due to the inhibitor molecular sulfur nanoparticles mixed with meloxicam drug adsorption on surface of carbon steel [12]. In the presence of an inhibitor, possible corrosion (Ecorr) has been transferred to more negative values. because the resistance of corrosion [13] Cathodic Tafel slope and Anodic Tafel slope values indicated that the inhibitor was affected by both carbon steel dissolution and evolution of hydrogen [14]. Inhibition efficiency (IE%) values were calculated from equation1:

$$\%IE = \frac{icorr * - icorr}{icorr *} X100 \ldots\ldots\ldots 1$$

Where icorr* corrosion current density of without inhibited. icorr corrosion current density of inhibited.
Effects of inhibition efficiency (percent %IE) values improved in the presence of an inhibitor with increasing temperature. because the desorption of the sulfur nanoparticles mixed with meloxicam drug on surface carbon steel [15]. The resistance of polarization (R_P) can be calculated from equation 2

$$Rp = \frac{bcba}{2.303\ (bc + ba)icorr} \ldots\ldots\ldots 2$$

Where (ba) anodic slope of Tafel, (bc) cathodic slope of Tafel,(icorr) corrosion current density and (Rp) resistance of polarization. Tables 2,3 show that the polarization resistance decreased with increasing temperature in with and without of inhibitor while the polarization resistance increased in the presence of inhibitor [16]. Figure 5 shows different Tafel plots and Table 3 shows all the measurements and calculations established from these curves.

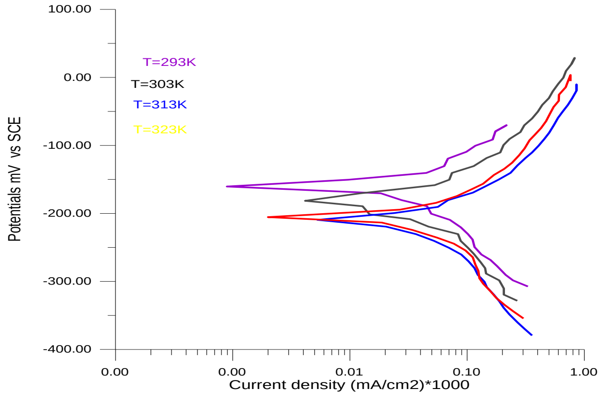

Figure (5) Tafel plots of carbon steel by sulfur nanoparticles mixed with meloxicam drug at various temperatures in (3.5% sodium chloride)

Table (3)Tafel parameters of the carbon steel by sulfur nanoparticles mixing with meloxicam drug at various temperatures in (3.5% sodium chloride)

T (K)	Icorr (μA/corr)	-Ecorr (mV)	ba mV/Dec	-bc mV/Dec	W.L (g/m^2.d)	P.L (mm/a)	IE%	θ	Rp Ω.cm2
293	25.62	164.5	107.6	95.7	6.40E+000	2.97 E001	69.17	0.6917	858.44
303	27.39	184.2	115.5	87.6	6.85 E+000	3.18E-001	74.25	0.7425	789.75
313	33.47	208.2	135.3	77	8.37E+000	3.88E-001	75.71	0.7571	636.63
323	50.93	203.9	193.1	112.2	1.27E+000	3.91E-001	81.94	0.81.94	665.03

3.5.Thermodynamic

Corrosion reaction thermodynamic parameters, (A) Arrhenius factor, activation energy Ea, activation entropy ΔS * and activation enthalpy ΔH * were determined using Arrhenius equation 3 and its alternative formulation called transition state equation 4. Activation energies were determined from the Arrhenius plots, representing the relationship between log (icorr) and (1 / T) in Figure 6 and 7. The log (icorr) vs1 / T plot gives the line slope (-Ea / 2.303 R) and the extrapolated line intercept gives log A [17].

$$Log\ Icorr = \frac{\log A - Ea}{2.303RT} \ldots\ldots\ldots.3$$

$$Log\ Icorr = log\frac{R}{Nh} + \frac{\Delta S*}{2.303R} - \frac{\Delta H*}{2.303RT} \ldots\ldots.4$$

If Icorr is the density of the corrosion current, Ea is the activation energy, R is the universal gas constant (8,314 J mol-1 K-1), T is the temperature, (A) Arrhenius factor, activation energy (Ea), activation entropy (Δ S *) and activation enthalpy (Δ H *), (h) the constant of the Plank (6,626176 x 10-34 Js), (N) the number of Avogadro (6,022 x 1023 mol-1) [18]. Figure (8 and 9) displays the log CR / T plot against 1 / T. Straight lines were obtained with a gradient of (Δ H * / 2.303 R) and an intercept of [(log (R / Nh) + (Δ S*/2.303 R)] from which the values of Δ H * and Δ S * were determined, respectively, while the free energy of activation Δ G * was calculated using the following equation. [19].

$$\Delta G *= \Delta H * - T\Delta S * \ldots\ldots..5$$

Table 4 shows that the activation energy of the carbon steel metal increases when the inhibitor is present and this indicates that the absorption of the retarder particles by the metal. The value of the activation energy of the carbon steel metal is 22.48 kJ / mol, the activation energy in the presence of the inhibitor is 131.1 kJ / mol, as well as the decrease in the corrosion current of the carbon metal Steel pioneered the inhibitor focus, Equation 3 shows that the corrosion current is affected by the activation energy and the , (A) Arrhenius factor [20]. When the inhibitor is present, it increases to 111.819 kJ / mol. This indicates that the presence of an inhibitor reduces the corrosion process and thus more energy is needed to break down the nanoparticles mixed with a drug and reacted with the mineral carbon steel. Positive energy values of enthalpy indicate that the process is endothermic [21]. The corrosion carbon steel in absences inhibitor and in presence inhibitor in 3.5 % NaCL solution, the positive values of ΔG that mean, these reaction are occurring unspontaneous.The values of ΔG are increased with increasing temperature presence inhibitor more than in absences inhibitor. [22].

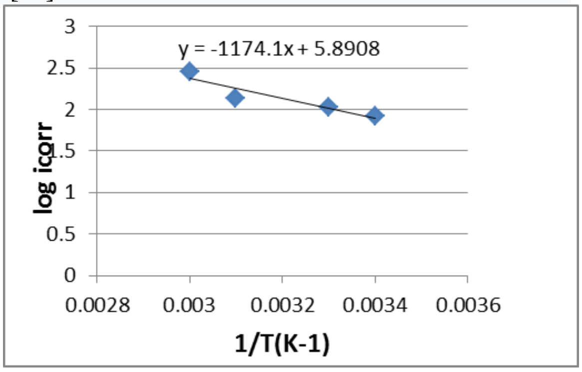

Figure (6) For carbon steel specimens, Arrhenius plots log icorr against 1 / T. at various temperatures in (3.5% sodium chloride)

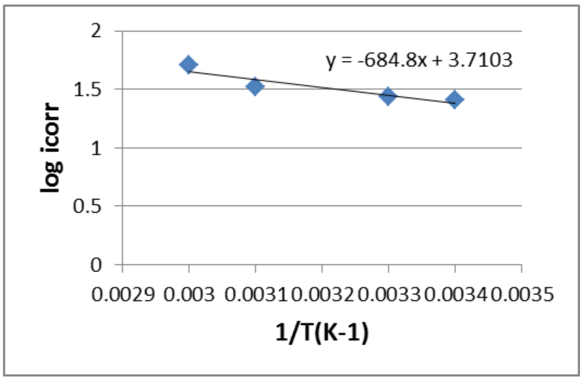

Figure (7) For carbon steel specimens, Arrhenius plots log icorr against 1 / T. by sulfur nanoparticles mixed with meloxicam drug at various temperatures in (3.5% sodium chloride)

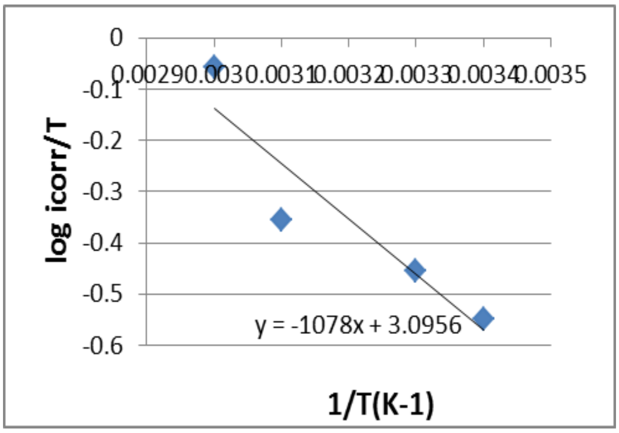

Figure (8) plots log icorr / T for carbon steel specimens against 1 / T at various temperatures in (3.5% sodium chloride)

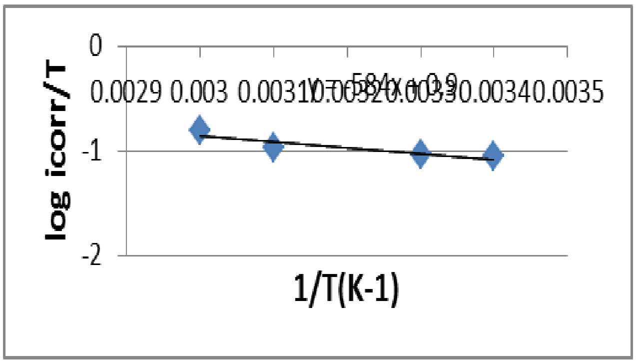

Figure (9) plots log icorr / T for carbon steel specimens against 1 / T by sulfur nanoparticles mixed with meloxicam drug at various temperatures in (3.5% sodium chloride).

Table (4) calculated thermodynamic parameters of carbon steel specimens and carbon steel by sulfur nanoparticles mixed with meloxicam drug at various temperatures in (3.5% sodium chloride)

carbon steel	T(K)	$\Delta G*10^3$/ KJ/mol	Ea/ KJ/mol	A Molecules. cm^{-2}.S	ΔH*/ KJ/mol	-ΔS*/ J/mol
	293	40.539	22.48	$3.67*10^{19}$	20.64	138.289
	303	41.922				
	313	43.305				
	323	44.687				
carbon steel by sulfur nanoparticles mixing with meloxicam.	293	52.945	131.1	$23.15*10^{19}$	111.819	180.32
	303	54.748				
	313	56.551				
	323	58.355				

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Thank you for Department of Chemistry /College of Science of Women /University of Baghdad, to help me to complet pepare the title of pepare is Protection of Carbon Steel from Corrosion by Sulfur Nanoparticles Mixed with Meloxicam Drug.

5.Conclusions

The sulfur nanoparticles were prepared by using Alhagi extra plant with thiosulphate sodium and mix with drug. The surface morphology of nanoparticle was studied using the Atomic Force Microscope (AFM) with a size of 100.32 nm. The inhibition was used protection Carbon Steel from corrosion in 3.5% NaCl Sodium chloride solution, the study corrosion in different temperature, the inhibition efficiency (%IE) was increased with increasing temperature, around 81.94% in 50 ºC. With the absence of an inhibitor, the polarization resistance decreased with increasing temperature, although the resistance to polarization increased in the presence of the inhibitor. therefore the sulfur nanoparticle mixed with meloxicam drugs were active inhibition for Carbon Steel in salt media .

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