Original Research Article

The Effect of H₂SO₄ Concentration on Corrosion of Kirkuk's Oil and Gas Pipelines with Studying Corrosion Reaction Rates Kinetically

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ARTICLE INFO

ABSTRACT

Acidic corrosions for oil and natural gas pipelines have been investigated by studying the effect of sulfuric acid (H_2SO_4) on carbon steel surface sample. Three different concentrations of sulfuric acid (0.1, 1, and 2 M) and two distinct kinds of carbon steel were used in this research. The results demonstrates that when the concentrations of acid medium (H_2SO_4 solutions) increased, the corrosion rates also increased due to the effect of high concentration of the acid. In addition, kinetic of corrosion rates were studied in which the corrosion rates followed the pseudo first order from the values of R^2 for the samples. Furthermore, polymer electrolyte liquid of polymethyl methacrylate (PMMA) has been used to decrease the acidity strength. The PMMA was indicated that the medium acidity decreased leading to supply further protection from corrosion. These results can be applied to successfully manage pipelines and improve the pipeline protection in acidic corrosion condition. Likewise, polymer electrolyte liquid PMMA oligomer should be considered as a novel form in polymer electrolyte field that might be employed in electrochemical devices for corrosion control purposes in acid media.

GRAPHICAL ABSTRACT

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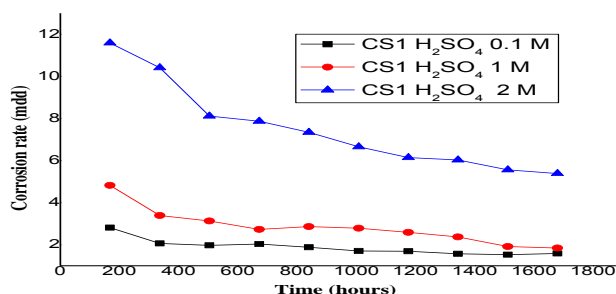
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Introduction

Corrosion is the destructive attack on a substance caused by interactions with its environment, and it is a serious natural concern associated with oil and gas production and transportation infrastructure [1, 2]. In oil refineries, contamination of oil products by corrosion products takes place as refineries age with time. Pipelines of refined and crude oil, that are rich in sulfur compounds, are also exposed to corrosion attacks [3]. In present era, corrosion is one of the most difficult challenges to solve in the business. Most industrial designs are impossible to be designed without taking into account the rust impact on the equipment's lifespan. Steel is one of the most common building materials used in the chemical and associated industries to handle acid, alkali, and salt solutions. Acid descaling, oil well acidizing, industrial acid cleaning, and acid pickling are just a few applications for acid solutions in industry field. HCl, H_2SO_4, and HNO_3 are the most often used acids [4, 5].

Corrosion is a major problem that affects most industries worldwide, causing devastating issues to the global economy. Corrosion is the deterioration of a material as a result of its interaction with its surroundings, and it can occur at any point or at any time during petroleum and natural gas processing. Although this definition applies to any material, it is mostly commonly associated with metallic alloys. Furthermore, corrosion processes affect not only the chemical properties of metal or metal alloys, but also cause changes in their physical properties and mechanical behaviors [6].

It was documented that corrosion rates of mild and high carbon steels in various acidic media increased with corrosion media concentration and exposure duration. In all acidic conditions, the corrosion rates of high carbon steel were greater than those of mild steel due to the carbon content of the former [7].

Combating corrosion in the oil and gas sector is crucial because the economic loss caused by corrosion in these industries is astronomical [8]. The use of corrosion inhibitors is one of the most effective and cost-effective strategies for combating corrosion in the oil and gas sector. In terms of corrosion and material composition, HCl and H2SO4 are the most challenging of the common acids to be managed. It is well-known that even at relatively dilute concentrations or in process solutions containing substantial amounts of sulphuric acid require to extraordinary dealing. The majority of metals and alloys are severely corroded by these acids [9].

The effect of temperature and acid concentrations has been investigated on the corrosion of low carbon steel in hydraulic acid medium using a nonlinear regression approach. It was found that the corrosion rate increased as the temperature and concentration of hydraulic acid increased [10].

The weight loss method has been applied to evaluate the corrosion resistance of uncoated medium carbon steel, nickel-coated medium carbon steel, and 18/8 stainless steel samples in a cassava fluid environment for thirty days. The results indicate a low corrosion rate (corrosion attack) on nickel-plated steel and a very high corrosion rate on the unplated steel [8].

This study is aimed to assess the effect of varying concentrations of H_2SO_4 solution as a corrosive media on the surface corrosion rates for carbon steel samples with two distinct metal contents in addition to the evaluation of polymethyl methacrylate role (PMM) for the steel surface protection in acidic media (H_2SO_4).

Materials and Methods

Sulfuric acid has been purchased from Posh-SA (95%), the acid diluted into three morality concentrations (0.1, 1, and 2M). Three pieces (equal dimensions) of sample carbon steels sample1 (CS1) and sample 2 (CS$_2$ were made by North Oil Company/Iraq oil pipelines with specific properties as shown in Table 1. These pieces were cut into the rectangular shapes and used to prepare uniform surfaces by grinding and smoothing to remove the surface roughness and unwanted sharp angles.

Table 1: The chemical composition by weight % of carbon steel samples

Elements / Samples	Fe Wt%	C Wt%	Mn Wt%	Ni Wt%	Co Wt%	Si Wt%	Cr Wt%
CS1	97.50	0.61	0.70	0.18	0.16	0.56	0.28
CS2	96.31	0.69	1.29	0.32	0.27	0.52	0.60

Synthesis of Liquid-Based PMMA Oligomer Electrolyte

5 mL of methyl methacrylate (MMA) monomer (purchased from ARCOS) with a molecular weight of 100.12 g/mol was mixed with 10% benzoyl peroxide (supplied by MERK) of the monomer mass. The test tubes were then immersed for a few minutes in a hot water bath to expedite the polymerization process. After that the mixture left at room temperature for 24 hours to complete the polymerization of PMMA. The tested tubes containing PMMA in liquid state were dipped into 1 mL of 0.5, 1, 2, 4, 6, 8, 10, and then H_2SO_4 acid (FLUKA) (9 M) for 24 hours was immediately used.

Samples weighting

The experimental work is used to calculate the weight loss measurements to determine the average of corrosion rates. A carbon steel specimen was immersed with a solution of H_2SO_4 (0.1, 1, and 2 M). The difference in weight between w_1 and w_2 has been calculated weekly after washing, grinding, drying, and weighting the samples using electronic balance. The surface area was measured using electronic Vernier to know the reduction.

Corrosion rate

The corrosion rate of each sample for a period of 11 weeks was calculated using the weight lost method, as identified in Equation (1):

$$corrosion\ rate\ (mdd) = \frac{(K*W)}{(A*T)} \qquad (1)$$

Where, K is a constant (2.4×10^6), A is the surface area in (cm^2), W is the difference in weight between w_1 and w_2 in (g), and T is the time in (hours). The results are listed in Table 2.

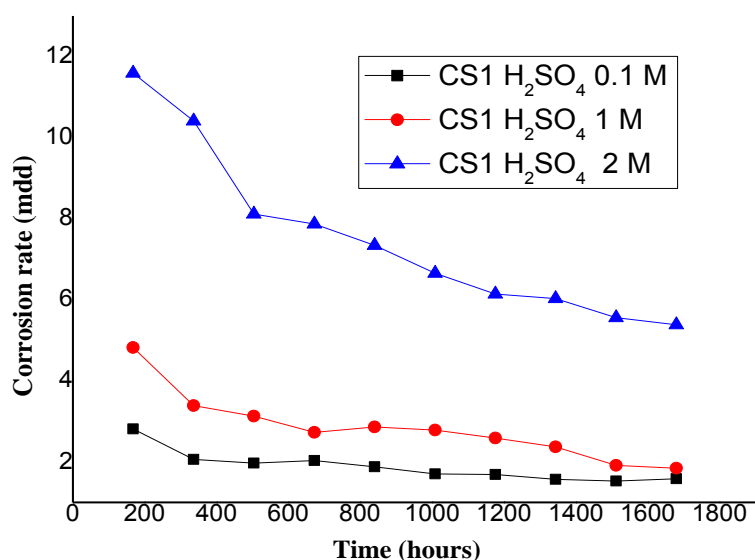**Results and Discussion**

Effect of acid concentration

All the results for corrosion rates on the carbon steel surfaces with different concentrations of sulfuric acid have been collected in Table 3.

Table 2: Weight loss measurements for CS1 and CS2 at different concentrations of H_2SO_4 acid

Weight (g)					
CS1			CS2		
H_2SO_4 0.1 M	H_2SO_4 1 M	H_2SO_4 2 M	H_2SO_4 0.1 M	H_2SO_4 1 M	H_2SO_4 2 M
170.10	169.66	168.78	108.10	105.99	106.86
170.03	169.53	168.44	108.06	105.86	106.64
169.93	169.36	168.03	107.99	105.72	106.42
169.82	169.18	167.48	107.92	105.59	106.22
169.68	168.96	166.91	107.86	105.47	106.03
169.50	168.72	166.22	107.80	105.37	105.86
169.30	168.42	165.45	107.75	105.26	105.69
169.09	168.08	164.64	107.69	105.18	105.53
168.85	167.72	164.07	107.64	105.10	105.39
168.60	167.35	163.13	107.60	105.02	105.28
168.33	167.02	162.05	107.56	104.98	105.18
168.03	166.67	161.03	107.54	104.94	105.06

Table 3: Corrosion rates (CR) for CS1 and CS2 samples in different concentrations of H_2SO_4 acid

Sample / Date	CS1 CR (mdd)			CS2 CR (mdd)		
	in H_2SO_4 0.1 M	in H_2SO_4 1 M	in H_2SO_4 2 M	in H_2SO_4 0.1 M	in H_2SO_4 1 M	in H_2SO_4 2 M
1/2/2021	2.81	4.82	11.59	1.97	3.95	6.23
8/2/2021	2.06	3.39	10.41	1.31	2.45	3.79
15/2/2021	1.97	3.13	8.11	0.84	1.71	2.71
22/2/2021	2.03	2.73	7.87	0.67	1.13	1.94
1/3/2021	1.88	2.86	7.34	0.48	1.04	1.62
8/3/2021	1.70	2.78	6.65	0.47	0.65	1.32
15/3/2021	1.69	2.59	6.14	0.35	0.57	1.02
22/3/2021	1.57	2.37	6.03	0.25	0.51	0.71
29/3/2021	1.53	1.91	5.56	0.22	0.25	0.58
5/4/2021	1.58	1.84	5.38	0.11	0.20	0.63

Figure 1: The acid concentration effect on the corrosion rates for CS1 samples

a) CS1 sample

The results indicated that the corrosion rates increase as H_2SO_4 solution concentrations increased, as displayed in Figure 1. This is due to the acid content leading to an increase in the amount of hydrogen ions (active species). In addition, sulphide and/or sulphate (SO_4^{2-}) ions are one of the most significant corrosion contributors [11].

b) CS2 samples

Figure 2 depicts the corrosion rates increase as H_2SO_4 solution concentrations increased. This is related to the effect of high concentration when acid concentration rises, the amount of hydrogen ions (active species) rises. In addition, sulphide and/or sulphate (SO_4^{-2}) ions are one of the most important corrosion contributors [11]. The effect of acid was clearly higher in CS1 samples than those in the CS2, as demonstrated in Figure 3. This is described to the percentage of chromium in CS2 samples is greater than the case of CS1, as presented in Table 1.
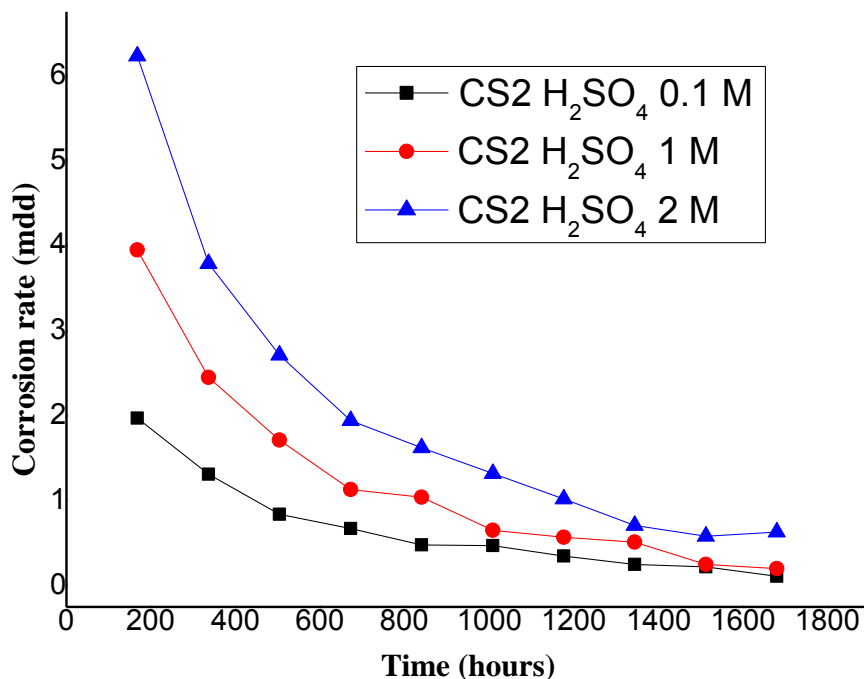
Figure 2: The effect of acid concentrations on the corrosion rates for CS2 samples
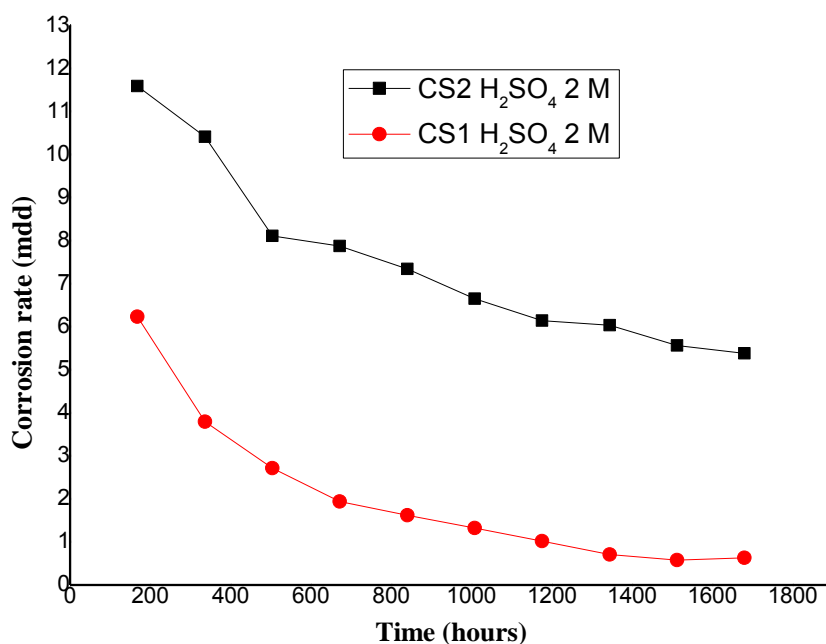

Figure 3: Comparison between the corrosion rates of CS1 and CS2 samples

Kinetic study

The kinetics study of the corrosion rate was investigated for two samples (CS1) and (CS2), where the time and data were fitted to a first-order rate model, as detailed in Equation (2):

$$ln\ (Wt\ /W0\ ) = -\ k\ t \qquad (2)$$

Where, k is the first-order rate constant, W_0 and W_t are the weights at time 0 and t, (min^{-1}) and t is the time. For the corrosion rate, R^2 was shown to be greatest for the first-order response compared to the second order. This means that the pseudo-first order kinetic is acceptable for the corrosion rate, as illustrated in Figures 4 and 5. The values of R^2 and k are shown in Tables 4 and 5 for the corrosion rate [12].
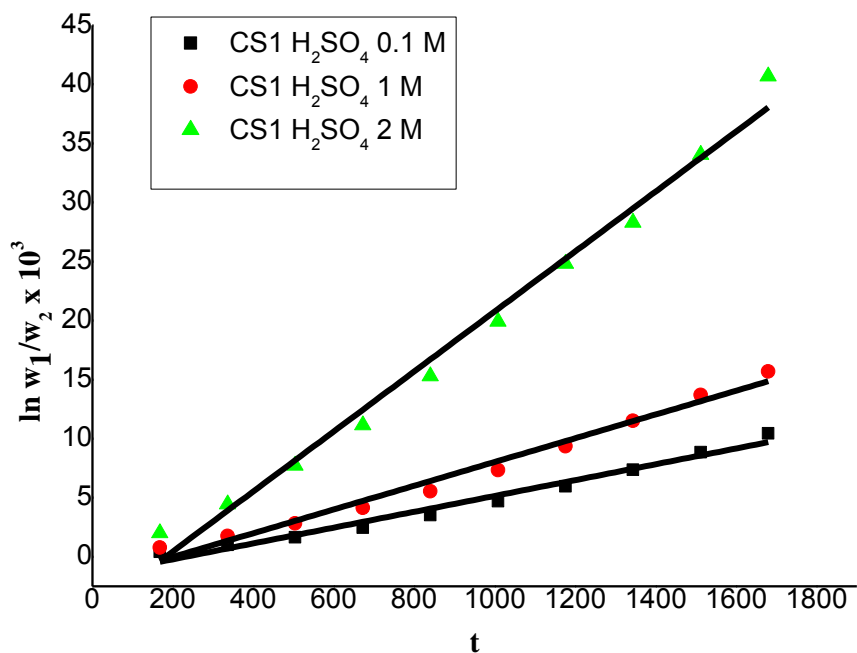
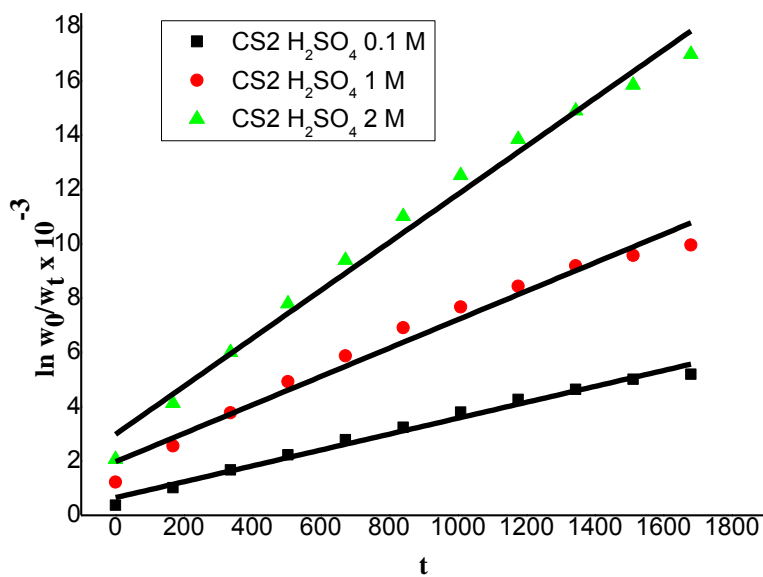**Figure 4:** Kinetic of corrosion rates for carbon-steel CS1 samples.

Figure 5: Kinetics of corrosion rates for CS sample

Table 4: R^2 and k values for the corrosion rates of CS1 samples

Carbon steel samples	R^2	k (min^{-1})
CS1 in H_2SO_4 0.1 M	0.97497	0.0067
CS1 in H_2SO_4 1 M	0.97989	0.0100
CS1 in H_2SO_4 2 M	0.98545	0.0254

Table 5: R^2 and k values for the corrosion rates of CS1 samples

Carbon-steel2 Samples	R^2	k (min^{-1})
CS2 in H_2SO_4 0.1 M	0.97155	0.0029
CS2 in H_2SO_4 0.1 M	0.98519	0.0052
CS2 in H_2SO_4 0.1 M	0.98496	0.0088

Some properties of doped Liquid PMMA and its Role with H_2SO_4

The synthesized of undoped liquid PMMA oligomer possess a high molecular weight up to 3000 g/mole. For 48 hours, this oligomer of PMMA can be preserved liquid. The significant point is that in the present of H_2SO_4, the PMMA has the ability to maintain in liquid state for additional 96 hours. In this case, the scenario will be different for the acid behaving as an inhibitor in the presence of the polymer, slowing down the polymerization process [13]. This leads to the decrease of corrosion rates due to the PMMA role.

Liquid PMMA oligomer electrolyte characterization: FT-IR analysis

The FT-IR spectra of H_2SO_4 doped PMMA oligomers are indicated in Figure 6. When H_2SO_4 was added into the system, a new peak was appeared around 3500-3000 cm^{-1}. This peak is reported to a hydrogen bond formation between the carbonyl (C=O) group of PMMA and the H$^+$ ion from the acid [13, 14]. This can be taken as evidence to the fact of an increase in the acid content along with a decreased in the intensity area ratio of the C=O band at 1730 cm^{-1}. The C=O band was also shifted to a lower frequency range, implying to strong interaction between the oligomer and the doping acid.

Figure 6: Doped liquid PMMA oligomer FTIR spectra

Conclusion

Carbon steel samples were successfully prepared and tested with different acid concentrations of sulfuric acid. For CS1 samples corrosion rates were increased faster than the case of CS2 samples at high concentrations of H_2SO_4 solutions due to the difference in chromium content. Furthermore, the corrosion rate decreases with increasing the time and it is followed the pseudo-first order kinetic. The PMMA has a significant role in decrease corrosion rate on carbon steel samples in H_2SO_4 conditions. This refers to that the liquid PMMA oligomer might be considered as a novel type for polymer electrolyte promising as an electrolyte in electrochemical devices for corrosion decreasing in the acid media.

Acknowledgements

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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