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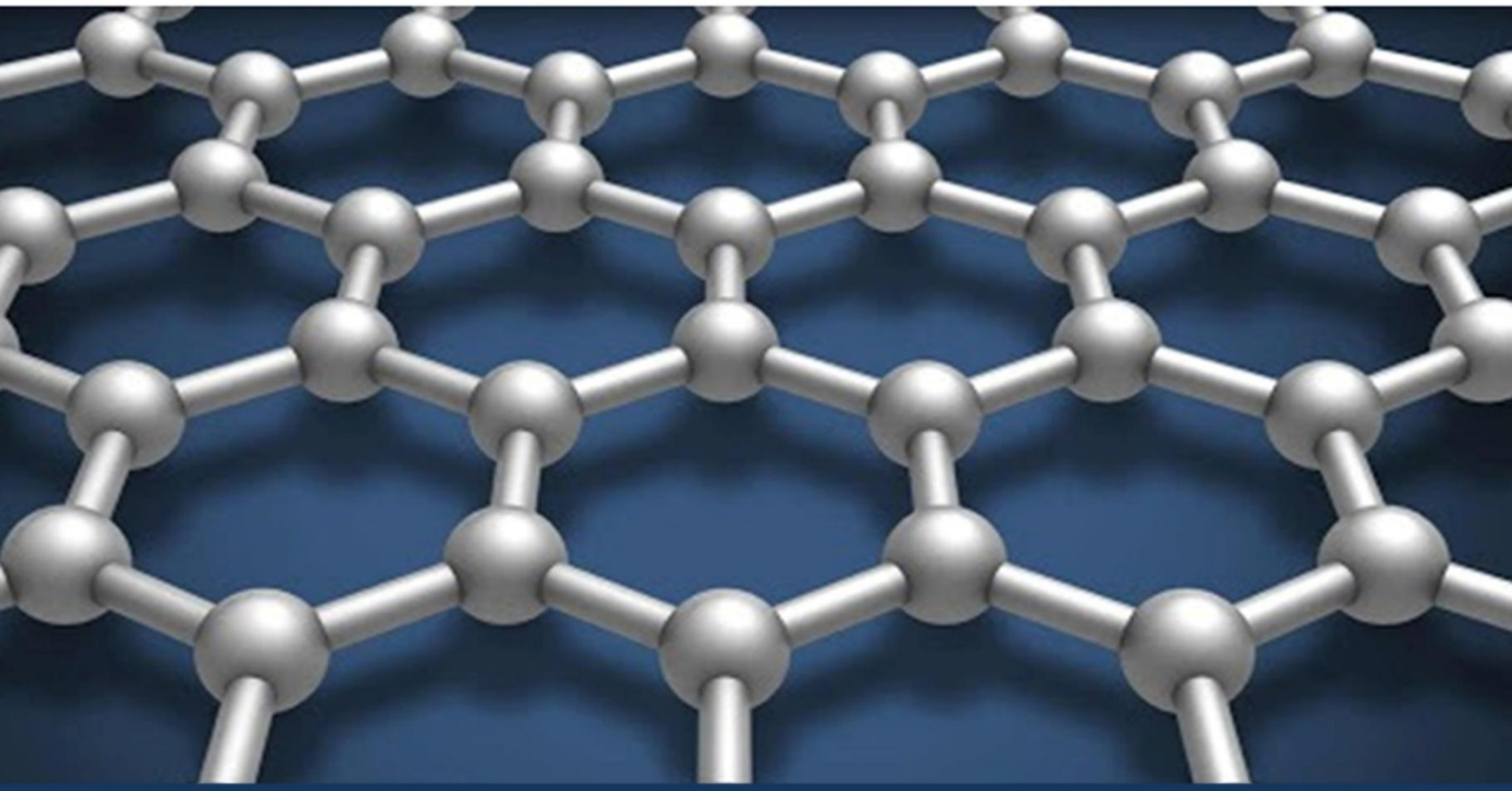

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Композиционные материалы

ЛИТЕРАТУРА

1. Драбкова Т. В., Абдуталипова Н. М., Рахматуллаев Ф. Н., Рахматов У. Н. Мониторинг водных ресурсов Узбекистана и перспективы использования ионообменных установок для очистки сточных вод // География и водные ресурсы. – Алматы. – 2025. – С. 3-12. https://doi.org/10.55764/2957-9856/2025-2-3-12.15
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SYNTHESIS OF CORROSION INHIBITOR BASED ON P-PHENYLENEDIAMINE, FORMALIN, AND ALANINE AND ITS INHIBITION EFFICIENCY BY ELECTROCHEMICAL METHOD

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Abstract. In this study, the synthesis, characterization, and corrosion inhibition performance of a novel inhibitor based on p-phenylenediamine, formalin, and alanine were investigated. The optimal synthesis conditions were established with a molar ratio of 1:2:2 for the starting materials and a reaction temperature range of 40–65 °C, resulting in a high reaction yield of 89.4%. The chemical structure of the synthesized inhibitor was confirmed using infrared (IR) spectroscopy, indicating the successful formation of the target compound. The corrosion inhibition efficiency was assessed using electrochemical measurements in acidic media, specifically for mild steel, revealing an excellent inhibition efficiency of 97.38% at a concentration of 150 mg/L. The results suggest that the inhibitor forms a protective adsorbed layer on the steel surface, effectively reducing metal dissolution.

Keywords: p-paraphenylenediamine, formalin, alanin, corrosion inhibitor, IR spectrium.

Introduction. Corrosion inhibitors are widely used to protect metals against various corrosive environments [1, 2]. A corrosion inhibitor is a compound that is added in low concentrations to a corrosive solution to reduce and/or minimize the corrosion rate [3].

Amines are the main part of organic substances that are among the inhibitors that reduce the process of corrosion of metals under the influence of the external environment[4]. Corrosion of aluminium in acidic environments causes serious material degradation in many industries. The use of organic corrosion inhibitors is an effective and economical way to control this problem. Diamine-type compounds are particularly interesting due to their strong electron-donating ability and high adsorption tendency on metal surfaces. In this study, (4S)-2,2,4-trimethylhexane-1,6-diamine (TMD) and (1R,3R)-3-(aminomethyl)-3,5,5-trimethylcyclohexane-1-amine (IPDA) were evaluated as corrosion inhibitors for aluminium in HCl solutions (0.2–0.4 M). Electrochemical and gravimetric results showed that inhibition efficiency increased with inhibitor concentration, reaching up to 98.3% for TMD at 50 mM [5].

A bi-Mannich base (BMT) was synthesized and evaluated as a corrosion inhibitor for carbon steel in an H_2S–HCl solution. At only 9 ppm, BMT achieved up to 98% inhibition efficiency. Adsorption followed the Langmuir isotherm, indicating spontaneous film formation. Quantum chemical results confirmed strong interaction between BMT and the steel surface, proving its effectiveness in sour and acidic environments [6]. A novel polyimide, poly(1,3-thiazine imide) (PTzI), and its copolymers were synthesized from a thiazine-based monomer. The polymers showed high thermal stability ($Td_5\%$ = 294–418 °C) and excellent corrosion inhibition for mild steel, with PTzI achieving up to 99.4% efficiency [7].

Cinnamaldehyde thiosemicarbazone (CT), synthesized via Schiff-base reaction, effectively inhibited mild steel corrosion in 1 M and 15% HCl with up to 97.6% efficiency. Adsorption followed the Langmuir isotherm, and DFT and FE-SEM analyses confirmed strong surface protection [8]. Amine units are essential in gas processing for removing H_2S and CO_2, but corrosion caused by heat-stable salts remains a major challenge. In a Gulf of Suez LPG plant, corrosion reached 14 MPY.

Using the NALCO CORR 11631A inhibitor reduced it to 3 MPY, with 50 ppm identified as the optimal concentration for effective corrosion control[9]. Salicylidene-p-toluidine (SPT) was investigated as a corrosion inhibitor for API X70 carbon steel in 1 M HCl at 25 °C. Using weight loss, electrochemical methods, and DFT calculations, SPT showed strong adsorption and high inhibition efficiency (up to 98.8% at 10^{-2} M), acting mainly as an anodic inhibitor[10].

The synthesized terpolymer (SPF), obtained from p-semidine, p-phenylenediamine, and formaldehyde, was also evaluated as a corrosion inhibitor for mild steel in sulfuric acid. Electrochemical and gravimetric studies revealed that SPF effectively reduced the corrosion rate, achieving up to 92.9% inhibition efficiency at 1×10^{-3} M. Adsorption and DFT analyses confirmed strong interaction of the polymer film with the steel surface through π-orbital and heteroatom coordination, suggesting its potential as an efficient anticorrosive material in acidic environments[11].

Poly(o-chloroaniline), poly(o-phenylenediamine), va ularning kopolimeri poly(OPD-co-OCA) sintez qilindi va tahlil qilindi. Kopolimer yuqori termal barqarorlik, redoks faollik va mild steel uchun 80% gacha korroziya inhibatsiya samaradorligini ko‘rsatdi[12].

Synthesis of the corrosion inhibitor (PFA). The synthesis of the corrosion inhibitor was carried out by adding 0.1 mol of p-phenylenediamine**,** 0.2 mol of formalin (37% aqueous formaldehyde), and 0.2 mol of alanine in a molar ratio of 1:2:2**.** The reaction was performed under an inert nitrogen atmosphere to prevent oxidation of *p-phenylenediamine* by atmospheric oxygen. The mixture was stirred at 40–45 °C for 45 minutes in the presence of a reflux condenser. During the reaction, the temperature was maintained within the range of 55–65 °C**.** The yield of the reaction mainly depended on the mole ratio of the starting materials and the reaction temperature table 1.

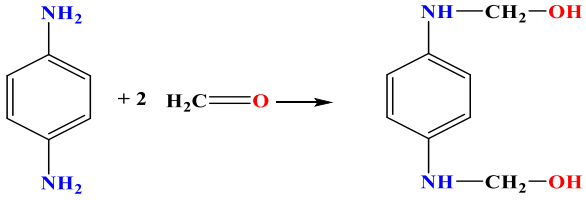
Table 1.

Dependence of the synthesis yield of PFA brand corrosion inhibitor on the mole ratio of starting materials and temperature

p-phenylenediamine formalin+alanin	Temperature^{0}C	Yield %	Temperature ^{0}C	Yield %
1:1:1	40÷65	49.67	65≤t	23.35
1:2:2		88,42		51.36
2:2:1		56.15		32.26
2:1:3		32.62		29.56
1:2:1		39.43		33.25

As shown in Table 1, the highest yield (89.4%) was obtained at a temperature range of 40–65 °C and a mole ratio of 1:2:2**.** Increasing the temperature above 65 °C resulted in a noticeable decrease in product yield. The obtained compound was well soluble in water, ethanol, and dimethylformamide (DMF) at temperatures above 40°C**.** After completion of the reaction, the mixture was cooled to room temperature, and the solid product was separated by filtration, washed several times with distilled water and ethanol to remove unreacted residues, and then dried under vacuum in an inert nitrogen atmosphere at 50°C until constant weight. The obtained compound was readily soluble in water, ethanol and dimethylformamide above40 °C.

IR spectrum analysis of inhibitor. It has been determined that the effectiveness of the inhibitors depends on the fact that they are adsorbed on the surface of steel and form chemical compounds with iron ions that are poorly soluble due to the functional groups in the composition. In addition, the structure of the molecule, the length of the oligomer chain is also important. Therefore, in order to discuss the mechanism of inhibition, we need to know the structure of the molecules of the obtained inhibitors. The structure of substances was studied using the IR spectroscopy method. For this purpose, IR spectra of the first reactant (1,4-phenylenebis(azanedyl)) dimethanol were obtained, newly formed bonds and groups were identified through absorption lines.



Synthesis 1. Reaction of (1,4-phenylenebis(azanedyl)) dimethanol

In Figure 1, the IR spectrometer results of (1,4-phenylenebis(azanedyl)) dimethanol show that in the IR- spectrum of (1,4-phenylenebis(azanedyl)) dimethanol, according to the results of the IR-spectrum, ν(OH) group's valence symmetric ν_s and 1458.81 cm^{-1} field, deformation d vibration frequency was formed. In the 3158.36 cm^{-1} and 1178.36 cm^{-1} regions, valence symmetric ν_s and deformation δ vibrations of the ν(NH_2) group were formed. At the same time, the frequency of valence asymmetric ν_{as}, valence symmetric ν_s and deformation δ vibrations of the ν(CH) bond belonging to the benzene ring at 2981.24 cm^{-1} and 1214.28 cm^{-1}, 2874.35 cm^{-1} and 1443.87 In cm^{-1} fields, the frequency of valence asymmetric ν_{as},

valence symmetric ν_s and deformational δ vibrations of $\nu(CH_2)$ group was formed figure 1.

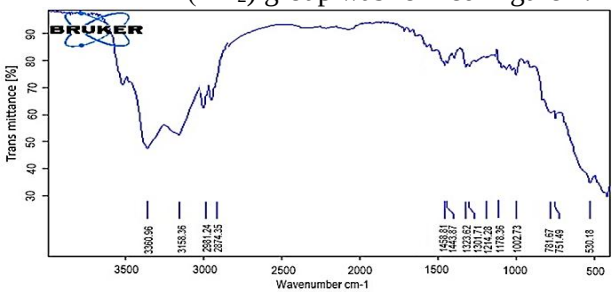


Figure 1. IR-spectrum of (1,4-phenylenebis(azanedyl))

According to the figure 2 IR-spectrometer results of PFA show that the IR-spectrum of PFA has 3480.52 cm^{-1}, 3366.81 cm^{-1}, 3217.83 cm^{-1}, and 1505.29 cm^{-1}, 1469.20 cm^{-1}, the frequency of valence symmetric ν_s and deformation δ vibrations of ν(NH) group was observed. At the same time, the frequency of valence asymmetric ν_{as}, valence symmetric ν_s and deformation δ vibrations of the ν(CH) bond belonging to the benzene ring at 3100.07 cm^{-1} and 1294.89 cm^{-1}, 2912.10 cm^{-1} and 1444.04 frequency of valence asymmetric ν_{as}, valence symmetric ν_s and deformation δ vibrations of $\nu(CH_3)$ group in cm^{-1} fields, valence asymmetric ν_{as}, valence symmetric ν_s and deformation δ vibrations of $\nu(CH_2)$ group in 2841.93 cm^{-1} and 1182.27 cm^{-1} fields δ is the frequency of oscillations. In the region of 1630.09 cm^{-1}, the valence ν vibration of the n(C=O) group was formed, as well as the frequency of the deformation δ vibration in the region of 836.57 cm^{-1}.

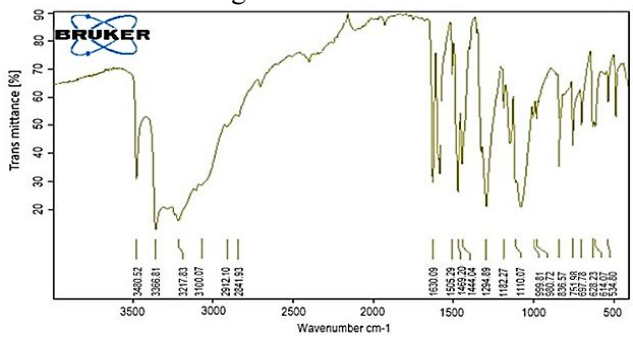
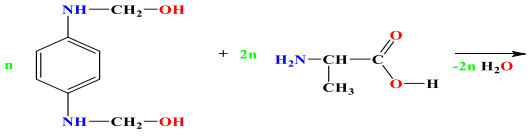
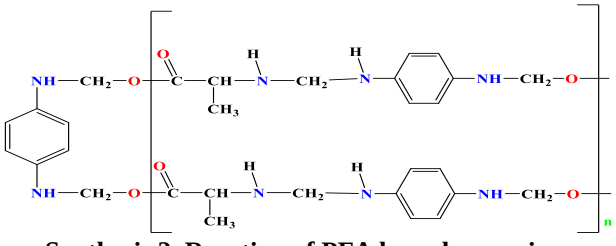


Figure 2. IR- spectrum of PFA brand corrosion inhibitor





Synthesis 2. Reaction of PFA brand corrosion inhibitor

Results and Discussion. ***Electrochemical studies.*** The inhibition efficiency of the synthesized corrosion inhibitor was studied using the CS-350 Corrosion Test device in figure 3.

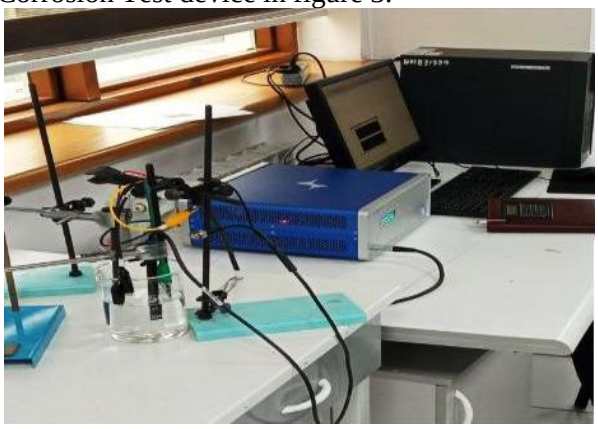


Figure 3. Photo of CS-350 "Cossion test" device

Three types of electrodes were used for electrochemical measurements: a working electrode, a reference electrode (Ag/AgCl), and a counter electrode (platinum wire). The St20 steel sample performs the task of the working electrode in the process, the surface of the electrode is cleaned with different brands of sandpaper, washed in distilled water, dried, and then cleaned again with acetone. Ag/AgCl was used as the reference electrode. Platinum was used as the counter electrode. For the experiment, only 1.2 cm^2 of each electrode was immersed in the corrosive medium. Each electrode was placed parallel to the other at a distance of 1 cm, and the Ag/AgCl electrode was placed between the other two electrodes. Polarization curves were performed from -160 mV to +160 mV at a scan rate of 1 mV s^{-1}. The electrochemical initial input range was 2.5 V, with a maximum potential resolution of 760 mV and a potential accuracy of 300 mV with an apparatus containing a noise module.

In this case, the corrosion rate (corrosion current density, i^0_c corr) was determined and compared. Corrosion current values obtained in this way in different environments and solutions containing inhibitors were evaluated for the effectiveness of inhibitors-film formers and passivation; Based on the formulas (1 and 2), the values of the braking coefficient g were found and the degree of protection Z% was calculated.

$$\text{Inhibition efficiency } \gamma = \frac{i_c}{i_c^o} \qquad (1).$$

$$\text{level of protection } Z = \frac{i_c - i_c^0}{i_c} 100\% \qquad (2)$$

It can be seen here: i_c and i^0_c –corrosion currents in inhibited and non-inhibited media.

During the study of the polarization curves of this corrosion inhibitor, the protection efficiency of the PFA-grade corrosion inhibitor for carbon steel at various concentrations was determined in a background solution based on 1M HCl (Figure 4).

In this process, the polarization curve method was used to investigate parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic (β_a) and cathodic (β_c) Tafel slopes, and inhibition efficiency (η_{PDP}). The results are presented in Table 4.

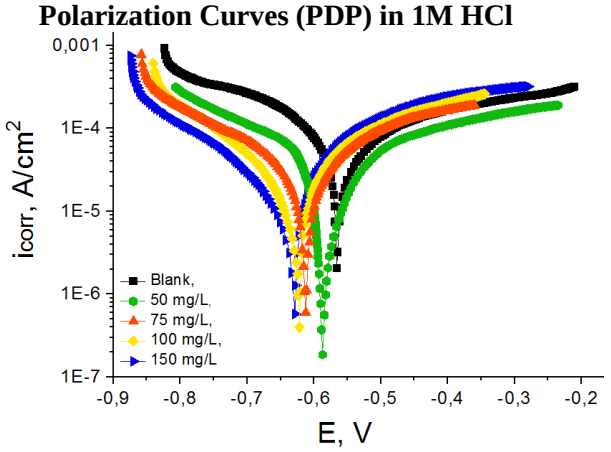


Figure 4. Polarization curves for samples containing PFA-grade corrosion inhibitor at various concentrations in a 1M HCl solution

Table 2.
Samples with PFG brand corrosion inhibitor at different concentrations in 1 M HCl solution

Parameters	C_{inh}, mg/L				
	Blank	50	75	100	150
i_{corr}, mA/cm²	247.05	24.10	17.02	13.01	3.98
E_{corr}, mV	–589	–601	–641	–614	–572
β_a, mV/decade	449	738	391	644	698
$-\beta_c$, mV/decade	722	514	174	268	366
η_{PDP}, %	–	90.24	93.11	94.73	97.38

Additionally, since the (E_{corr}) value did not show a significant difference between systems with and without the inhibitor, it was determined that this inhibitor belongs to the mixed-type category. The inhibition efficiency of this inhibitor at a concentration of 50 mg/L was found to be 90.24%, while at the optimal concentration of 150 mg/L, it reached 97.38%.

Polarization Curves (PDP) in 0.5 M H_2SO_4. Using this method, the polarization curves of the PFA brand inhibitor in a 0.5 M H_2SO_4 environment were determined. The polarization curves of St2 steel at different concentrations, both with and without the PFA inhibitor, were obtained (Figure 5). In this method, key parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), and inhibition efficiency (η_{PDP}) were studied. The cathodic and anodic polarization curves were examined both in the presence and absence of the inhibitor. The obtained results showed that the polarization curves exhibited more negative potential values, indicating that this corrosion inhibitor predominantly inhibits the anodic process.

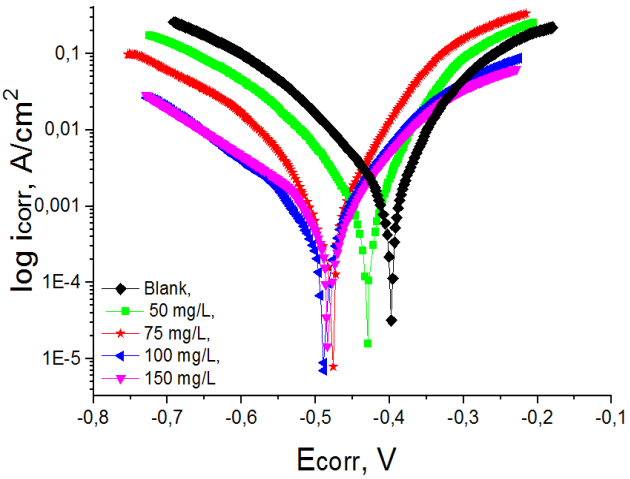


Figure 5. Polarization curves for samples with different concentrations of PFA brand corrosion inhibitor in a 0.5 M H_2SO_4 solution

As seen in Table 5 the values of the Tafel slopes β_c and β_a have significantly changed in the presence of the inhibitor.

Table 3.
Inhibition efficiency in the presence and absence of PFA at different concentrations in 0.5 M H_2SO_4 solution

Parameters	C_{inh}, mg/L				
	Blank	50	75	100	150
i_{corr}, mA/cm²	14.23	2.23	1.21	0.81	0.36
E_{corr}, mV	-419	-449	-465	-472	-467
β_a, mV/decade	285.3	272.2	231.2	212.5	269.1
$-\beta_c$, mV/decade	239.2	179.6	171.3	104.9	100.7
η_{PDP}, %	-	83.98	91.49	94.31	97.47

According to the obtained results, the i_{corr}, value for inhibitor-free solutions was 14.23 mA/cm². However, with the addition of the inhibitor and an increase in its concentration, the i_{corr}, value significantly decreased—from 14.23 mA/cm² to 0.36 mA/cm².

As the inhibitor concentration increased and i_{corr}, decreased, the η_{PDP} (inhibition efficiency) increased. For example, at an inhibitor concentration of 50 mg/L, i_{corr}, was 2.23 mA/cm², and η_{PDP} reached 83.98%. Furthermore, when the inhibitor concentration increased from 50 mg/L to 150 mg/L, i_{corr} reached its minimum value (0.36 mA/cm²), while η_{PDP}achieved its maximum value of 97.47%. These results indicate that the inhibitor strongly adsorbs onto the metal surface, effectively protecting it from corrosion.

Polarization Curves (PDP) in 1 M HCl + 200 mg/L NaCl

The protection efficiency of the PFA brand corrosion inhibitor for St2 steel in a 1 M HCl + 200 mg/L NaCl corrosive environment was studied.

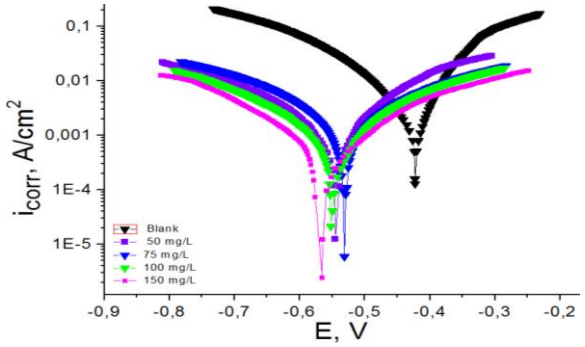


Figure 6. Polarization curves for samples with different concentrations of PFA brand corrosion inhibitor in a 1 M HCl + 200 mg/l NaCl solution

Table 4

PDP Tafel characteristics of the PFA brand corrosion inhibitor

Parametrs	C_{inh}, mg/L				
	Blank	50	75	100	150
i_{corr}, mA/cm^2	75.2	8.21	6.14	3.78	1.82
E_{corr}, mV	–437	–560	–531	–536	–538
β_a, mV/decade	135.2	262.1	287.1	246.2	252.7
– β_c, mV/decade	188.2	317.2	252.3	243.2	249.9
η_{PDP}, %	-	89.08	91.83	95.33	97.57

According to the conclusions drawn from Figure 8, the values of (i_{corr}) in the system without inhibitor were (75.2 mA/cm^2), but with the introduction of the inhibitor into the system and its concentration increasing, the values of (i_{corr}) decreased significantly (8.21 mA/cm^2 at 50 mg/L, 6.14 mA/cm^2 at 75 mg/L, 3.78 mA/cm^2 at 100 mg/L, and 1.82 mA/cm^2 at 150 mg/L (Table 6).

Conclusion. In this study, a novel corrosion inhibitor (PFA) was successfully synthesized from *p*-phenylenediamine, formalin, and alanine under optimal conditions (mole ratio 1:2:2, temperature range 40–65 °C), with a yield of 89.4%. The structural features of the inhibitor were confirmed by IR spectroscopy, indicating the formation of characteristic functional groups capable of coordinating with metal surfaces. Electrochemical measurements electrochemical measurements (PDP) showed that the PFA inhibitor exhibits mixed-type inhibition behavior for carbon steel in acidic media (HCl, H_2SO_4, and HCl + NaCl solutions). The inhibition efficiency increased with concentration, reaching 97.4–97.6% at 150 mg/L.

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