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Synthesis, characterization, and evaluation of polymeric surfactants derived from PET plastic waste as green corrosion inhibitor of steel surfaces in marine environment for heavy industry†

 Reda Abdel-Hameed,^{ID}*^{ab} Ghadah M. S. Aleid,^a Hanan Ragab,^a Hussin Alshafey^c and Abeer M. Alosaimi^d

The aim of this work was to prepare a nonionic polymeric surfactant from a recycled product of poly(ethylene terephthalate) plastic waste, PET. In this respect, PET waste was subjected to reverse polymerization (depolymerization) *via* reaction with both ethylene diamine (EDA) in the presence of a catalyst and propylene glycol (PG) in the presence of a transesterification catalyst. The corresponding products obtained were poly amino amide (PETAA) and poly glycol ester (PETPG), respectively. The obtained materials reacted with oleic acid to produce *N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl) terephthalamide (PETAA-OL) and 2-(2-(((*E*)-octadec-8-enoyl)oxy)propoxy)ethyl (2-(2-(((*E*)-octadec-9-enoyl)oxy)propoxy)ethyl) terephthalate (PETPG-OL). The prepared materials were characterized by FT-IR, ¹HNMR, and elemental analysis. It was evaluated as a corrosion inhibitor for carbon steel used in the petroleum industry in the marine environment. Chemical, analytical, and electrochemical techniques were used for the evaluation of the corrosion inhibition efficiency of the prepared polymeric surfactants. The effects of the polymeric surfactant concentration and reaction temperature were studied. The inhibition efficiency was found to increase with increasing concentration and decrease with rising temperature. The inhibition due to the adhesion and adsorption of the polymeric material on the steel surface agrees with the Langmuir adsorption isotherm model. The amount of dissolved iron in the corrosive medium due to the corrosion process was estimated using atomic absorption spectroscopy (AAS). It was found that the dissolution of iron was decreased by adding the prepared nonionic surfactants. Potentiodynamic polarization data indicate the mixed-type nature of surfactant inhibitors. According to the potentiodynamic polarization data, the prepared surfactant boosts polarization resistance and inhibition performance by adsorbing on the metal/electrolyte interface. The addition of inhibitor molecules to the aggressive medium produces a negative shift in the open-circuit potential due to the retardation of the cathodic reaction. The surface morphology of steel was examined using SEM. A protective coating of inhibitor molecules forms on the steel surface, according to the SEM measurements of the surface. The data obtained from different techniques are in good agreement, indicating good inhibition efficiency of the prepared nonionic surfactants derived from plastic waste in a marine environment.

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^aBasic Science Department, Preparatory Year, University of Ha'il, Hail, 1560, Saudi Arabia. E-mail: r.abdelghany@Uoh.edu.sa

^bChemistry Department, Faculty of Science, Al-Azhar University, 11884, Cairo, Egypt

^cPetroleum Applications Department, Egyptian Petroleum Research Institute, Cairo, 11727, Egypt

^dDepartment of Chemistry, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia

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1 Introduction

Polymeric surfactants are polymers that have high surface-active properties. Classified as ionic (cationic or anionic), and nonionic surfactants consist of a hydrophilic head with a hydrophobic long polymer chain (tail). Polymeric surfactants have widespread applications in many industrial fields, involving emulsion emulsifiers, and corrosion inhibitors.^{1–4} The wide range of applications of the polymeric surfactant is related to its unique properties, such as good adsorption and long stabilizing blocks. Polymeric surfactants are prepared from the recycling product of polyethylene terephthalate plastic waste



(PET). Plastic bottles (PET) are produced annually in large quantities; due to the single use of PET bottles, they are left in the environment, causing environmental pollution.¹⁻⁴ Finding quick solutions to remove the solid and plastic trash represented by water bottles is also critical. A majority of PET was used to produce approximately 30 million tons of polyester produced worldwide in 2000, which increased to 55 million tons in 2012. Because of its wide range of applications in a wide range of consumer products, a lot of PET trash is generated, including waste from the production of polymers and products that have reached the end of their useful lives. Environmental contamination caused by the accumulation of solid and plastic trash causes major environmental issues. PET is a semi-crystalline, thermoplastic polyester that is clear, strong, and non-biodegradable.¹⁻⁴ PET is not a harmful product, but the amount of garbage it generates increases dramatically. Because of the increasing pressure to keep the environment clean, the only solution is to recycle PET waste in an environmentally sustainable manner. PET waste can be recycled in several ways, including chemical and physical recycling. The widely used thermoplastic polyethylene terephthalate (PET) produces tons of waste due to its non-biodegradability in the environment, which could upset the ecosystem's balance. The chemical recycling of PET to useable materials is a recognized process among mechanical, thermal, and chemical recycling techniques that adhere to the principles of sustainable development.¹⁻⁷ Several chemical depolymerization techniques, such as methanolysis, glycolysis, hydrolysis, aminolysis, aminolysis, and hydrogenation are being used for PET chain scission based on the types of chemical reagents.¹⁻⁷ Chemical

recycling can depolymerize PET trash into base monomers or oligomers. The two main pathways for polymer solvolysis, also known as solvent for depolymerization, are methanolysis and glycolysis.⁴⁻⁷ In 1973, Nathaniel Wyeth applied for a patent on the PET bottle, which became widely used in the 1980s for the production of single-use soft drink bottles. In 1987, more than 700 million pounds of PET was used in its production.⁴⁻⁷ Steel corrosion control is critical from technical, economic, and environmental standpoints. Corrosion inhibitors are commonly used to reduce corrosion attacks on steel surfaces.⁴⁻⁷ Steel's lifetime increases due to inhibitors' ability to slow down the corrosion process.⁴⁻⁷ The majority of effective acid inhibitors are organic compounds containing nitrogen, oxygen, and/or sulfur; these compounds adsorb on steel surfaces to slow corrosion.⁸⁻¹² The chemical composition of the inhibitors, the presence of electron-donating or repelling groups, inhibitor's molecular weight, temperature, and the electrochemical potential at the metal/solution interface influence the strength of the adsorption.^{13,14} Surfactant inhibitors have many advantages, including high inhibition efficiency, low toxicity, and ease of manufacture.^{7,15} Adsorption of the surfactant on the metal surface can significantly alter the metal's ability to resist corrosion,^{16,27-29} making research into the relationship between adsorption and corrosion inhibition critical.^{31,33,40-43} PET was depolymerized using monoethanolamine and ethylene diamine in previous studies,¹⁶⁻²⁴ and the resulting nonionic surfactants were proven to be effective steel corrosion inhibitors in HCl. This article is part of a series aimed at reducing environmental pollution caused by the accumulation of plastic waste by recycling waste into modified products and evaluating the abilities of those

Table 1 Summary and review of the corrosion inhibition efficiencies reported in the literature

Studied metal	Corrosive media environment	Inhibitors used	Reported corrosion inhibition efficiency (%)	Ref.
Mild steel	Marine environment	Amide of phthalimide derivative	(83-92)	1
Mild steel	Phosphoric acid 1.0 M H ₃ PO ₄	Ethylene di amine and ethylene glycol products with PET	(88-95)	2
Mild steel	Nitric acid 0.1 M HNO ₃	Products of diethanol amine and triethanol amine with PET	(75-89)	3
C-steel	Sulfuric acid 1.0 M H ₂ SO ₄	Glycolized product of PET with propylene glycol	(65-84)	5
C-steel	Acetic acid 1.0 M CH ₃ COOH	Ethoxylated poly(ethylene terephthalate) derived from plastic waste	(73-91)	9
Mild steel	2 M NaCl	Recycled poly ethyleneterephthalate (PET) with both of diethanolamine (DEA) and triethanolamine	(67-75)	10
C-steel	Hydrochloric acid 1.0 M HCl	Nonionic surfactants from plastic waste (diethanol and triethanolamine derivatives)	(83-94)	11
C-steel	Hydrochloric acid 1.0 M HCl	Nonionic polymeric surfactants as corrosion inhibitors for the C-steel alloy in hydrochloric acid	(87-92)	14
Mild steel	Marine environment	Recycling of poly(ethylene terephthalate) waste	(83-91)	15
C-steel	Sulfuric acid 1.0 M H ₂ SO ₄	Aminolysis product of PET	(87-96)	18
C-steel	Methanoic acid 1.0 M HCOOH	Poly(oxyethylene)terphthylamine	(81-91)	32
C-steel X60 carbon steel	3.5% NaCl solution	Amide derived from the waste	(85-95)	72



modified products to prevent corrosion of metals and alloys in various aqueous conditions.^{16–24} The present work is one from a series aimed at alleviating the environmental pollution caused by the accumulation of PET waste and evaluation of the products as corrosion inhibitors for metals and alloys in different corrosive environments.^{1–18} The previously published papers focusing on the study of the corrosion in an acidic media such as HCl, H₂SO₄, and HNO₃, all contain H⁺ ions (investigate the effects of H⁺ presence), with the conclusion of different inhibition efficiencies. A review of the reported inhibition efficiencies in the literature is summarized in Table 1. In this study, PET plastic waste was recycled using ethylene diamine EDA *via* aminolysis and propylene glycol PG *via* glycolysis in the presence of a transesterification catalyst; the corresponding products are poly amino amide (PETAA) and poly glycol ester (PETPG). The obtained materials were reacted with oleic acid to produce the *N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide (PETAA-OL) and 2-(2-(((*E*)-octadec-8-enoyl)oxy)propoxy)ethyl 2-(2-(((*E*)-octadec-9-enoyl)oxy)propoxy)ethyl terephthalate (PETPG-OL). The product materials were characterized and evaluated as corrosion inhibitors for carbon steel in a marine environment. Chemical, analytical, and electrochemical techniques were used for the evaluation of the corrosion inhibition efficiency of the prepared materials. The effects of the concentrations, temperatures, and adsorption isotherms were also studied.

2 Experimental

2.1. Materials and solutions

All chemicals used in this experiment were of analytical grade and were obtained from Sigma Aldrich Chemicals Co., with the exception of the PET waste, which was collected from beverage drinking water bottles.^{25,26} The bottle labels and other contaminants were removed, and the PET waste was chopped into 1 mm² pieces, washed with soap and water, dried, and recycled in a green manner. Table 2 shows the gravimetric composition of the steel materials used in this study (type-X60 carbon steel rods, CSX60, SABIC, Kingdom of Saudi Arabia) with a composition similar to that of the steel used in the manufacturer of the petroleum pipelines and tanks in the petroleum industry in the SABIC carbon steel used in Saudi Arabia. It has a comparable composition to the carbon steel used in many heavy industries such as boilers, automobiles, and water tanks. The corrosive solution used in this study is aggressive with 3.5% sodium chloride solution as artificial seawater prepared from analytical grade sodium chloride (99.9%, Sigma Aldrich).

2.2. Recycling of PET waste

With a weight ratio of PET to ethylene diamine (EDA) and/or propylene glycol (PG) of 1 : 3 (wt% of PET : wt% of EDA), PET

waste was depolymerized with 1,3-diamino ethane (EDA) utilizing 1.0 percent sodium acetate and 1.0 percent acetic acid as a co-catalyst (by weight based on the weight of PET). Whereas PET waste was depolymerized with propylene glycol (PG) in the presence of manganese acetate as a transesterification catalyst (1% by weight to the weight of the total reactants). The reaction mixtures in both cases were heated for 4 hours at a temperature of about 170–190 °C and for 3 hours at 200 °C while being vigorously stirred in a nitrogen environment.^{25,26} The reaction temperature was subsequently decreased to 100 °C for one hour. It took some time for the combination to cool to room temperature. Phase separation was performed once the reaction was complete, and the products were separated in an organic layer. The product obtained in the case of depolymerization with ethylene diamine EDA was (*N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide), whereas, the product obtained in the case of depolymerization with propylene glycol (PG) was bis(2-(2-hydroxypropoxy)ethyl) terephthalate, as shown in Fig. 1 and 2.

2.3. Synthesis of polymeric surfactants from the recycled product of PET

Nonionic polymeric surfactants were prepared from the reaction of recycled products of PET with both EDA and PG, which are (*N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide), and bis(2-(2-hydroxypropoxy)ethyl) terephthalate compounds (PETAA) and (PETPG), respectively. Reactions of both the compounds with oleic acid in the presence of sodium acetate as a catalyst and acetic acid as a co-catalyst in the presence of *p*-toluene sulfonic acid were performed by refluxing for 7 hours in xylene until the calculated amount of water was removed. A schematic diagram of the complete synthesis process is shown in Fig. 1 and 2. The obtained polymeric surfactants were *N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide (PETAA-OL) and 2-(2-(((*E*)-octadec-8-enoyl)oxy)propoxy)ethyl 2-(2-(((*E*)-octadec-9-enoyl)oxy)propoxy)ethyl terephthalate (PETPG-OL). The prepared polymeric surfactants (PETAA-OL) and (PETPG-OL) were used for the preparation of the corrosion inhibitor.

2.4. Elemental and spectroscopic analysis

Spectroscopic and elemental analyses were performed at the Micro Analytical Center, Cairo University. Fine chemicals were supplied by the Aldrich Co. The resulting compounds were crystallized and then further purified using a column chromatography process while the reactions were being tracked using TLC.

Table 2 Gravimetric composition of the used steel materials

Element	Mn	Si	S	P	C	Fe
Composition weight (%)	0.517	0.201	0.009	0.007	0.157	About 99%



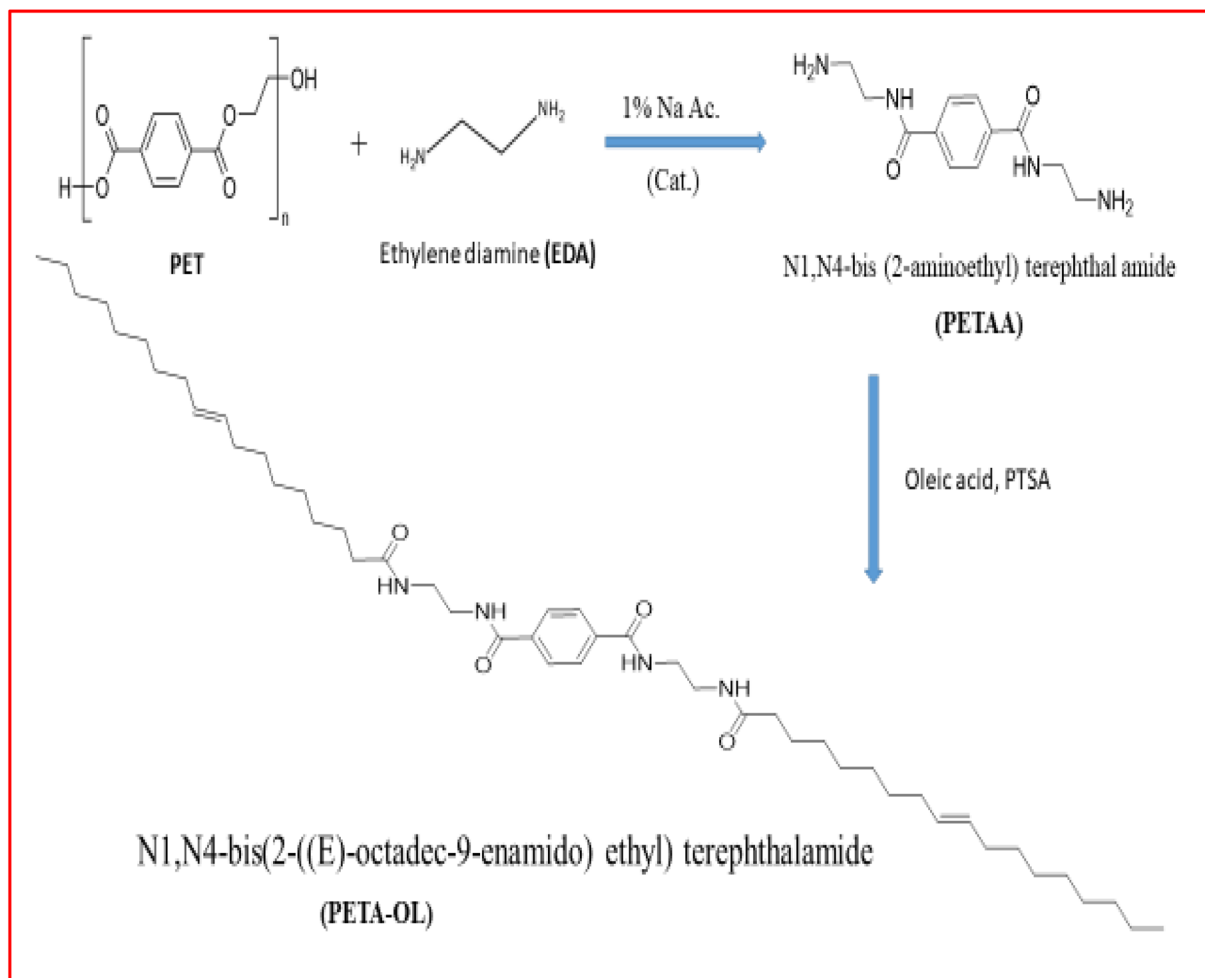


Fig. 1 Chemical structure of the prepared non-ionic polymeric surfactant (PETA-OL) inhibitor compound, and scheme 1 of the aminolysis process.

2.5. Infrared spectroscopy analysis

The chemicals produced were studied using an ATI Mattson Genesis Series FT-IR spectrophotometer. Thin films of the materials were examined using two KBr discs.

2.6. Analysis using nuclear magnetic resonance spectroscopy

In order to determine the chemical structure and the HLB, by comparing the integral traces of various peaks, the produced surfactants were dissolved in DMSO and subjected to spectroscopic analysis using a JEOL NMR spectrometer, model JNM-EX (270 MHz).

2.7. Gravimetric measurements

2.7.1. Measurement of weight loss (chemical technique).

The method is based on calculating the weight loss (WL) of a sample (coupon) of the surface (S) that has been submerged in the abrasive solution for a period of time (t). The tests were carried out in non-aerated media in 100 ml glass vials at room temperature. The iron samples were cleaned with distilled

water, degreased with acetone, and dried before and after the 48 hours immersion. The weight loss technique was applied for all the studied temperatures ranging from 303, 313, 323, and 333 K. The following relationship¹⁶⁻¹⁹ was used to calculate the corrosion rate W :

$$W = \frac{m_i - m_f}{St} \quad (1)$$

where W ($\text{mg cm}^{-2} \text{ h}^{-1}$) is the corrosion rate, m_i (mg), and m_f (mg) are the masses before and after exposure to the test solution, respectively, S (cm^2) is the surface area of the specimen, t (h) is the immersion time. Regarding the inhibitory efficiency, IE% and the surface coverage (θ), which represents the part of the metal surface covered by the inhibitor molecules, were calculated according to the following equations:¹⁶⁻¹⁹

$$\text{IE (\%)} = ([W^0 - W]/W^0) \times 100 \quad (2)$$

$$\theta = ([W^0 - W]/W^0) \quad (3)$$

where W^0 and W represent the corrosion rates in the absence and presence of the inhibitors, respectively.



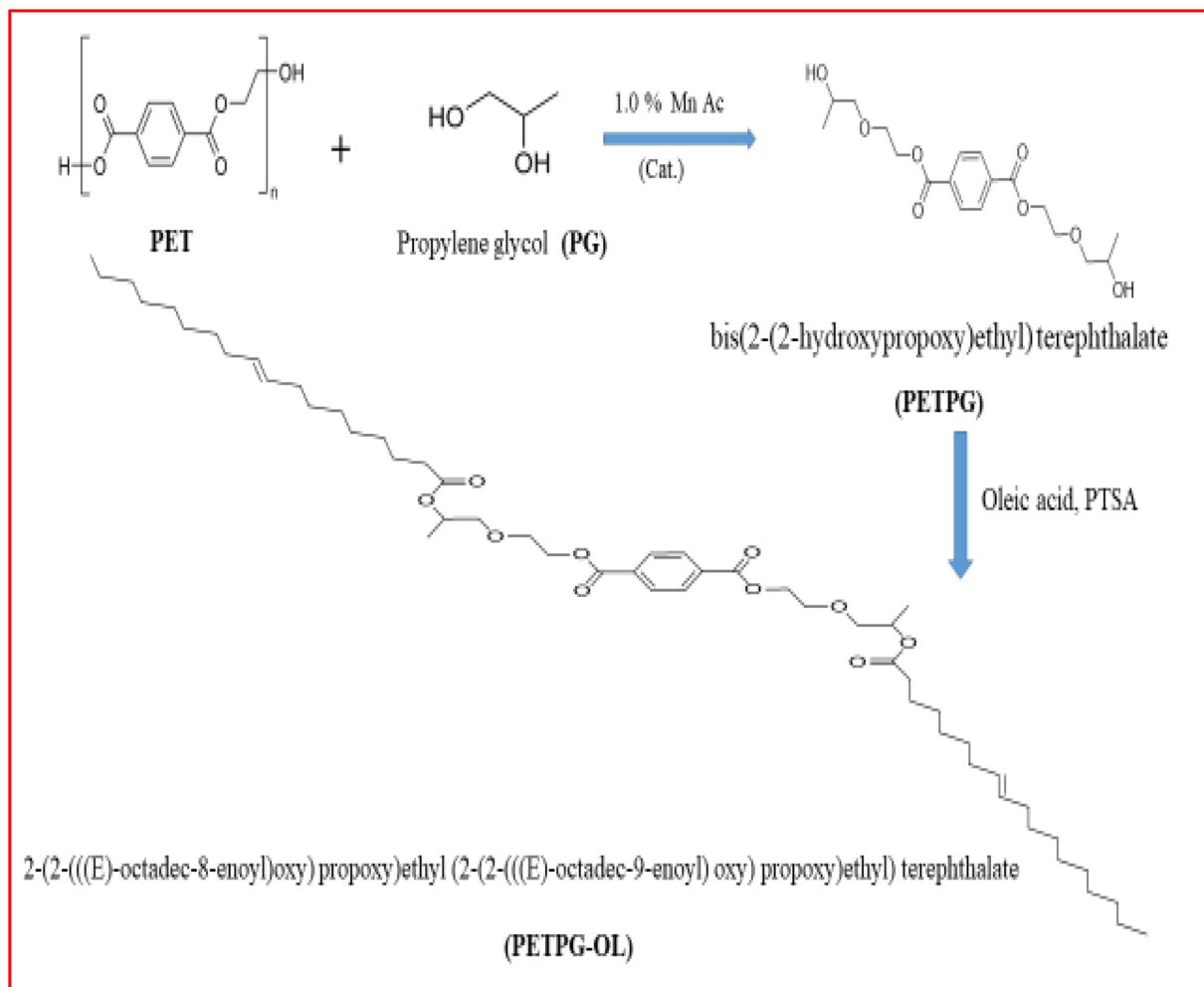


Fig. 2 Chemical structure of the prepared non-ionic polymeric surfactant (PETPG-OL) inhibitor compound, and scheme 2 of the glycolysis process.

2.7.2. Atomic absorption spectroscopy (AAS) (analytical technique). Atomic absorption spectroscopy was utilized to quantify the concentration of iron in corrosive solutions, both in the absence and presence of the employed inhibitor (AAS) at 303 K as the experimental temperature. Atomic absorption spectroscopy on a Varian Spectra AA 220 was used to concentrate the ferric ions introduced into the solution. We dissolved the corrosive medium with aqua regia in order to measure the amounts of iron in the corrosive solution, both when the inhibitor was absent and present.^{34–39}

2.8. Thermometric measurements

The carbon steel sheet was press cut $2 \times 2 \times 0.1$ cm with chemical composition as mentioned in Table 1. The measurements were carried out in a Dolvacpyrex flask covered with aluminum foil. The reaction vessel consisted of 50 ml of the test solution placed into the flask covered with aluminum foil, corked using a Check temp digital thermometer in place. The metal coupon was introduced into the corrosive solution and was quickly covered. Thermometric measurements depend on

measuring the temperature variation during the reaction of a metal with a test piece with a definite volume of a corroding solution.^{34–39} The variation in the temperature of the system was monitored with time, and the reaction number (RN) is defined as^{34–39}

$$\text{RN } (^{\circ}\text{C min}^{-1}) = (T_m - T_i)/t_m \quad (4)$$

where T_m and T_i are the maximum and initial temperatures, respectively, t_m is the time in minutes taken to attain the maximum temperature.

2.9. Open-circuit potential measurement

At 30 °C, the potential of the carbon steel electrode was measured in 3.5% NaCl solution against a saturated calomel electrode (SCE) in the absence and presence of varying amounts of the employed inhibitor. The multi-tester was used for all measurements until the steady-state potentials were attained.



2.10. Potentiodynamic polarization measurements (electrochemical studies)

The tests were carried out utilizing the radiometer analytical, Volta master for all electrochemical measurements (PGZ301, Dynamic Els Voltammetry). A platinum wire counter electrode is employed. Calomel is used as a reference electrode because it is a standard and all potential is attributed to it. In addition, as a working electrode, a steel cylindrical electrode (1 cm² in area) is used. Silicon carbide abrasive sheets of grades 600, 1000, 1200, 1500, and 2000 are used to abrade and clean it. The electrode was then rinsed with distilled water, degreased with ethyl alcohol, cleaned with water, and dried to be ready to serve as a functioning electrode. Before each experiment, this protocol was followed. For 50 minutes, the working electrode was immersed in the corrosive solution. The electrical scanning is done at a 1 mV s⁻¹ scan rate. Using the following mathematical equation the inhibition efficiency percent IE% and surface coverage (θ) were computed.¹⁶⁻¹⁹

$$IE (\%) = ([I - I_0]/I) \times 100 \quad (5)$$

$$\theta = ([I - I_0]/I) \quad (6)$$

where I and I_0 are the corrosion current densities in the absence of inhibitors and in the presence of inhibitors, respectively. The corrosion potential (E_{corr}), corrosion current (I_{corr}), and Tafel constants (β_a and β_c) were computed and tabulated using the values of the cathodic and anodic Tafel slopes obtained from the Tafel plot.

2.11. Electrochemical impedance measurements (electrochemical studies)

A three-electrode assembly with calomel as a reference electrode, platinum wire as a counter electrode, and carbon steel specimens with an exposed surface area of 1 cm² as a working electrode were used in the electrochemical studies. Impedance responses were measured at an open circuit potential (frequency range: 10–100 kHz, 5 mV amplitude). All tests and measurements were conducted at room temperature in a motionless or unstirred environment. The inhibitory efficiency was calculated using charge-transfer resistance, which is represented as R_p in the Nyquist plots' impedance data.⁶⁵⁻⁷¹

The inhibition efficiency was determined using the charge-transfer resistance, which is labeled as R_{ct} in the Nyquist plots' impedance data, as follows:⁶⁵⁻⁷¹

$$IE (\%) = [(R_{\text{ct}} - R_{\text{ct}0})/R_{\text{ct}}] \times 100 \quad (7)$$

The charge transfer resistance with an inhibitor is R_{ct} , while the charge transfer resistance without the inhibitor is $R_{\text{ct}0}$.

2.12. Scanning electron microscope (SEM)

The surface morphology of the carbon steel was examined before and after treatment using scanning electron microscopy (SEM). Scanning electron microscopy was used to obtain information on the changes that occurred on the surface of the corrosive samples before and after the addition of the selected inhibitors. The specimens were first immersed in 3.5% NaCl solutions in the absence and presence of optimal concentrations (200 ppm) of the tested compounds for 48 h at room temperature, then taken out from the test solutions, cleaned with bi-distilled water and acetone, and dried with cool air. The SEM images were collected using a JEOL, model JSM-53000, scanning electron microscope (SEM).

3 Results and discussion

3.1. Chemistry of the synthesis process (the recycling process)

Polyethylene terephthalate plastic waste PET was subjected to degradation depolymerization with both ethylene di amine EDA and propylene glycol PG to produce the corresponding amide and ester. Both the produced amide and ester were separately reacted with oleic acid to produce the corresponding oleic acid ester and the details of the chemistry of the synthesis procedures are described in detail as follows.

3.1.1. Synthesis of (N1,N4-bis(2-((E)-octadec-9-enamido)ethyl)terephthalamide), (PETAA-OL). Polyethylene terephthalate (PET) (1% w/w) and a tri-molecular ratio of ethylene diamine (EDA) (3% w/w) were refluxed for 6 hours at temperature (190–200 °C), as indicated in Section 2.2. The reaction proceeded in the presence of a co-catalyst comprising 1.0% sodium acetate as a catalyst and 1.0% acetic acid as a co-catalyst (W% from the total weight of the reactants).⁴⁻⁶ Saline water was added to the reaction mixture after it had been cooled to 100 °C and brought to room temperature in order to remove the bi-

Table 3 Elemental analysis and composition of the resulting compounds

Compound	Analysis	Molecular Formula (Mol. F)	Molecular Weight (Mol. wt)	C%	H%	N%	O%
PETAA	Calculated	C ₁₂ H ₁₈ N ₄ O ₂	250.4	54.6	7.2	22.4	22.2
	Found		294.6	53.8	6.9	20.8	21.6
PETAA-OL	Calculated	C ₄₈ H ₈₂ N ₄ O ₄	779.21	74.3	10.8	7.9	8.5
	Found		778.63	73.99	10.61	7.19	8.21
PETPG	Calculated	C ₁₈ H ₂₆ O ₈	370.40	58.37	7.08	0.0	34.56
	Found		370.16	85.35	7.02	0.0	34.57
PETPG-OL	Calculated	C ₅₄ H ₉₀ O ₁₀	899.30	72.12	10.09	0.0	17.79
	Found		898.65	72.08	10.01	0.0	17.79



product glycol. The result was a yellowish, viscous residue, which was further purified using column chromatography. Fig. 1 depicts the product's chemical makeup and the synthesis method in the diagram form. The obtained **PETAA** compound was reacted with oleic acid in the presence of sodium acetate as a catalyst and acetic acid as a co-catalyst in the presence of *p*-toluene sulfonic acid and refluxed for 7 hours in xylene until the calculated amount of water was produced. The schematic of the complete synthesis process is shown in Fig. 1. The reaction produces the corresponding oleic acid phthalimide compound, (*N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide); this compound is designated as (**PETA-OIL**) and used as a corrosion inhibitor for carbon steel in marine corrosive environments. Fig. 1 shows the chemical structure of the nonionic surfactant (**PETA-OL**) inhibitor molecule and a schematic of the synthesis process (Table 3).

3.1.2. Synthesis of 2-(2-(((*E*)-octadec-8-enoyl)oxy)propoxy)ethyl (2-(2-(((*E*)-octadec-9-enoyl)oxy)propoxy)ethyl) terephthalate (PETPG-OL**).** Polyethylene terephthalate (PET) (1% w/w) and a tri-molecular ratio of propylene glycol (PG) (3% w/w) were refluxed for 6 hours at 190–200 °C, as indicated in Section 2.3. The reaction proceeded in the presence of anhydrous manganese acetate ((CH₃COO)₂Mn) as a transesterification catalyst (1% by weight compared to the total weight of the reactants.^{4–6} Hot saline water was added to the reaction mixture after it had been cooled to 100 °C and brought to room temperature in order to remove bi-product glycol. The result was a white gelatinous residue, which was further purified using column chromatography. Fig. 2 depicts the product's chemical compounds and the synthesis method in the diagram form. The obtained **PETPG** compound was reacted with oleic acid in the presence of sodium acetate as a catalyst and acetic acid as a co-catalyst in the presence of *p*-toluene sulfonic acid and refluxed for 7 hours in xylene until the calculated amount of water was produced. The schematic diagram of the full synthesis process is shown in Fig. 2. The reaction produces the corresponding oleic acid ester compound, 2-(2-(((*E*)-octadec-8-enoyl)oxy)propoxy)ethyl (2-(2-(((*E*)-octadec-9-enoyl)oxy)propoxy)ethyl) terephthalate. The prepared compound in this step was designated as **PETPG-OL** and used as the corrosion inhibitor for carbon steel in 1.0 M HCl corrosive environment. Fig. 2 shows the chemical structure of the nonionic surfactant inhibitor molecule (**PETPG-OL**) and the scheme of the synthesis process.

3.2. Spectroscopic characterization of the prepared polymeric compounds

The four prepared polymeric surfactant compounds were characterized using FT-IR, ¹HNMR, and elemental analysis as follows.

3.2.1. Spectroscopic characterization of the PETAA compound. IR spectroscopy was used to identify the characteristic functional groups in the organic and inorganic materials, in the reported works the frequency scaling factors for the stable configuration were calculated theoretically by scaling the IR spectrum.⁷³ The prepared PETAA compound with the IUPAC name *N*1,*N*4-bis(2-aminoethyl)terephthalamide was elucidated

using FT-IR and ¹HNMR. The resulting IR spectra of this compound show strong bands at 3421–3274 cm⁻¹ (NH₂, NH), 2830–2950 cm⁻¹ (C–H methylene groups), and 1665 (C=O) cm⁻¹. The products' end group with amino groups is indicated by the appearance of a prominent band at 3421 cm⁻¹ in the spectra. On the other hand, the band seen at 810 cm⁻¹ for all the depolymerized PET is attributed to *p*-substituted phenyl's –CH out-of-plane bending. This band verifies that the depolymerized materials include phenyl rings. Strong peaks at 1745 cm⁻¹, which are attributed to the amide group C=O stretching, show that all depolymerized PET products contain the amide functional group.

¹HNMR provides additional support for PET products with ethylene diamine (EDA). In this regard, the **PETAA** spectra display signals at chemical shifts of 8 ppm and 4.5 ppm, which stand for the *p*-substituted phenyl group and COOCH₂CH₂O–H of the generated PET. The signal at 6.93 ppm was also observed (s, NH). The product made from PET waste contained active amino amide groups, according to the results of FT-IR and ¹HNMR analysis.

3.2.2. Spectroscopic characterization of the PETAA-OL compound. The prepared PETAA-OL compound resulted from the reaction between oleic acid and the PETAA compound, which was obtained as described in the previous section (3.2.1). The IUPAC name of this compound was suggested to be (*N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide) based on its FT-IR and ¹HNMR data.

The resulting IR spectra of this compound show the disappearance of the strong band at 3421 cm⁻¹ (NH₂) due to the change of the terminal (NH₂) into amide (CONH) through the reaction with the carboxylic group of the oleic acid, which was confirmed from the presence of the strong absorption band at V cm⁻¹, 3274 (NH), and band at V cm⁻¹, 1665 (CO), indicating the presence of the amide linkage in the PETAA-OL compound. Proton nuclear magnetic resonance ¹HNMR of the prepared PETAA-OL compound provided additional support. ¹HNMR spectra displayed signals at chemical shifts of 8 ppm and 4.5 ppm, which represent the *p*-substituted phenyl group and COOCH₂CH₂O– of the generated PET. The 8.3 ppm signal was observed (s, NH). The signal at 5.4 ppm was observed (d, HC=CH) for the unsaturated double bond of the oleic acid reacting backbone. In addition, to the appearance of (m, CH₂) signals at (1.28, 1.3, 1.33, and 2.16), all observations proved that the product compound made from PETAA and oleic acid was the PETAA-OL compound of IUPAC name (*N*1,*N*4-bis(2-((*E*)-octadec-9-enamido)ethyl)terephthalamide), as shown in Fig. 1. This confirmation was based on the synthesis procedure and the results of the FT-IR and ¹HNMR analysis.

3.2.3. Spectroscopic characterization of PETPG compound. The compound symbolized PETPG, prepared by recycling of PET with propylene glycol PG with the suggested IUPAC name of bis(2-(2-hydroxypropoxy)ethyl) terephthalate; its structure was confirmed by FT-IR and ¹HNMR analysis.

A significant broad band appeared in the IR spectrum at 3350 cm⁻¹, (OH), which is a characteristic band of the terminal hydroxyl group (OH) with the presence of bands at 2900 cm⁻¹ and 1100 cm⁻¹ (aliphatic groups) with the significant sharp



band at 1740 cm^{-1} and 1171 cm^{-1} ($\text{C}=\text{O}$, $\text{C}-\text{O}$ ester group). The $^1\text{H NMR}$ spectrum of the resulting PETPG compound displayed signals at chemical shifts of 8 ppm and 4.5 ppm, which are for the *p*-substituted phenyl group and $\text{COOCH}_2\text{CH}_2\text{O}-$ of the generated PET. The signals at 5.3 ppm (s, OH), and 1.11 ppm (t, CH_3 terminal) were seen and signals at 3.9 ppm (s, CH), and 3.8, 4.7 ppm were for the m, $-\text{O}-\text{CH}_2\text{CH}_2-\text{C}=\text{O}$, methylene groups.

3.2.4. Spectroscopic characterization of the PETPG-OL compound. The compound symbolized as PETPG-OL derived from the reaction of oleic acid with the PETPG compound prepared as described in the previous step (Section 3.2.3) was characterized by FT-IR, $^1\text{H NMR}$ spectroscopic analysis. The IR spectrum of this compound showed the disappearance of the broad band at 3350 cm^{-1} due to the incorporation of a hydroxyl group in the reaction with the carboxylic acid group of the oleic acid molecule, forming the corresponding ester group with bands appearing at 1740 cm^{-1} and 1115 cm^{-1} ($\text{O}=\text{C}-\text{O}-\text{C}$). The $^1\text{H NMR}$ analysis of the PETPG-OL compound showed the disappearance of the 5.3 signal (s, OH), proving the incorporation of the (OH) group in the formation of the ester group when it reacted with oleic acid in the presence of PTSA. The presence of a signal at 5.4 ppm (d, $\text{HC}=\text{CH}$) indicated the unsaturated

double bonds for the oleic acid reacting backbone. In addition, to the appearance of (m, CH_2) signals at (2.16, 1.29, 1.33, 1.66, and 2.35) for ($\text{HC}=\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$). All these observations prove that the product compound made from PETPG and oleic acid is the PETPG-OL compound of IUPAC name 2-(2-(((*E*)-octadec-8-enoyl)oxy)propoxy)ethyl (2-(2-(((*E*)-octadec-9-enoyl)oxy)propoxy)ethyl) terephthalate, as shown in Fig. 2. This confirmation suggestion was based on the synthesis procedure and the results of the FT-IR and $^1\text{H NMR}$ analysis.

3.3. Corrosion protection of steel substrate using synthesized materials

The four prepared polymeric surfactants (PETAA-OL, PETAA, PETPG-OL, and PETPG) of nonionic type were applied for the protection of steel substrate in the marine environment. For the evaluation of the inhibition performance of the prepared surfactants towards the carbon steel substrate, chemical, analytical, and electrochemical techniques were used. The chemical techniques (weight loss method) were used for studying the effect of all inhibitor's concentrations range (50–200 ppm). Atomic absorption spectroscopy (AAS) and thermometric measurements as the analytical techniques were used for

Table 4 Effect of the inhibitor concentrations on steel corrosion characteristics in 3.5% NaCl solutions determined by weight loss measurements at 303 K

Type of surfactant inhibitors	Glycol-based polymer				Amide-based polymers			
	PETPG		PETPG-OL		PETAA		PETAA-OL	
	IE (%)	θ	IE (%)	θ	IE (%)	θ	IE (%)	θ
Blank	—	—	—	—	—	—	—	—
50	81.9	0.819	83.5	0.835	85.3	0.853	87.6	0.876
100	82.3	0.823	84.5	0.845	87.4	0.874	89.8	0.898
150	83.4	0.834	85.3	0.853	89.6	0.896	91.2	0.912
200	84.5	0.845	86.2	0.862	90.7	0.907	92.3	0.923

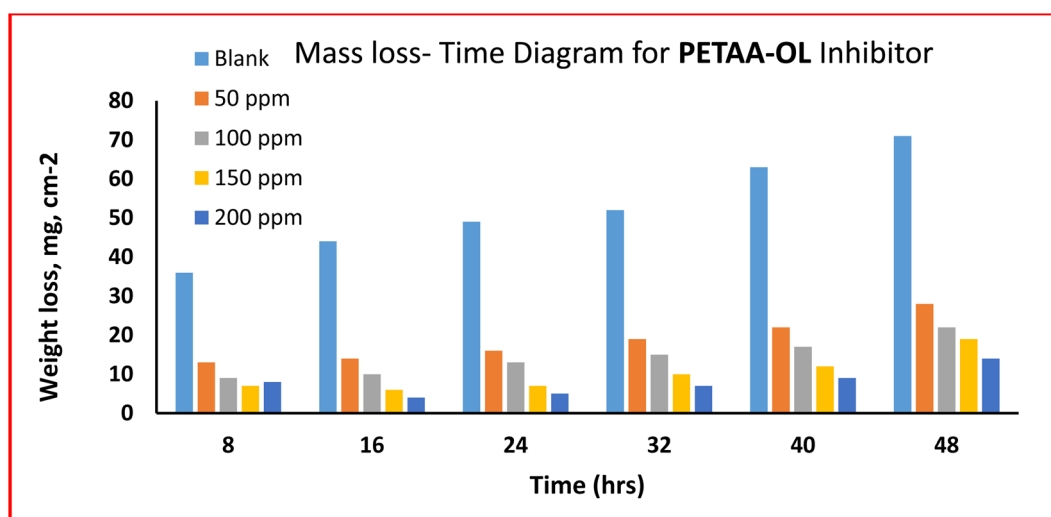


Fig. 3 Weight loss of steel in 3.5% NaCl over time in the presence and absence of the prepared polymeric surfactant (PETAA-OL) inhibitor derived from the plastic waste.



the evaluation of different concentrations (50–200 ppm) from the four prepared polymeric surfactant materials (**PETAA-OL**, **PETAA**, **PETPG-OL**, and **PETPG**). From the results of the chemical and analytical techniques, it was concluded that the order of corrosion inhibition performance of the four prepared nonionic polymeric surfactants was **PETAA-OL** > **PETAA** > **PETPG-OL** > **PETPG**. The effect of temperatures (30, 40, 50, and 60 °C) on the corrosion inhibition efficiency was also studied using a 200 ppm inhibited solution from the four prepared materials. Finally, the electrochemical techniques (potentiodynamic polarization (**PDP**), open circuit potential (**OCP**), and electrochemical impedance spectroscopy (**EIS**), as accurate, fast, and high-performance techniques, were used for the evaluation of the efficiency of the esterified amide derivative (**PETAA-OL**) towards the protection of the steel substrate used in the manufacture of the petroleum pipelines, in the petroleum industry.

3.3.1. Weight loss measurements (chemical measurements). The loss in the weight of the steel materials (compounds) in the presence and absence of the different concentrations (50–200 ppm) from the four prepared nonionic polymeric surfactants (**PETAA-OL**, **PETAA**, **PETPG-OL**, and **PETPG**) were studied using the mass loss method.^{16–19} A sodium chloride solution of 3.5% concentration as an artificial seawater was used as the blank solution, which causes the corrosion of steel materials in the marine environment. Table 4 illustrates the surface coverage (θ), corrosion rate, and corrosion inhibition efficiency of the four prepared nonionic polymeric surfactant materials (**PETAA-OL**, **PETAA**, **PETPG-OL**, and **PETPG**) at four selected concentrations (50, 100, 150, and 200 ppm). The corrosion rate, corrosion inhibition efficiency, and surface coverage (θ) were calculated using the mathematical formulas (eqn (1)–(3)) respectively. From Table 4, we can conclude that

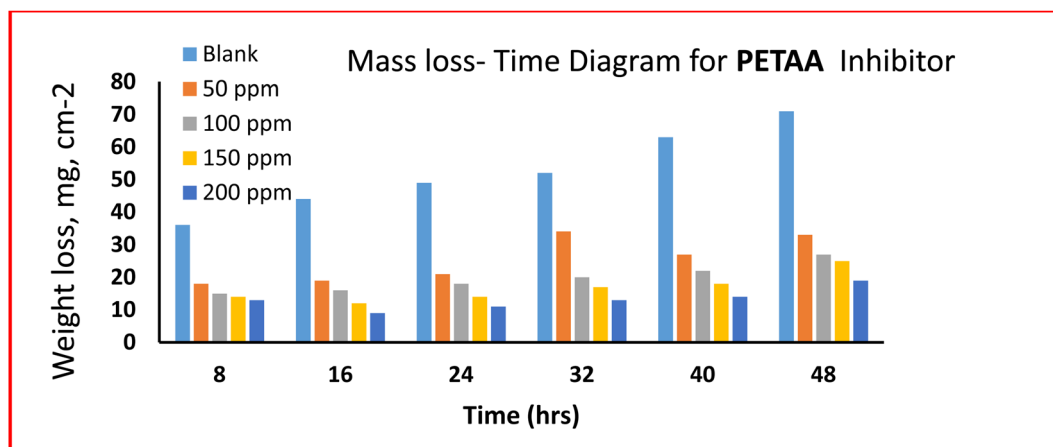


Fig. 4 Weight loss of steel in 3.5% NaCl over time with and without the presence of a polymeric surfactant (PETAA) inhibitor derived from plastic waste.

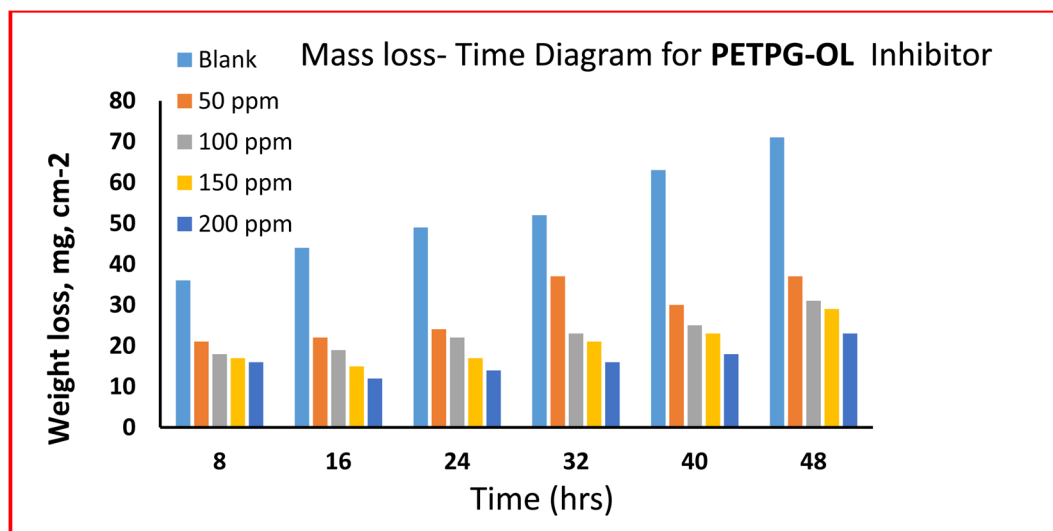


Fig. 5 Weight loss of steel in 3.5% NaCl over time with and without the presence of a polymeric surfactant (PETPG-OL) inhibitor derived from plastic waste.



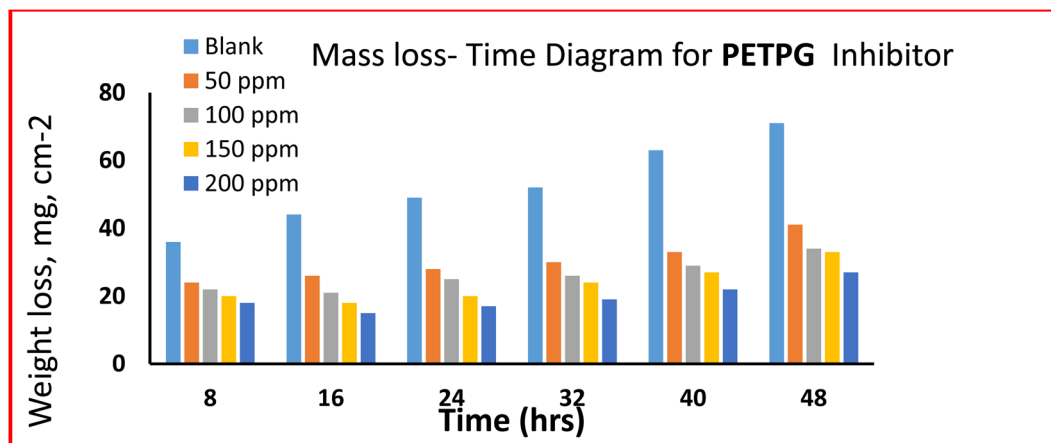


Fig. 6 Weight loss of steel in 3.5% NaCl over time with and without the presence of a prepared polymeric surfactant (PETPG) inhibitor derived from plastic waste.

the inhibition efficiency of all the prepared materials was found to increase upon increasing the inhibitor concentrations, reaching a maximum inhibition efficiency of 93% at 200 ppm of the (PETA-OIL) inhibitor. The observed inhibition efficiency in the case of amide-based inhibitor compounds (PETAA-OL and PETAA) is more than the inhibition efficiency in the case of glycol-based inhibitor compounds (PETPG-OL and PETPG). From Table 4, it is concluded that the order of corrosion inhibition performance of the four prepared nonionic polymeric surfactants is: PETAA-OL > PETAA > PETPG-OL > PETPG. This observation may be due to the strong linkage formed between the amide bond and the steel surface.¹⁻⁵ Fig. 3–6 depict the weight loss of steel in 3.5% NaCl as the artificial seawater over time in the presence and absence of four-prepared polymeric surfactant inhibitor materials derived from the recycling of PET plastic waste. As shown in Fig. 3–6, the weight loss of steel materials increased due to the corrosion process with a time of immersion in the corrosive environment; this observation was

for both blank and inhibited solutions as well. The corrosion rates increase as the immersion time increases but decrease as the inhibitor concentration increases. The efficiency of the corrosion inhibition improves as the concentration of inhibitors rises. The inhibition of the prepared nonionic polymeric surfactants due to the adsorption, adhesion, and passive layer generation on the steel surface, the formed passive layer protecting the steel against corrosion in the marine corrosive environment.¹⁶⁻¹⁹

3.3.2. Effect of temperature. Fig. 7 shows the temperature inhibition relationship for the 200 ppm from the four prepared nonionic polymeric surfactant materials. To understand the inhibitory mechanism and determine the kinetic parameters of the corrosion process, gravimetric (weight loss) measurements were taken at different temperatures, 303, 313, 323, and 333 K. The percentage of steel that is inhibited in the presence of the inhibitor is graphically depicted in Fig. 7, and as observed, it is affected by temperature, indicating that the protective film of

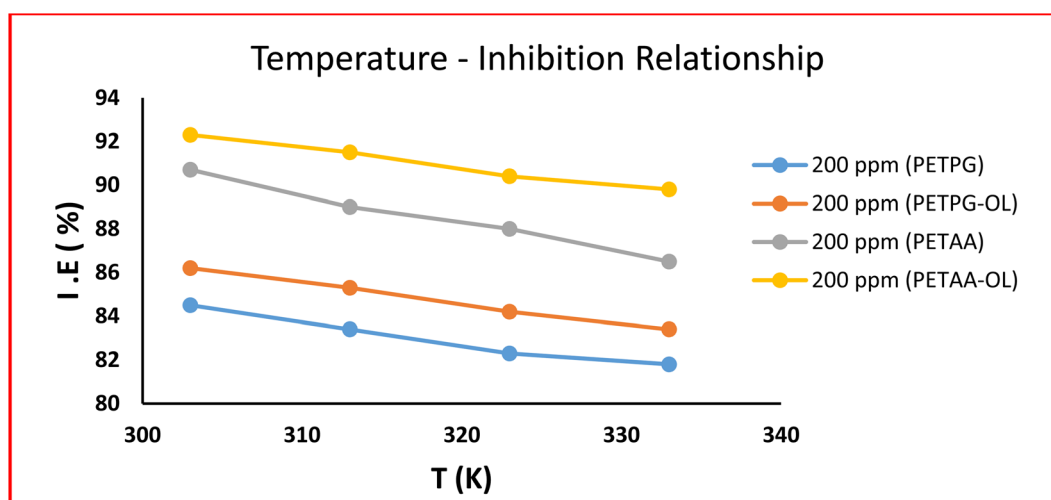


Fig. 7 Weight loss data at 200 ppm of the four studied inhibitor polymeric surfactant materials derived from plastic waste and the effect of temperature on the percent I.E. for steel in 3.5% NaCl solution.



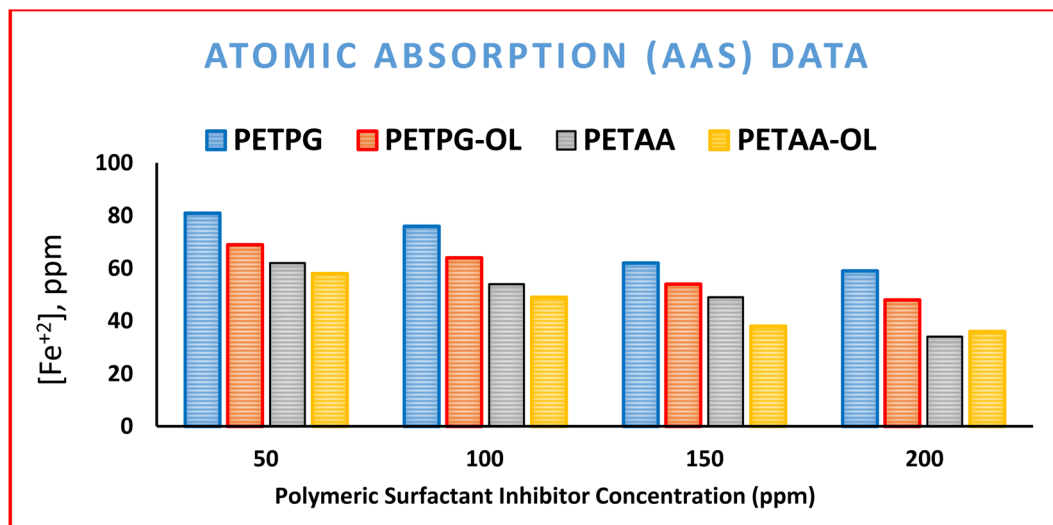


Fig. 8 Effect of four prepared polymeric surfactant inhibitor concentrations on ferrous ion concentration $[\text{Fe}^{2+}]$ in the presence of 3.5% NaCl solution, as measured by atomic absorption spectroscopy (AAS).

these compounds generated on the surface of the steel is less stable at higher temperatures. It is evident that the IE% values declined as the temperature increased. This might be because more of the metal was exposed to the corrosive environment at higher temperatures because certain molecules that were adsorbed desorbed from the surface of the steel.^{16–19}

3.4. Analytical measurements

3.4.1. Atomic absorption spectroscopy (AAS). The AAS technique was used to determine the concentrations of Fe ions in mineral waters and natural waters.^{34–36} The iron ions released into the solution as a result of corrosion were immediately identified using atomic absorption spectroscopy, and their concentration was calculated using a calibration curve. High salinity, falling pH, chloride ion presence, and temperature accelerated the corrosion of iron samples in the solution.^{34–36} When iron is exposed to oxygen, humidity, and chloride ions, a complex process known as iron corrosion occurs. Following the characteristics of the corroding material allows the calculation of the societal costs of the corrosion of iron structures or

other components.^{34–36} The current study employed atomic absorption spectroscopy to determine the concentrations of ferrous ions Fe^{2+} produced due to the corrosion of steel by 3.5% NaCl. The ions flowing into the solution were concentrated using AAS to determine the amount of ferrous ions in the corrosive solution when the green inhibitor was absent or present. According to the AAS data shown in Table 4 and Fig. 8, the ferrous ion Fe^{2+} concentrations in the corrosive medium decreased with increasing inhibitor concentration. The concentration of ferrous ions in the solution is modeled as a function of the corrosion rate, in this case, as a result, as the concentration of ferrous ions in the solution increases, so does the corrosion rate, and *vice versa*. Every step is affected by the addition of an inhibitor. From Table 5 it can be seen that the concentration of ferrous ions in the corrosive solution was found to decrease by increasing the inhibitor concentrations. The observed ferrous ion concentration in the case of amide-based inhibitor compounds (PETAA-OL and PETAA) is lower than that of the observed ferrous ion concentrations in the case of glycol-based inhibitor compounds (PETPG and PETPG-OL). The lowest ferrous ions concentrations were observed in the

Table 5 Effect of concentrations of the polymeric surfactant inhibitors on the ferrous ion concentrations as a result of atomic absorption spectroscopy (AAS) due to steel corrosion in 3.5% NaCl

Kind of surfactants inhibitors	Glycol-based polymer		Amide-based polymers	
	PETPG	PETPG-OL	PETAA	PETAA-OL
Concentrations (ppm)	Ferrous ion concentrations $[\text{Fe}^{2+}]$, ppm			
Blank	162	149	143	139
50	81	69	62	58
100	76	64	54	49
150	62	54	49	38
200	59	48	34	36

Table 6 Thermometric parameters for the carbon steel corrosion in 3.5% NaCl solution in the presence of four nonionic polymeric surfactant inhibitors compounds

Types of surfactant inhibitors	Glycol-based polymer		Amide-based polymers	
	PETPG	PETPG-OL	PETAA	PETAA-OL
Thermometric Parameters				
T_m , °C	43	41	39	37
t_m , min	319	365	380	398
RN, °C/min	0.0407	0.0301	0.0237	0.0176
RR (%)	90	91	93	94
Δt_m	297	343	368	397



case of amide-based nonionic polymeric surfactant material (PETAA-OL) inhibitor compound. The data in Table 5 show that the results of the two gravimetric approaches (weight loss method and ASS method) are in good agreement, demonstrating that the addition of prepared inhibitor materials inhibits steel corrosion in a marine environment and reduces the iron dissolution process.

3.4.2. Thermometric measurements (analytical technique).

Reaction number (RN) values are known as a relative measure of the retardation of the dissolution process.^{34–37} The extent of corrosion inhibition can be expressed in terms of the percentage reduction in the reaction number (RR%) given by the following equation.^{34–37}

$$\% \text{RR} = \frac{\text{RN uninhibited} - \text{RN inhibited}}{\text{RN uninhibited}} \times 100 \quad (8)$$

The thermometric parameters and inhibition efficiency are summarized in Table 6. The inhibition efficiency and Δt_m increased upon increasing the inhibitor concentrations. The reduction in the reaction number and time delay (Δt_m) of the four studied polymeric surfactant inhibitor materials increased in the case of amide-based inhibitors than in glycol-based inhibitors and it followed the order PETAA-OL > PETAA > PETPG-OL > PETPG. This observation agrees well with the data obtained from both mass loss measurement and atomic absorption spectroscopy (AAS). Meaning that the data of different studied techniques are in good agreement with each other to prove the good protection efficiency of the four prepared nonionic polymeric surfactants towards the steel surface.

3.5. Adsorption of polymeric materials on the steel surface

The adsorption behavior of the inhibitor materials on the metal substrate is a function of the protection and inhibition performance. The protection of steel from corrosion in the corrosive

environment is due to the adsorption and adhesion of inhibitor molecules on the steel surface, forming a barrier layer. The charge and type of the metal surface, its electronic properties, the adsorption of solvent and other ionic species, the temperature at which corrosion occurs, and the electrochemical potential at the solution interface are the primary factors influencing the adsorption process. The inclusion of the electro-repelling or electro-donating groups in derivatives. Adsorption of the four studied inhibitor materials on the steel surface was studied using the weight loss data.

The calculated values of the surface coverage (θ) at various inhibitor concentrations were used to explain the best fit isotherm for the adsorption process. The Langmuir adsorption isotherm best fits the results, according to the following equation:^{45–64}

$$C_i/\theta = 1/K_{\text{ads}} + C_i \quad (9)$$

where K and C are the equilibrium constant and the inhibitor concentration of the adsorption process, respectively.^{45–64} The straight line obtained by plotting C_i/θ vs. C_i is shown in Fig. 9. $1/K$ is the intercept of the line with an approximately unit slope. The standard free energy of adsorption ΔG_{ads} is calculated using the following equation:^{44–46}

$$K_{\text{ads}} = 1/55.5 \exp(-\Delta G_{\text{ads}}/RT) \quad (10)$$

where T is the absolute temperature, R is the gas constant, and the majority of the solution per litre contains 55.5 moles of water. The adsorption equilibrium constant is denoted by K_{ads} . In the case of amide-based polymeric surfactant material (PETAA-OL) inhibitor, the ΔG_{ads} was calculated to be $-37.46 \text{ kJ mol}^{-1}$. The absence of a positive value for ΔG_{ads} indicates that inhibitor molecules were adsorbed spontaneously on the metal surface.^{44–46} However, the obtained value was less than the -40 kJ mol^{-1} the threshold value required for

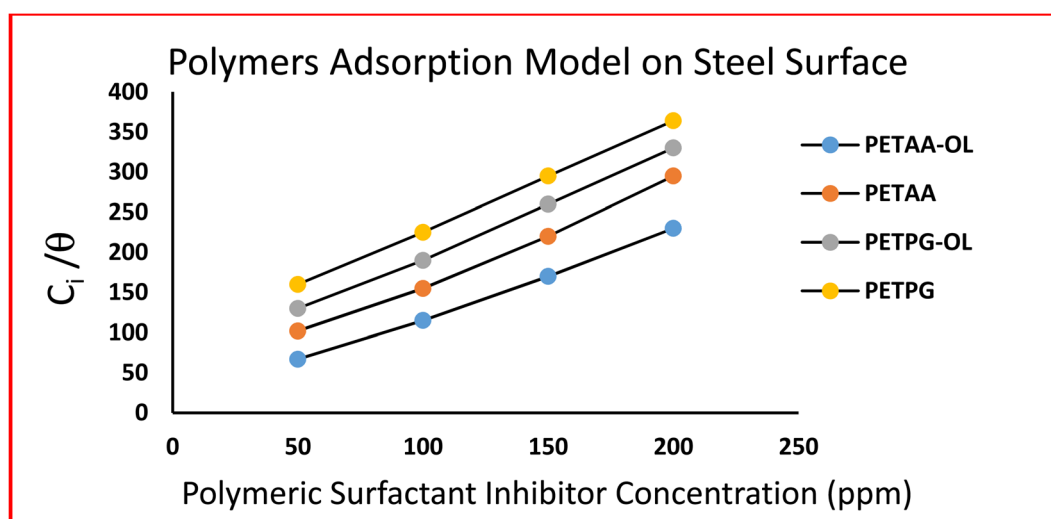


Fig. 9 Langmuir adsorption isotherm model for the adsorption of the four prepared polymeric surfactant inhibitors on the steel surface immersed in 3.5% NaCl solution at 30 °C.



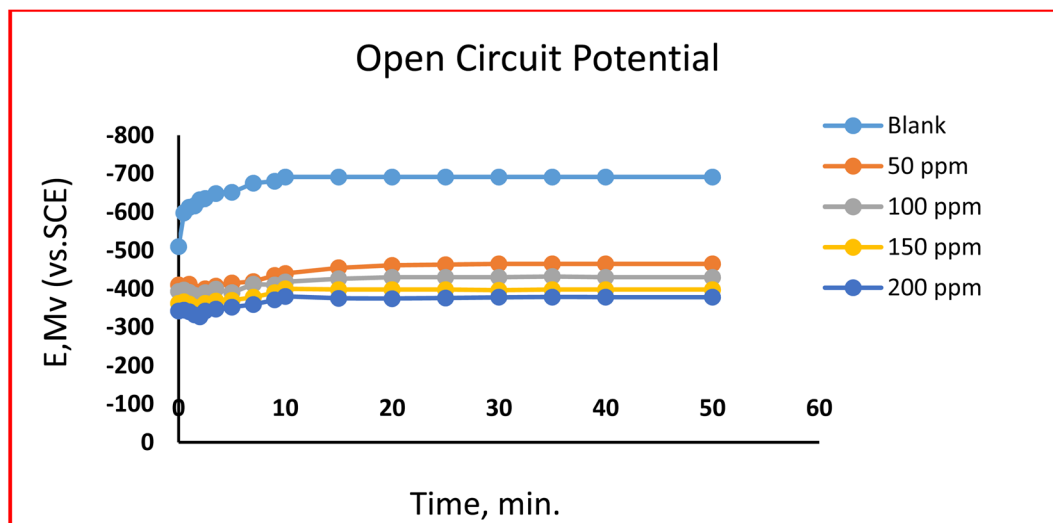
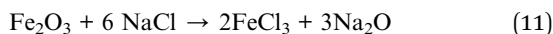


Fig. 10 Potential–time curves for carbon steel immersed in 3.5% NaCl solution in the absence and presence of nonionic surfactant inhibitor (PETA-OL).

chemical adsorption, indicating that the adsorption mechanism is physical.^{16–19} The investigated compound is widely acknowledged to inhibit corrosion by adhering to the metal/solution contact. Furthermore, it is believed that the development of a solid organic molecule complex with a metal atom has piqued the interest of many.^{45–64}

3.6. Open-circuit potential measurements

Fig. 10 shows the relation between the open-circuit potential (OCP) and time of the immersion for the blank solution and inhibited solution of different concentrations (50, 100, 150, and 200 ppm) of the nonionic polymeric surfactant compound (PETA-OL) prepared from the recycling of PET plastic waste. The steady state was observed after 50 min of immersion time. The potential of a steel electrode immersed in 3.5% NaCl solution (blank curve) clearly moves to a higher negative potential first, resulting in a short step. According to the equation:^{16–19}



Following this, a new oxide film forms within the solution, shifting the potential back to a more noble direction until a steady-state potential is reached. When inhibitor molecules are added to the aggressive medium, the cathodic reaction is

slowed, resulting in a negative shift in the open-circuit potential.^{16–19}

3.7. Potentiodynamic polarization measurements (PDP)

Electrochemical techniques (potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS)), as accurate, fast, and high-performance techniques, were used for the evaluation of the efficiency of the esterified amide derivative (PETAA-OL) towards the protection of the steel substrate used in the manufacturer of the petroleum pipelines, in the petroleum industry. Potentiodynamic polarization curves were used to investigate the components of the corrosion inhibition process that caused an anodic/cathodic process change. Table 7 lists the parameters that were estimated. The polymeric surfactant inhibitor compound (PETA-OL) was shown to have an excellent ability to form a surface coating on the steel surface *via* adsorption. Inhibitors can alter the process by slowing down the rate of corrosion. The corrosion current density and potential were determined from the intersection of the anodic and cathodic curves. When compared to a blank, E_{corr} tended toward the value in the presence of an inhibitor, but no discernible difference was found (Fig. 11). As a result, the nonionic surfactant inhibitor compound (PETA-OL) functions as a mixed-type. The I_{corr} values decreased as the concentrations

Table 7 Potentiodynamic (PDP) characteristics for the carbon steel corrosion in 3.5% NaCl solution at 303 K with and without different dosages of nonionic polymeric surfactant (PETA-OL) inhibitor

Solution type	Solution concentration, ppm	I_{corr} , mA cm ⁻²	$-E_{\text{corr}}$, mV (SCE)	β_a , mV dec ⁻¹	β_c , mV dec ⁻¹	θ	IE, %
Blank solution	Free	1.45	489	113	134	—	—
Inhibitor solution	50	0.19	572	147	161	0.869	86.9
nonionic polymeric surfactant (PETA-OL)	100	0.17	579	158	172	0.883	88.3
	150	0.14	576	163	177	0.903	90.3
	200	0.11	574	168	185	0.924	0.924



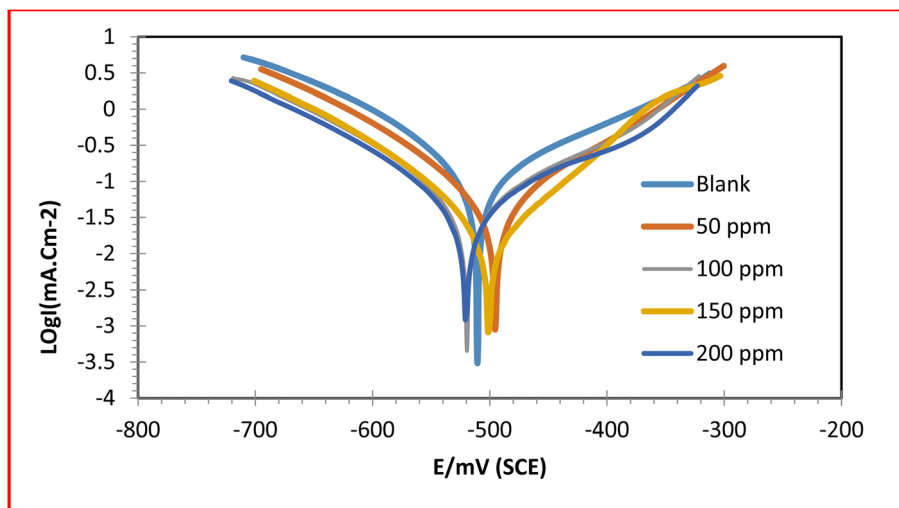


Fig. 11 Steel potentiodynamic polarization (PDP) curves with various concentrations of the prepared nonionic surfactant (PETA-OL) inhibitor derived from plastic waste at 30 °C in 3.5% NaCl solution.

of the inhibitor polymeric surfactants were increased, indicating that the formation of a shield on the carbon steel surface in the presence of inhibitors impedes electrochemical processes.^{65–71}

3.8. Electrochemical impedance spectroscopy, EIS, (electrochemical studies)

Electrochemical impedance spectroscopy (EIS) is an accurate, fast, and powerful tool for investigating corrosion, and inhibitory mechanisms. Electrochemical impedance spectroscopy (EIS) with and without polymeric surfactant inhibitor was used to investigate corrosion inhibition at various concentrations of nonionic surfactant inhibitor (PETA-OIL). The electrical resistance of the steel electrode immersed in 3.5% sodium chloride corrosive solution was measured using different concentrations (50, 100, 150, and 200 ppm) from the amide-based surfactant compound (PETA-OIL), and the obtained EIS data are tabulated and discussed. Table 8 displays the results for the characteristic impedance diagram parameters. R_{ct} , a measure of electron transmission across a contact, is found to be inversely proportional to the corrosion rate. The semicircle fitting method was used to calculate the electrochemical impedance parameters. A single time constant is represented as a perfect semicircle in Nyquist plots. Impedance tests revealed surface resistance and

capacitance, as well as a substance's ability to inhibit corrosion and the nature of the inhibition process. Deviations from perfect circular shapes are attributed to interfacial impedance frequency dispersion, which is linked to surface non-homogeneity and metal roughness.^{65–71} Our investigation yielded a pattern that was not a perfect semicircle. This could be related to the addition of an inhibitor, which completely distracts the semicircle. Single semicircles are shifted in lock-step with the true impedance of the x -axis in the Nyquist plot (Fig. 12). The impedances increased as the concentrations of the plant extract increased. In addition, the impedance profiles were consistent across all concentrations. Inhibitors can alter the process by slowing down the rate of corrosion. Furthermore, the rate-controlling mechanism can be determined to be a reaction-controlled mechanism due to inhibitor corrosion.^{65–71} As inhibitor concentrations increase, R_{ct} values rise. As a result, the charge transfer mechanism is in charge of the vast majority of corrosion responses. Furthermore, an increase in inhibitor concentration results in a decrease in C_{dl} values due to the increased surface coverage of the inhibitor. This is because the inhibitory efficiency was increased. The decrease in the C_{dl} value could be explained by a lower local dielectric constant and/or a thicker electric double layer on the carbon steel surface.^{65–71}

Table 8 Electrochemical impedance (EIS) parameters of carbon steel corrosion in 3.5% NaCl with and without different doses of nonionic surfactant inhibitor (PETA-OL) at 303 K

Solution type	Solution concentration ppm	R_1 (Ohm cm^{-2})	R_{ct} (Ohm cm^{-2})	C_{dl} ($\mu\text{F cm}^{-2}$)	θ	IE (%)
Blank solution	Free	2.87	21.5	2.35	—	—
Inhibitor solution nonionic surfactant (PETA-OIL)	50	10.8	153	12.3	0.859	85.9
	100	11.7	188	13.5	0.886	88.6
	150	12.9	251	13.6	0.914	91.4
	200	13.7	289	14.1	0.925	92.5



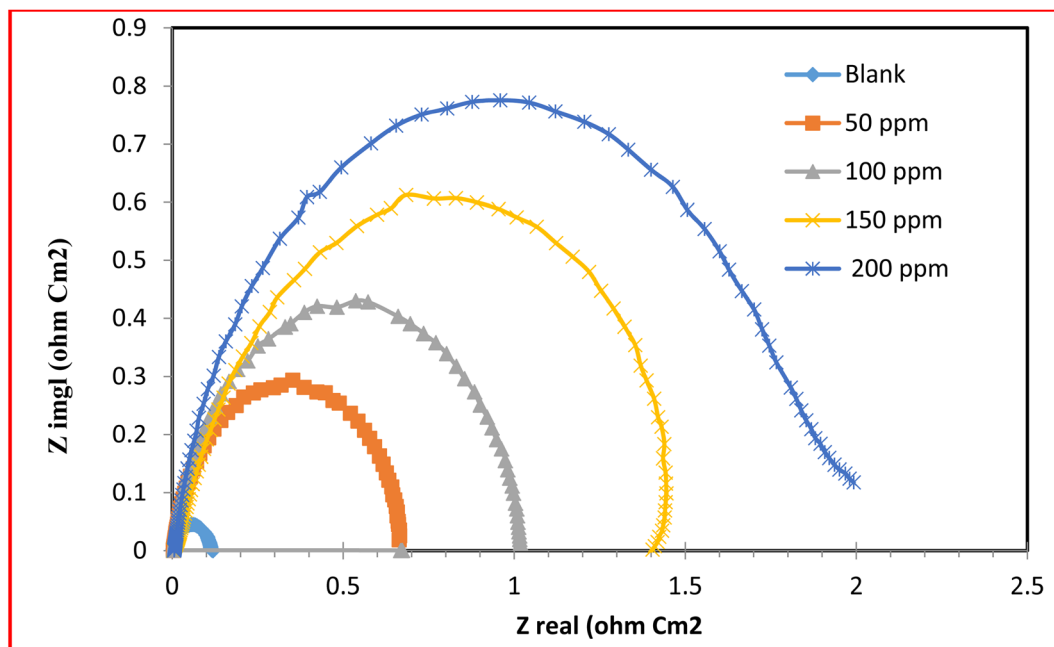


Fig. 12 Nyquist plots for a carbon steel electrode in 3.5% NaCl solution at 30 °C with various concentrations of the prepared nonionic surfactant (PETA-OL) inhibitor derived from the plastic waste.

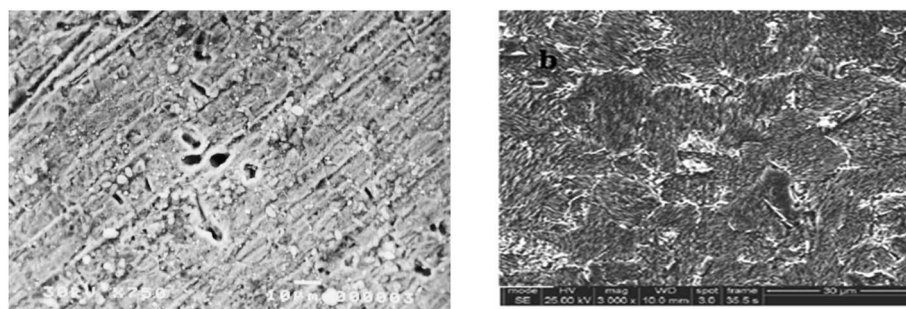


Fig. 13 (a) SEM micrographs of the carbon steel sample after immersion in 3.5% NaCl solution for 48 h in the presence of 200 ppm of the inhibitor (PETA-OL) at 30 °C. (b) SEM micrographs of the steel sample after immersion in 3.5% NaCl solution without inhibitor for 48 h at 30 °C.

3.9. Scanning electron microscopy studies (SEM)

Scanning electron microscopy (SEM) imaging was used to study the surface morphology of the carbon steel samples. A narrowly focused electron beam was employed using the scanning electron microscope (SEM) to scan over the area of interest. The signals produced by the electrons' interactions with the atoms that make up the sample (at or near its surface) conveyed information about the topography of the sample's surface.³⁰ Fig. 13b displays an SEM image of the carbon steel specimen's surface following immersion in a 3.5% NaCl solution for 48 hours, while (Fig. 13a) displays an SEM image of a different steel specimen following the same procedure in the presence of 200 ppm of the inhibitor (PETA-OL). A protective coating of the inhibitor molecule forms on the steel surface, according to SEM measurements of the surface. At a concentration of 200 ppm of the inhibitor (PETA-OL), the protective coating that is shown on the surface of steel (Fig. 13a) appears to be very smooth and

covers the entire surface without any imperfections. This supports the previously reported high percentage inhibition efficiency (IE%) of the utilized polymeric surfactants inhibitor chemical (PETA-OL), which is generated from plastic waste.

3.10. Corrosion inhibition mechanism

The first stage of the inhibitory mechanism, which regulates corrosion, is the adsorption of inhibitor molecules at the metal/solution contact.^{68–72} At the metal/solution interaction, four different types of adsorptions may take place when organic molecules are inhibited:

- (1) Electrostatic forces that draw charged molecules and metals together.
- (2) The manner in which the metal interacts with the molecules' unshared electron pairs.
- (3) Pi-electron interactions with the metal.
- (4) A combination of the first three.



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 generation of metallic complexes are a few variables that influence an inhibitor's ability to inhibit.⁷² Physical adsorption requires the presence of charged species in the bulk of the solution and metal with a vacant low-energy electron orbital, an inhibitor with molecules that are extremely loosely connected to electrons, or a heteroatom with lone pair electrons. Chemical interactions coexist with electrical connections as well. Chemical contact was initiated by non-bonding oxygen, nitrogen, and benzene ring electrons.^{68–72}

The current effort will provide a concise description of the interaction of both amido amide inhibitor compounds and ester derivative inhibitor compounds with steel through an electrical contact between the unshared electron pairs and the steel material's d-orbital. The amide and ester functional group's heteroatoms are adsorbed on the surface. Furthermore, the alkyl chain is adsorbed on the material's surface *via* unsaturated orbitals from the aromatic nucleus. As a result, the molecules are found on the steel. In order to keep the medium from coming into contact with steel, the alkyl chain is placed closer to the surface than the amido amide and ester compounds prepared from waste plastic. The combination of these two forms improves the capacity of amido amide produced from plastic waste to resist corrosion.

4 Conclusion

From the experimental results and theoretical calculations, the following conclusions can be drawn:

(1) Recyclability, by reacting with both ethylene diamine (EDA) and propylene glycol (PG) in the presence of an adequate catalyst, of PET plastic waste is efficient and yielding. Recycling is a solvent-free and efficient technology that is considered a green synthesis process.

(2) The four obtained product materials from the recycling process are characterized by FT-IR, ¹HNMR, and elemental analysis. The spectroscopic analysis proved the structure of the prepared materials as nonionic polymeric surfactants prepared from the reaction of recycled PET products with both EDA and PG; they are (N1,N4-bis(2-((E)-octadec-9-enamido)ethyl)terephthalamide), and bis(2-(2-hydroxypropoxy)ethyl) terephthalate, compounds (PETAA) and (PETPG), respectively.

(3) The obtained polymeric surfactants are N1,N4-bis(2-((E)-octadec-9-enamido)ethyl)terephthalamide (PETAA-OL) and 2-(2-(((E)-octadec-8-enoyl)oxy)propoxy)ethyl (2-(2-(((E)-octadec-9-enoyl)oxy)propoxy)ethyl) terephthalate (PETPG-OL). The prepared polymeric surfactants (PETAA-OL) and (PETPG-OL) were used for the preparation of corrosion inhibitors for steel in marine environments.

(4) The four prepared nonionic polymeric surfactant materials act as good inhibitors for steel substrates in a 3.5% NaCl marine corrosive environment.

(5) The protection performance of steel material by the prepared inhibitors was found to increase with concentrations but decrease with increasing temperature.

(6) Corrosion protection due to the adhesion and adsorption of polymeric materials on the steel surface obeyed the Langmuir adsorption isotherm model.

(7) The inhibition efficiency in the case of amide-based inhibitor compounds (PETAA-OL and PETAA) is more than glycol-based inhibitor compounds (PETPG-OL and PETPG). The order of corrosion inhibition performance of the four prepared nonionic polymeric surfactants is PETAA-OL > PETAA > PETPG-OL > PETPG.

(8) The AAS data demonstrated that increasing the inhibitor doses led to a decrease in ferric ion Fe²⁺ concentrations.

(9) The addition of inhibitor molecules to the aggressive medium produces a negative shift in the open-circuit potential due to the retardation of the cathodic reaction.

(10) Potentiodynamic polarization data indicate the mixed-type nature of surfactant inhibitors. According to potentiodynamic polarization data, the prepared surfactant boosted the polarization resistance and inhibited the performance by adsorbing on the metal/electrolyte interface.

(11) R_{ct} values increase as inhibitor concentrations increase. As a result, the charge transfer mechanism controls the majority of the corrosion response. Furthermore, an increase in inhibitor concentration leads to a decrease in C_{dl} values due to the inhibitor's increased surface coverage. This is due to an increase in the inhibitory efficiency. A lower local dielectric constant and/or a thicker electric double layer on the carbon steel surface could explain the decrease in the C_{dl} value.

(12). The reduction in the reaction number and time delay (Δt_m) of the four studied polymeric surfactant inhibitor materials increases in the case of amide-based inhibitors compared to glycol-based inhibitors. It was found in the following order: PETAA-OL > PETAA > PETPG-OL > PETPG. This observation agrees well with the data obtained from both mass loss measurements and atomic absorption spectroscopy (AAS). This means that the data of the different studied techniques are in good agreement with each other to prove the good protection efficiency of the four prepared nonionic polymeric surfactants towards the steel surface.

(13) SEM observations of the steel surface revealed the formation of a protective coating film of the inhibitor molecules on the steel surface.

(14) The protective coating film formed on the steel surface appeared to be very smooth and covered the whole surface without any flaws. This confirmed the observed high percentage inhibition efficiency (IE%) of the used polymeric surfactant inhibitor compound (PETAA-OL) derived from plastic waste.

Abbreviations

PET	Poly(ethylene terephthalate) plastic waste
EDA	Ethylene diamine
PG	Propylene glycol
PETAA	The symbol for the corresponding products of poly amino amide obtained from the reaction of PET with DEA



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PETPG	The symbol for the corresponding products of polyester obtained from the reaction of PET with PG
PETAA-OL	The symbol for the compound with IUPAC name: <i>N</i> 1, <i>N</i> 4-bis(2-((<i>E</i>)-octadec-9-enamido)ethyl) terephthalamide. This compound was obtained from the reaction of PETAA with oleic acid in the presence of a catalyst
PETPG-OL	The symbol for the compound with IUPAC name: 2-(2-(((<i>E</i>)-octadec-8-enoyl)oxy)propoxy)ethyl (2-(2-(((<i>E</i>)-octadec-9-enoyl)oxy)propoxy)ethyl) terephthalate This compound was obtained from the reaction of PETPG with oleic acid in the presence of a catalyst
(AAS)	Atomic absorption spectroscopy
SEM	Scanning electron microscopy
PDP	Potentiodynamic polarization measurements
EIS	Electrochemical impedance spectroscopy
WL	Weight Loss
TLC	Thin-layer chromatography
OCP	Open circuit potential measurement

Conflicts of interest

The authors declare that they have no conflict of interest.

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