

Solvent Free Glycolysis of Plastic Waste as Green Corrosion Inhibitor for Carbon Steel in Sulfuric Acid

R.S. Abdel Hameed^{1,2}

¹Chemistry Department, Faculty of Science, Al-Azhar University, 11884, Cairo, Egypt

²Chemistry Department, Faculty of Science, Hail University, Hail, 1560, KSA

Received: June 08, 2017, Accepted: July 18, 2017, Available online: August 07, 2017

Abstract: Solvent free efficient green glycolysis of Polyethylene terephthalate waste, PET, in this respect, PET waste was subjected to depolymerization with propylene glycol in the presence of manganese acetate as a catalyst, the product is Bis-(3-hydroxy-propyl)-terephthalate, BHPT, as non-ionic surfactant was separated, characterized by FT-IR and ¹HNMR, BHPT was evaluated as corrosion inhibitor for steel in the presence of 1.0 M sulfuric acid by chemical and electrochemical methods, the corrosion inhibition efficiency increase with inhibitor concentration and decrease with temperatures, the galvanostatic polarization curves indicate that the BHPT, compound act as mixed inhibitor, the impedance of the inhibited solution has increased with the increase in the concentration of the inhibitor. the inhibition due to adsorption of the inhibitor molecules on the steel surface, the adsorption obey Langmuir adsorption isotherm. Thermodynamic parameters were computed and discussed, Scanning electron microscope (SEM) was used to study the surface morphology of steel in absence and presence of the used inhibitor, hydrogen evolution techniques was used to evaluate the inhibition efficiency of the BHPT inhibitor compound. the data obtained from different techniques are in good agreement to each other and show the BHPT, surfactant derived from PET, waste considered as good corrosion inhibitor for steel in sulfuric acid.

Keywords: green inhibitor; recycling; glycolysis; EIS; polarization; SEM

1. INTRODUCTION

The overall world production of polyester was about 30 million tons in 2000, this value increased to 55 million in 2012 and most consisted of PET. As a result of the diversity of its applications in a high volume of consumer products, large amount of PET waste is also generated, which includes polymer manufacturing waste as well as the products after the end of their useful life. PET is semi-crystalline, thermoplastic polyester of characteristic high strength, transparency, and not biodegradability [1]. The PET bottle was patented in 1973 by Nathaniel Wyeth and began to be used popularly for the production of disposable soft drink bottles in the 1980s. In 1987, more than 700 million pounds of PET were consumed in their production [2]. PET is not a hazardous product, but its waste quantity increases drastically. With the increasing pressure of keeping the environmental clean. Recycling of PET waste in an ecofriendly manner is the only solution. PET waste can be recycled by different methods like physical recycling and chemical

recycling. Chemical recycling is the reaction of PET with various reagents to obtain products that are used in the chemical industry [3]. During chemical recycling, PET waste can be depolymerized to base monomers or oligomers. With the use of solvent of depolymerization, generally called solvolysis of polymer, methanolysis [4] and glycolysis [5] are the main possible routes. Steel is a backbone of heavy industries, Corrosion control of steel is of technical, economical, and environmental importance, corrosion inhibitors are commonly used to reduce the corrosion attack on the steel surface [6]. The presence of the inhibitors lead to decline in the rate of corrosion of steel and hence the lifetime increases [7]. Most of the effective acid inhibitors are organic compounds containing nitrogen, oxygen and /or sulfur and these compounds adsorb at the steel surface and hence slow down the rate of corrosion [8-12]. The strength of the adsorption depends on the several factors such as the chemical structure of the inhibitors, the presence of electrodonating or electropelling group, molecular weight of the inhibitor, temperature and electrochemical potential at the metal / solution interface [13,14]. surfactant inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity

*To whom correspondence should be addressed:
Email: r.abdelghany@uoh.edu.sa, rsabdelhameed@yahoo.com

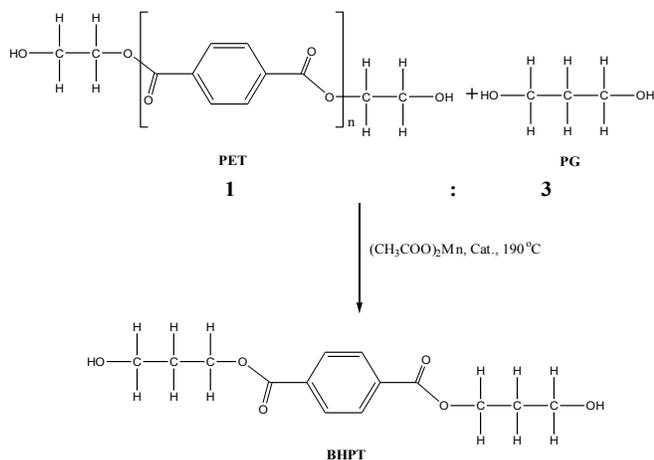


Figure 1. the chemical scheme of the green synthesis process for the Bis-(3-Hydroxy- Propyl) Terephthalate, BHPT compound.

and easy production [15]. The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting property of the metal [16], and so the study of the relationship between the adsorption and corrosion inhibition is of great importance. In the previous works depolymerization by aminolysis of PET, with monoethanolamine [17], and ethylene di amine [18] the products nonionic surfactants act as good corrosion inhibitors for steel in HCl. This work is one from the series aimed to alleviate the environmental pollution by accumulation of plastic waste by converting waste into modified products, and to evaluate the modified products as corrosion inhibitors for metals and alloys in different aqueous media [17-22]. In the present work Propylene glycol was used to convert PET waste into Bis-(3-hydroxy-propyl)-terephthalate, BHPT, via solvent free green recycling, the product was evaluated as corrosion inhibitor for carbon steel in 1.0 M H_2SO_4 by weight loss, hydrogen evolution (gasometry), open circuit potential, potentiodynamic polarization, Electrochemical impedance spectroscopy (EIS), and SEM. The effect of inhibitor concentrations and temperatures were studied. Thermodynamic parameters were computed and discussed. Corrosion inhibition mechanism was discussed.

2. EXPERIMENTAL

2.1. Materials

Poly(ethyleneterephthalate) (PET) waste is collected from beverage bottles. Propylene glycol (PG) and manganese acetate were obtained from Aldrich Chemical Co., England. The carbon steel specimen of the type (L-52) used for this study has the following chemical composition : (wt%); C :0.26, Mn :1.35%, P: 0.04%, S: 0.03 Nb:0.005, V:0.02, Ti:0.03, and the remainder is iron. The aggressive solution (1.0 M H_2SO_4) was prepared by appropriate dilution of analytical grade H_2SO_4 with double distilled water.

2.2. Recycling Process

PET waste was depolymerized with propylene glycol glycol (PG), at weight ratio of PET to Glycol (PG) 1:3 (wt% of PET: wt% of PG) using 0.5% of manganese acetate as catalyst (by weight based on weight of PET). The reaction mixtures were heated under vigorous stirring in nitrogen atmosphere at temperature about 170–

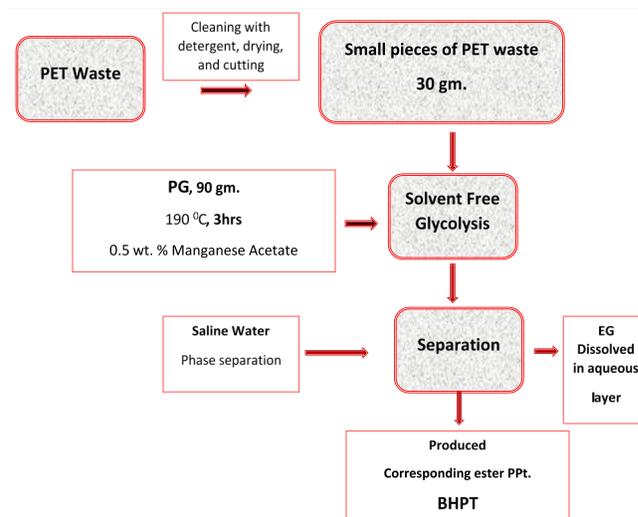


Figure 2. Flow Diagram of the solvent free green synthesis Processes.

190 °C for 3 h and at 200 °C for 1 h. The temperature of the reaction was then lowered to 100 °C for 1 h. The mixture was allowed to cool to room temperature. at the end of the reaction, saline water was added to the reaction mixture with vigorous agitation followed by phase separation, the product, poly(bis(2-Hydroxy ethylene)terephthalate) (BHPT) was obtained in organic layer as white viscous product, which have the chemical structure as showed in Figure 1. The general diagram for the green synthesis procedure as presented in Figure 2.

2.3. Weight loss measurements

Coupons of steel of 4 x 8x 0.1cm dimensions were used as test specimens, the specimens were polished by 410 and 610 emery papers, respectively, degreased with acetone, washed with distilled water and finally dried using two filter papers. The described treatment was carried out immediately before each measurement. The specimen of the given metal was immersed in 100 ml of the test solution (i.e., 1.0 M H_2SO_4) with different inhibitors concentrations, samples maintained in test solution up to 8hours. Experiments were carried out under different temperature 30, 40, 50, and 60°C.

2.4. Open circuit potential

The potential of steel electrode was measured against saturated calomel electrode (SCE) in 1.0 M H_2SO_4 solution in absence and presence of different concentrations of the used inhibitor at 30 °C. All measurements were carried out using Multi-tester until the steady-state potentials are reached.

2.5. Galvanostatic Polarization Measurements

The working electrode was made from carbon steel rod that has the same composition as mentioned in point 2.1. The rod was axially embedded in araldite holder to offer an active flat disc shaped surface of an area 1 cm^2 . Prior to each experiment, the working electrode was polished successively with fine emery paper, rinsed

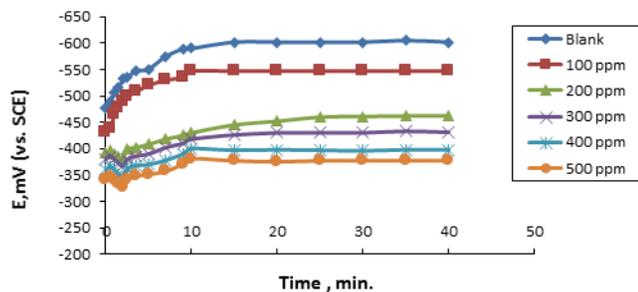


Figure 3. Potential–time curves for carbon steel immersed in 1.0 M H₂SO₄ solution in the absence and presence of inhibitor (BHPT).

with acetone, washed with double distilled water and finally dried before dipping into the electrolytic cell. A platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode to which all potentials are referred. The electrochemical experiments are performed using radiometer analytical, Volta master (PGZ301, DYNAMIC ELS VOLTAMMETRY). Under stirring with scan rate 1 Mv/s and potential was scanned in the range of -800 to 0 mV.

2.6. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance were obtained using a Voltalab 40 for all EIS measurements with a frequency range of 100 kHz to 50 mHz with a 4 mV sine wave as the excitation signal at open circuit potential. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a Nyquist Plot. The charge transfer resistance values (R_{ct}) was calculated from the difference in impedance at lower and higher frequencies.

2.7. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. The surface morphology of the carbon steel was analyzed before and after the corrosion tests, by a Joel (840 X Japan) scanning electron microscope. This instrument was operated in a secondary electron imaging made with an accelerating voltage of either 10 or 20Kev. Magnifications ranging from 50 to 10000X could be obtained by this tool in the present investigation three magnifications were selected 950, 1200 and 2400X.

2.8. Gasometry Measurements (hydrogen evolution measurements)

The progress of the corrosion reaction was determined at 30 °C. by volumetric measurement of the evolved hydrogen. The metal sample was put in a Büchner flask containing the test solution. The flask is sealed with a rubber bung, and from its hose barb protruding from its neck, rubber tubing is connected to the bottom of an inverted measuring cylinder which is fitted above a basin. The cylinder and the basin are filled with distilled water. The evolved hydrogen gradually displaces the distilled water and is collected at the top inside the cylinder, and its volume is measured directly with time. The experiment is done in the absence and presence of different concentrations of the tested inhibitor.

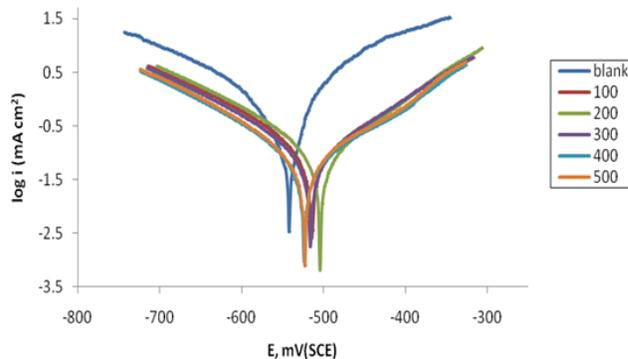


Figure 4. Galvanostatic polarization curves of carbon steel in 1.0M H₂SO₄ solution containing different concentrations of inhibitor (BHPT) derived from PET waste.

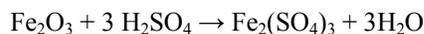
3. RESULTS AND DISCUSSION

3.1. Solvent Free Green Synthesis of Bis-(3-Hydroxy-Propyl) Terephthalate, (BHPT) compound.

The (BHPT) compound was synthesized without using any solvent via the direct catalytic reaction of PET and PG (1:3 wt. %) in the presence of 0.5% manganese acetate as a trans esterification catalyst, the reaction was carried out in nitrogen atmosphere. The product of bis-(3-hydroxy-propyl) Terephthalate (BHPT) was separated by phase separation using aqueous saline water. The structure of (BHPT) was established on the basis of its spectral data, since the IR spectrum showed absorption bands at 3350–3300 assignable to the (OH) groups, indicates the termination of the products with hydroxyl groups. On the other hand, the band observed at 810 cm⁻¹ for all depolymerized PET is assigned to –CH out-of-plane bending of p-substituted phenyl. This band confirms the presence of phenyl rings in depolymerized products. The presence of strong absorption bands at 1737 and 1170 cm⁻¹ assignable to C=O stretching and C-O stretching of ester groups. While, the ¹H-NMR spectrum revealed signal at δ 1.94 (m, 4H, 2CH₂), 3.53 (m, 4H, 2CH₂), 4.25 (t, 4H, 2CH₂), 4.92 (s, 2H, 2OH, D₂O exchangeable) and 7.90 (m, 4H, Ph-H), represent p-substituted phenyl group.

3.2. Open Circuit Potential Measurements

The potential of carbon steel electrodes immersed in 1.0 M H₂SO₄ solution was measured as a function of immersion time in the absence and presence of BHPT inhibitors derived from waste, as shown in Figure 3. It is clear that the potential of steel electrode immersed in 1.0 M H₂SO₄ solution (blank curve) tends towards more negative potential firstly, giving rise to short step. This behavior was reported by other investigators [23-25] which represents the breakdown of the pre-immersion air formed oxide film presents on the surface according to the following equation:



This is followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established. Addition of inhibitor

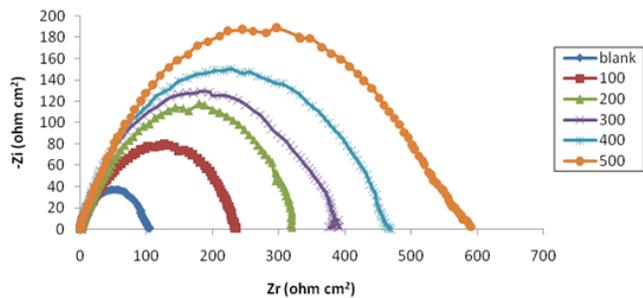


Figure 5. Nyquist plots for carbon steel in 1.0 M H₂SO₄ solution at 30°C containing various concentrations of inhibitor (BHPT) derived from PET waste.

molecules to the aggressive medium produces a negative shift in the open circuit potential due to the retardation of the cathodic reaction.

3.3. Galvanostatic Polarization Measurements

Figure 4. illustrates the galvanostatic polarization curves for carbon steel electrode in 1.0 M H₂SO₄ solution with and without different concentrations of used inhibitor derived from plastic waste, (BHPT). Some electrochemical corrosion parameters such as the values of cathodic (β_c) and anodic (β_a)Tafel slopes were determined from the linear region of the polarization curves. , The values of corrosion current density (I_{corr}) were computed from the intersection of the anodic and cathodic lines with the corrosion potential (E_{corr}). Inspection of Table 1. It is concluded that, The values of anodic (β_a) and cathodic (β_c) Tafel slopes are approximately changed slightly proved that these compounds acted as mixed inhibitors . The surface area available for anodic dissolution of iron and cathodic hydrogen evolution reaction decreases without affecting the reaction mechanism. The values of E_{corr}. change slowly to negative values indicating that these inhibitors are of mixed type inhibitors mainly cathodic. The values of I_{corr}. decrease and hence the values of IE's increase, indicating that the inhibiting effect of these compounds toward the corrosion of carbon steel in 1.0M H₂SO₄ solutions.

The inhibition efficiency is given by the following equation [23-25]:

$$\%IE = 1 - (I_{inh} / I_{uninh}) \times 100 \tag{1}$$

Where: I_{uninh} and I_{inh} ae the corrosion current densities in the absence and presence of inhibitor respectively.

3.4. Electrochemical Impedance Spectroscopic Measurements (EIS)

The impedance spectra (Nyquist plots) of carbon steel in 1M HCl containing various concentrations of the inhibitor at 30 °C is shown in Figure 5. Nyquist plots contain depressed semicircle with center under real axis. The size of the semicircle increases with the inhibitor concentration, indicating the charge transfer process as the main controlling factor of the corrosion of carbon steel. It is apparent from the plots that, the impedance of the inhibited solution has increased with the increase in the concentration of the inhibitor. The experimental result of EIS measurements for the corrosion of carbon steel in 1.0 M H₂SO₄ in the absence and presence of inhibitor is given in Table 2.

It can be observed that polarization resistance (R_p) value increased with increase in the concentration of the inhibitor. Whereas values of the capacitance of the interface (C_{dl}) starts decreasing, with increase in inhibitor concentration, which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor acts via adsorption at the metal/solution interface [26] and the decrease in the C_{dl} values is caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the electrode surface, which decreases the extent of metal dissolution [27].

The inhibition efficiency [28] is given by the following equation:

$$\% IE (R_{ct}) = \frac{R_{ct} (inhi) - R_{ct} \times 100}{R_{ct} (inhi)} \tag{2}$$

Where R_{ct} is polarization resistance without inhibitor, and R_{ct}(inhi) is polarization resistance with inhibitor. The proposed equivalent circuit is represented in Figure 6.

3.5. Weight Loss Measurement

3.5.1. Effect of inhibitor concentrations

BHPT compound derived from green glycolysis of plastic waste was evaluated as corrosion inhibitor for carbon steel alloy in 1 M sulfuric acid by weight loss methods at different concentration,

Table 2. AC impedance data of carbon steel in 1.0 M H₂SO₄ solution at 30 °C

Sample	R _{ct} Ohm cm ²	R _s Ohm cm ²	C _{dl} μF cm ⁻²	IE%	θ
Blank	104.269	2.18	40.95	---	---
100	237.012	1.64	8.56	56.0	0.56
200	322.789	1.58	4.19	67.6	0.67
300	392.478	2.23	3.13	73.4	0.73
400	470.124	1.86	2.25	77.8	0.78
500	591.568	1.74	1.42	82.4	0.82

Table 1. Electrochemical corrosion parameters obtained from the galvanostatic polarization measurements for carbon steel in 1.0M H₂SO₄ solution containing different concentrations of (BHPT) inhibitor derived from plastic waste.

Sample	Conc., ppm	-E _{corr} mV (SCE)	I _{corr} mA cm ⁻²	b _c mVdec ⁻¹	b _a mVdec ⁻¹	θ	% IE
Blank	-	485	0.723	98	86	-----	
BHPT	100	508	0.448	114	102	0.380	38.03
	200	516	0.375	120	108	0.481	48.13
	300	522	0.224	126	114	0.690	69.02
	400	530	0.180	132	126	0.751	75.10
	500	534	0.112	138	130	0.845	84.51

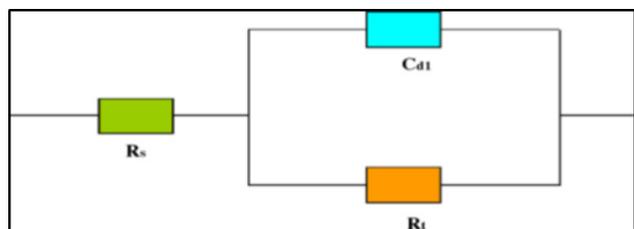


Figure 6. The equivalent circuit model for the electrochemical impedance measurements.

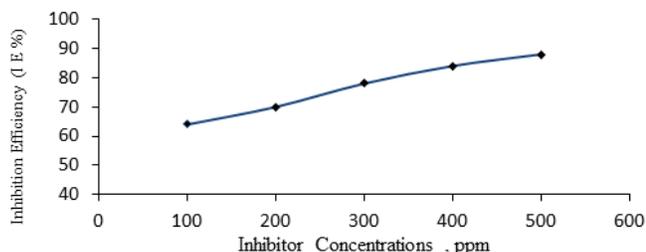


Figure 7. Plot of inhibition efficiency vs. inhibitor concentration (ppm).

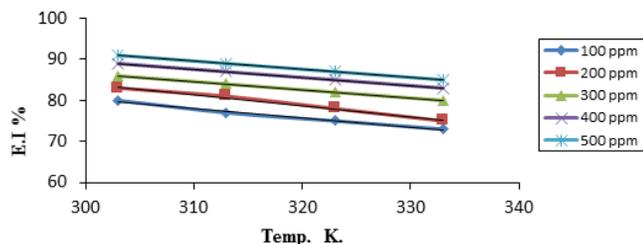


Figure 8. Effect of temperature on I.E. for carbon steel in 1.0 M H₂SO₄ in the presence of different concentrations of the used inhibitor (BHPT).

from 100 to 500 ppm, Figure 7 presented plot of inhibitor concentration *V.S.* Inhibition efficiency from figure 7 it can be seen that as the concentrations increase the corrosion inhibition efficiency increase this is due to increase the number of adsorbed molecules at higher inhibitor concentrations.

3.5.2. Effect of solution temperature

To elucidate the mechanism of corrosion inhibition and to determine the kinetic thermodynamic parameters of corrosion process, weight loss were performed at 303, 313, 323, and 333k. Figure 8 presented the effect of solution temperature on the corrosion inhibition efficiency, the inhibition efficiency decreased with increasing solution temperature as showed in figure 8 this due to the protective film formed on the steel surface is less stable at higher temperature, which may be due to the desorption of some adsorbed molecules from the steel surface at higher temperature leaving greater area exposed to acidic environment.

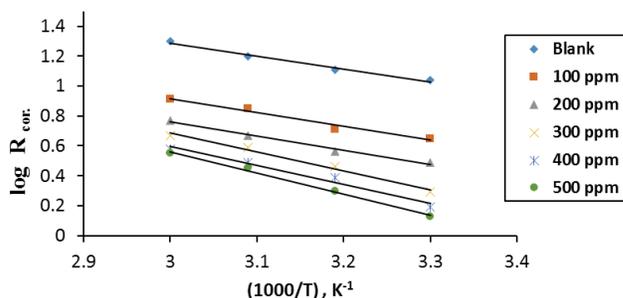


Figure 9. Arrhenius plot for carbon steel in 1.0 M H₂SO₄ solution in the absence and presence of different concentrations of the inhibitor (BHPT).

3.5.3. Kinetics and thermodynamic consideration

The dependence of the corrosion rate on temperature can be expressed by Arrhenius equation and transition state equation:

$$\ln R_{\text{corr.}} = (-E_a/RT) + A \quad (3)$$

$$R_{\text{corr.}} = (RT/h) \exp(\Delta S_a/R) \exp(-\Delta H_a/RT) \quad (4)$$

Where E_a is the apparent activation energy, R is the universal gas constant, A is Arrhenius pre exponential factor, T is the absolute temperature, h is the Plank's constant, N is the Avogadro's number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation. The apparent activation energy can be calculated by linear regression between $\log R_{\text{corr.}}$ and $1/T$, Figure 9 showed an Arrhenius plot for carbon steel immersed in 1.0 M sulfuric acid in absence and presence of different inhibitor concentrations. The plots obtained are straight lines and the slope of each straight line gives the apparent activation energy, the results were shown in table 3. In the present study the higher value of E_a for carbon steel in presence of (BHPT) inhibitor compared to that in its absence is attributed to its physical adsorption. The increase in E_a can be attributed to an appreciable decrease in the adsorption of the inhibitor on the carbon steel surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to acid environment [32]. The relation between $\log R_{\text{corr.}}/T$ and $1/T$ where shown in figure 10. Straight lines are obtained with slope $(-\Delta H_a/2.303R)$ and an intercept of $[\log(R/h) + (\Delta S_a/R)]$, from which the values of ΔH_a and ΔS_a were calculated and listed in table 3. The positive sign of enthalpy reflect the endothermic nature of steel dissolution process, the increase in ΔH_a with

Table 3. Values of activation parameters for carbon steel in 1.0M H₂SO₄ in the absence and presence of different concentrations of the inhibitor (BHPT).

Inhibitor concentrations (ppm)	E_a (kJmol ⁻¹)	ΔH_a (kJmol ⁻¹)	ΔS_a (Jk ⁻¹ mol ⁻¹)
Blank	53.82	53.43	185.16
100	57.97	54.3	171.4
200	61.2	58.4	168.1
300	63.14	63.3	162.5
400	64.2	65.4	154.4
500	66.3	68.3	147.3

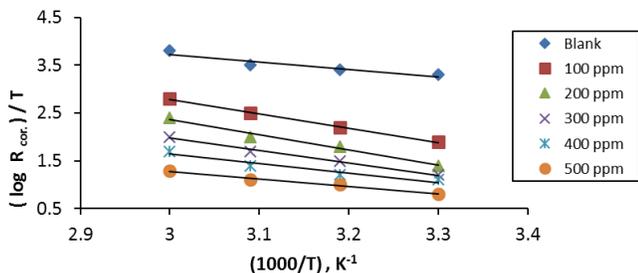


Figure 10. Transition state plot for carbon steel in 1.0 M H₂SO₄ solution in the absence and presence of different concentrations of the inhibitor (BHPT).

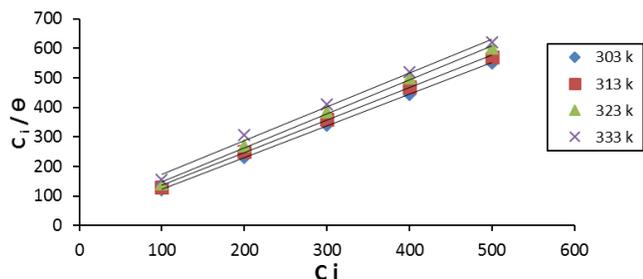


Figure 11. Langmuir adsorption isotherm for carbon steel in 1.0 M H₂SO₄ inhibited solution at various temperatures.

increase in the concentration of the inhibitor for carbon steel corrosion reveals that decrease in carbon steel corrosion rate is mainly controlled by kinetic parameters of activation [11, 33, and 34]. The entropy of activation values are less negative for inhibited solutions than that for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from reactants to the activated complex [11, 34].

3.6. Adsorption Isotherm

Adsorption depends mainly on the charge and nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent and other ionic species, temperature of corrosion reaction and on the electrochemical potential at solution-interface. Adsorption of inhibitor involves the formation of two types of interaction responsible for bonding of inhibitor to a metal surface. The first one (physical adsorption) is weak undirected interaction and is due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of metal [33, 35]. In order to obtain the adsorption isotherm the degree of surface coverage (Θ) for various concentration of the inhibitor (C_i) has been calculated. The data were tested graphically by fitting to various isotherms. A straight line with correlation coefficient nearly equal to 1.0 was obtained on plotting C_i/Θ against C_i as shown in figure 11. The adsorption of the inhibitor compound (BHPT) on the carbon steel surface followed Langmuir adsorption isotherm model at all studied temperatures.

The surface coverage (Θ) is related to inhibitor concentration C_i by the following equation[36]:

$$C_i / \Theta = 1 / K_{ads} + C \tag{5}$$

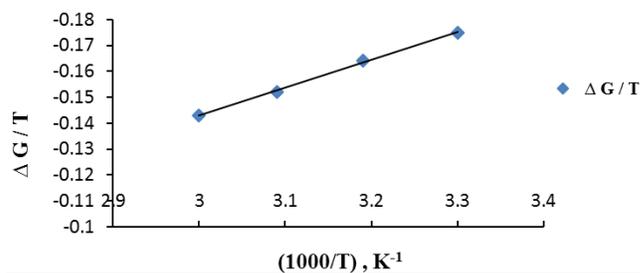


Figure 12. ΔG_{ads}/T versus 1/T plot for carbon steel in 1.0 M H₂SO₄ inhibited solution.

Where, K_{ads} is equilibrium constant of the equilibrium adsorption process. Langmuir isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species. The K_{ads} values can be calculated from the intercept lines on the C_i/Θ axis. This is related to the standard free energy of adsorption (ΔG_{ads}) by the following equation:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \tag{6}$$

Where, R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L. The values of ΔG_a for the inhibitor on the surface of carbon steel are given in table 4. The negative value of ΔG_{ads}, indicated spontaneous adsorption of the inhibitor on the carbon steel surface. Generally, the magnitude of ΔG_a around -20kJ/mol or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those around -40kJ/mol or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions). In the present work, the calculated values ΔG° at 303K for carbon steel is -39.3 kJ/mol, which indicate that adsorption of the inhibitor on the mild steel surface involves both physical and chemical process [37]. But the inhibition efficiency decreased with increasing temperature indicating inhibitor adsorbed predominantly physically on the surface of carbon steel. The enthalpy of adsorption (ΔH_{ads}) can be calculated from the rearranged Gibbs-Helmholtz equation[37-43]:

$$\Delta G_{ads}/T = (\Delta H_{ads} /T) + K \tag{7}$$

The variation of ΔG_{ads}/T with 1/T gave a straight line with a slope of ΔH_{ads} as shown in figure 12. The entropy of adsorption ΔS_{ads} was calculated using the following thermodynamic equation [38-43]:

Table 4. Thermodynamic parameters for the adsorption of the inhibitor in 1.0 M H₂SO₄ on the carbon steel at different temperatures.

Temperature (k)	-ΔG _{ads}	- ΔH _{ads}	ΔS _{ads}
303	39.3	10.3	94.9
313	40.1	10.3	94.5
323	41.1	10.3	94.9
333	42.1	10.3	94.8

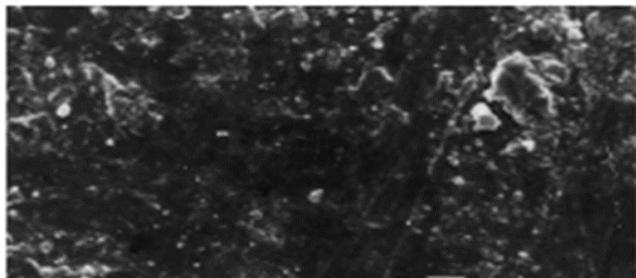


Figure 13. SEM micrographs of carbon steel sample after polishing

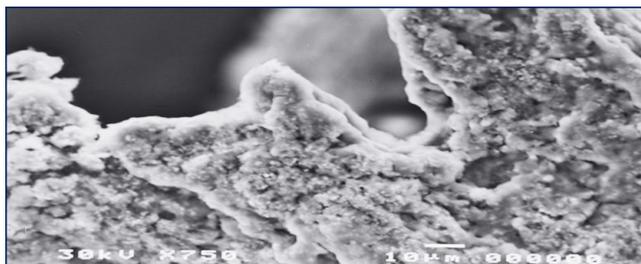


Figure 14. EM micrographs of carbon steel sample after immersion in 1.0 M H₂SO₄ solution without inhibitor for 24 hr. at 30 °C.

$$\Delta S_{\text{ads}} = (\Delta H_{\text{ads}} - \Delta G_{\text{ads}}) / T \quad (8)$$

The calculated values of heat of adsorption and entropy of adsorption are listed in table 4.

The negative sign of ΔH_{ads} indicated the exothermic process of adsorption of the inhibitor on carbon steel surface in sulfuric acid. The positive value of ΔS_{ads} in the presence of inhibitor can be attributed to the increase in the solvent entropy and more positive desorption entropy. It is also interpreted that the increase of disorderness is due to more water molecules which can be desorbed from the metal surface by one inhibitor molecule. Therefore it is revealed that decrease in the enthalpy is the driving force for the adsorption of the inhibitor on the surface of carbon steel [38-40].

3.7. Mechanism of Corrosion Inhibition

Corrosion inhibition mechanism in acidic medium is the adsorption of inhibitor onto metal surface. The adsorption of inhibitor at the metal/solution interface is the first step in the inhibition mechanism in acidic media. Four types of adsorption may take place during inhibition involving organic molecules at the metal/solution interface [29]:

1. Electrostatic attraction between charged molecules and the charged metal,
2. Interaction of unshared electron pairs in the molecule with the metal,
3. Interaction of π -electrons with the metal, and
4. A combination of the above.

Concerning inhibitors, the inhibition efficiency depends on several factors; such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface, and the formation metallic complexes [30].

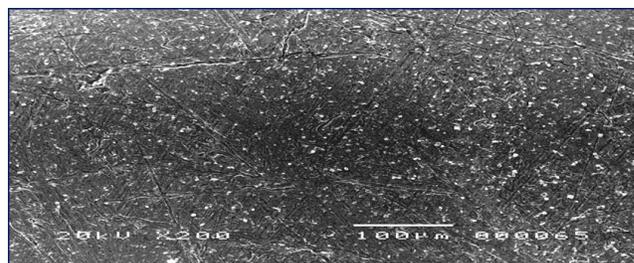


Figure 15. EM micrographs of carbon steel sample after immersion in 1.0 M H₂SO₄ solution with 500 ppm of the inhibitor (BHPT) at 30 °C.

Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatom with lone pair electrons. However, the compound reported can be protonated in an acid medium. Thus they become cations, existing in equilibrium with the corresponding molecular form:



The protonated BHPT, could be attached to the carbon steel surface by means of electrostatic interaction between SO_4^{2-} and protonated BHPT since the steel surface has positive charge in the H₂SO₄ medium [31]. This could further be explained based on the assumption that in the presence of SO_4^{2-} the negatively charged SO_4^{2-} would attach to positively charged surface and thereby protonated BHPT being adsorbed to the metal surface. Apart from electrostatic interaction, some chemical interaction is also involved. The non-bonding electrons of oxygen atoms and π -electrons of benzene ring caused chemical interaction.

3.8. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) depends on the using of a finely focused beam of electrons to scan over the area of interest. The electrons interact with the atoms (at or near the surface of the sample) that make up the sample producing signals that contain information about the sample's surface topography [32]. Figure 13 shows a characteristic inclusion observed on the polished carbon steel surface, which was probably an oxide inclusion, so that a comparison can be drawn with the morphology after exposure to the corrosive media. Figure 14 shows SEM image of the surface of carbon steel specimen after immersion in 1.0 M sulfuric acid for 24 hours, while Figure 15 shows SEM image of another carbon steel specimen after immersion in 1.0 M sulfuric for the same time interval in presence of 500 ppm of the inhibitors (BHPT). SEM observations of the steel surface showed that a protective film of inhibitor molecules is formed on the carbon steel surface. The protective film presented on the surface of carbon steel at a concentration of 500 ppm of Inhibitor (BHPT) Figure 15, appears to be very smooth and to cover the whole surface without any flaws. This confirms the observed high percentage inhibition efficiency (% IE) of Inhibitor (BHPT) derived from PET, plastic waste as it was discussed in the previous sections.

3.9. Gasometry

The hydrogen evolution method (gasometric method) was used for evaluation of the inhibition efficiency of BHPT compound derived from green glycolysis of plastic waste for corrosion process of steel in 1.0 M H₂SO₄ corrosive medium. The volume of hydrogen evolved during the corrosion reaction of c-steel in 1.0 M H₂SO₄ in absence and presence of different concentrations of the inhibitors was measured with time at room temperature (25 °C). The inhibition efficiency was calculated using the following equation [40-43].

$$I.E \% = [1 - (V_{inh.} / V_{free})] \times 100 \quad (10)$$

Where V_{inh} is the volume of hydrogen gas evolved for inhibited solution and V_{free} for the uninhibited solution. The values of evolved hydrogen volumes and inhibition efficiencies at different concentrations are shown in table 5, the inhibition efficiency increase with increasing the inhibitor concentration. Which indicate that the used inhibitors BHPT compound derived from waste act as good inhibitor for carbon steel in 1.0 M sulfuric acid. The volume of the evolved hydrogen decrease gradually with increasing inhibitor concentration which may due to inhibitor compounds control the hydrogen evolution reaction.

4. CONCLUSION

From the experimental data we can concluded that:

1. PET waste could be depolymerized using propylene glycol in the presence of manganese dioxide catalyst to give Bis(Hydroxy Propylene) terephthalate, BHPT, the process is solvent free efficient green process.
2. BHPT compound act as mixed inhibitor for carbon steel in 1.0 M H₂SO₄.
3. The corrosion inhibition efficiency increase with inhibitor concentration and decrease with temperatures.
4. The impedance of the inhibited solution has increased with the increase in the concentration of the inhibitor.
5. SEM observations of the steel surface showed that a protective film of inhibitor molecules is formed on the carbon steel surface.
6. The protective film formed confirms the observed high percentage inhibition efficiency (% IE) of Inhibitor (BHPT) derived from plastic waste.
7. The volume of the evolved hydrogen decrease gradually with increasing inhibitor concentration which may due to inhibitor compounds control the hydrogen evolution reaction.
8. The data obtained from different techniques are in good agreement.

Table 5. hydrogen volumes and inhibition efficiency for the corrosion of C- Steel in 1.0 M H₂SO₄ with and without different concentrations of BHPT inhibitor compound at room temperature after 6 hrs.

Concentration	Volume of hydrogen (ml/ cm ²)	I.E %
Free	47	-
100 ppm	15	68
200 ppm	14	70
300 ppm	13	72
400 ppm	10	78
500 ppm	8	83

REFERENCES

- [1] L'opez-Fonseca R., Duque-Ingunza I., De Rivas B., Flores-Giraldo L., Gutierrez-Ortiz J. I., Chemical Engineering Journal, 168, 312 (2011).
- [2] Gargiulo C., Belletti G., Presented at Chemical fiber international, September 1997.
- [3] Khoonkari Mohammad, Haghghi Amir Hossein, Sefidbakht Yahya, Shekoochi Khadijeh, and Ghaderian Abolfazl, International Journal of Polymer Science,1, (2015).
- [4] Colomines G., Robin J., Tersac G., Polymer, 46, 3230 (2005).
- [5] Ishihara K., Ishida K., Jpn Pat 11302227; 1999.
- [6] Shukla SR., Kulkarni KS. J. Appl. Polym. Sci., 85, 1765 (2002).
- [7] Golestani Gh., Shahidi M., Ghazanfari D., Appl. Surf. Sci., 308, 347 (2014).
- [8] Hosseini M.G., Ehteshamzadeh M., Shahrabi T., Electrochim. Acta, 52, 3680 (2007).
- [9] Abdallah M., Zaaferany I., Khairou K.S., Sobhi M., Int. J. Electrochem Soc., 7 (2012)1564.
- [10] Fouda A. S., Abdallah M., Medhat M., Prot. Met. Phys.Chem. Surf., 48(4) (2012) 477.
- [11] Abdallah M., Zaaferany I. A. , AL Jahdaly B.A. , J. Mater. Environ. Sci. 7, 1107 (2016).
- [12] Abdelhameed R. S. , , Adv. Appl. Sci. Res., 7, 92 (2016).
- [13] Hanane H., Douadi T., Al-Noaimi M., Issaadi S., Daoud D., Chafaa S., Corros. Sci., 88, 234 (2014).
- [14] Abdallah M., Asghar B.H., Zaaferany I., Sobhi M., Prot. Met. Phys. Chem. Surf., 49, 485 (2013).
- [15] Abdallah M., Al Jahdaly B.A., Al-Malyo O. A., Int. J. Electrochem Sci., 10, 2740 (2015).
- [16] Abdallah M., AL Jahdaly B.A., Sobhi M., Ali A.I., Int. J. Electrochem. Sci., 10, 4482 (2015).
- [17] Sobhi M., El-Sayed R., Abdallah M., Chem. Eng. Comm., 203, 758 (2016).
- [18] Abdel Hameed R. S., Adv. Appl. Sci. Res., 2, 483 (2011).
- [19] Abdel Hameed R. S., Elmetery Naser S., Alshemary Nawaf F., Shehata H. A., Mat. Sci. J., 14, 417 (2016).
- [20] Abdel Hameed R. S., Ph.D., Thesis, Al Azhar Uni., (2006).
- [21] Abdel Hameed R. S., Shehata H. A., Abdelbary H.M., Soliman S.A., Salem A.M., Atta A. M., , Mat. Sci. J., 8, 289 (2012).
- [22] Abdel Hameed R.S., Al-Shafey H. I. and Farghaly O. A., Research, Rev. Electrochem., 3, 41 (2012).
- [23] Abdel Hameed R. S., Al-Shafey H. I., Ismail E. A., Abu-Nawwas Abd-Alhakeem H., El Azabawy O.E.; Int. J. Engi. Res. Applic., 3, 1094 (2013).
- [24] Abdel Hameed R.S., El-Zomrawy A., Abdallah M., Abed El Rehim S.S., AlShafey H.I., Nour Edin Sh., Int. J. Corros. Scale Inhib., 6, 196 (2017).
- [25] Abdel Hameed R. S., Al Shafey H.I., Abu-Nawwas A.H., Int. J. Electrochem Sci., 9, 6006 (2014).
- [26] Abdel Hameed R. S., Al-Shafey H.I., Ismail E.A., Abu-Nawwas Abd-Alhakeem H. Int J Electrochem Sci., 10, 2098 (2015).

- [27]Emregul,K. C., Akay A. A., Atakol O., *Matter. Chem. Phy.*, 93, 325 (2005).
- [28]Khaled K. F., *Electro Chim. Acta*, 48, 2493 (2003).
- [29]Aljourani J., Raeissi K., Golozar M. A., *Corros. Sci.*, 51, 1836 (2009).
- [30]Bhajiwala H. M., Vashi R. T., *Bull. Electrochem.*, 17, 441 (2001).
- [31]Schweinsberg D., George G., Nanayakkara A., Steinert D., *Corros. Sci.*, 28, 33 (1988).
- [32]Fouda A.S., Moussa M., Taha F. I., ElNeanaa A. I., *Corros. Sci.*, 26, 719 (1986).
- [33]Alshafey H.I., Abdel Hameed R.S., Ali F.A., Aboul-Magd Abd El-Aleem S., Salah M., *Inter. J. Pharm. Sci. Revie. Res.*, 27, 146 (2014).
- [34]Singh Kumar Ashish, Kumar Shukla Sudhish, Quraishi M. A., *Int J Electrochem Sci.*, 10, 5802 (2011).
- [35]Abd El-Hameed R. S., *Port. Electrochim. Acta*, 29, 273 (2011).
- [36]Al Hamzi A.H., Zarrok H., Zarrouk A., Salghi R., Hammouti B., Al-Deyab S.S., *Int. J. Electrochem Sci.*, 8, 2586 (2013).
- [37]Abdel Hameed R. S., Al-Shafey H.I., Abul Magd A.S., Shehata H.A., *J. Mater. Environ. Sci.*, 3, 294 (2012).
- [38]Mansfeld F., Kending M.W., Tsai S., *Corrosion*, 37, 301 (1981).
- [39]Abdallah M., Kamar E. M., Salah Eid , El-Etre A. Y., *J Mol. Liq.*, 220, 755 (2016).
- [40]El-Etre A.Y., Ahmed H. Tantawy, Salah Eid, Doaa F. Seyam, *J. Basic Envi. Sci.*, 2, 128 (2017).
- [41]Abdel Hameed R. S., Abdallah M., protection of metals and surface chemistry of surface, in press N6 2017.
- [42]Abdallah M., Al –Tass H.M., AL Jahdaly B.A., .Fouda A.S, *J Mol Liquids*, 216, 590 (2016).
- [43]Abdel Hameed R. S., Shamroukh A. H., *Int. J. Corros. Scale Inhib.*, 6, 333 (2017).