Effect of food grade organic compounds on corrosion of carbon steel in environmental corrosive media like as peracetic acid solution

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Abstract

The effect of food grade organic compounds, tartaric acid and trisodium citrate, on the corrosion of carbon steel in environmental corrosive media like as peracetic acid solution (PAA) was investigated by weight loss and potentiodynamic polarization curves at 25 ^{o}C. The results show that both tartaric acid and trisodium citrate are effective corrosion inhibitor for carbon steel in different concentrations of peracetic acid solution (PAA). But trisodium citrate is better than tartaric acid as corrosion inhibitor. Weight loss and Tafel results show that corrosion rate of carbon steel decreases with increasing the concentration of both tartaric acid and trisodium citrate. Tafel curves reveal that both tartaric acid and trisodium citrate act as a mixed type inhibitor.

Keywords: Food grade; Carbon steel; Weight loss; Polarization; Acid inhibition.**.**

1. Introduction

Freedom from microbial and foreign body contamination is essential in food production, and the principal means for controlling the surface route of contamination is sanitation (cleaning and disinfection).

After the cleaning phase, disinfection plays a crucial role in further reducing microbial numbers and viability.

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However; disinfectants for use in the food industry may contaminate the product. Therefore, as well as being effective and suitable for factory use, such disinfectants must also be non-toxic and non-tainting. The author describes the usage criteria and operator safety requirements of disinfectants, together with methods to determine taint potential, toxicity and efficacy. Using these parameters, a limited number of disinfectants are judged suitable for general food industry use and these are compared.

The major importance in food manufacture is the freedom of the finished product from contamination by microbes (spoilage and pathogenic microorganisms) and foreign bodies. Contamination in food products may arise from four main sources: the constituent raw materials, surfaces, people (and animals), and the air. Food may become contaminated as it moves across product contact surfaces or if it comes into contact with food operatives or pests. The air may act both as a source of contamination (i.e. from outside the processing area) and as a transport medium, transferring [1].

The biocidal efficacy of disinfectants has been assessed for many years and, in relation to food hygiene, disinfectants are normally evaluated in suspension tests [2, 3].

A number of authors have shown that bacteria attached to various surfaces are more resistant to biocides than when the organisms are in suspension [3-10].

The old traditional chemicals which used before, some of those chemical may be more effective but also it is toxic and not matched with food industries and processes and also the chemicals which may safe for food and human being may be not effective enough. Therefore, the need to safe as human being and also highly effective disinfectants become a great need.

The health Canada has approved the sale of disinfectant for food premises which contain hydrogen peroxide base and per-acetic acid base disinfectants approved for using H_2O_2 & PAA in food industry [11]. The urgent need for usage new generation and stabilized H_2O_2 and PAA due to the highly effectiveness of those products and also safety criteria for it for both food and human being, because the dissociation by products are safe and not toxic, but those products have corrosion properties for the metal.

The selection of Tartaric acid as corrosion inhibitor due to the antioxidant properties as soon as the registration in European Union as food additives with E number 334, Tartaric acid also has several applications for industrial use. Tartaric acid and its derivatives have a plethora of uses in the field of pharmaceuticals. For example, tartaric acid has been used in the production of effervescent salts, in combination with citric acid, in order to improve the taste of oral medications. The acid has been observed to chelate metal ions such as calcium and magnesium. Therefore, the acid has served in the farming and metal industries as a chelating agent for complexing micronutrients in soil fertilizer and for cleaning metal surfaces consisting of aluminium, copper, iron, and alloys of these metals, respectively [12,13].

The objective of this investigation is to determine the effect of tartaric acid and trisodium citrate as food grade organic compounds on corrosion of carbon steel in environmental corrosive media like as peracetic acid solution. The corrosion inhibition performance of tartaric acid and trisodium citrate for carbon steel in peracetic acid solution was investigated using weight loss and potentiodynamic polarization. A probable inhibitive mechanism is presented to explain the experimental observations.

2. Materials and experimental methods

2.1. Materials

2.1.1. Carbon steel specimens

Carbon steel specimens of the following chemical composition (wt. %) were used in the experiment: 0.19% C, 0.05% Si, 0.94% Mn, 0.009% P, 0.004% S, 0.014% Ni, 0.009% Cr, 0.034% Al, 0.016% V, 0.003% Ti, 0.022% Cu, and balance Fe.

A pre-treatment was carried out prior to each experiment, in which specimen surface was mechanically grinded with 340, 400, 600, 800, 1000 and 1200 grades of emery paper, rinsed with bidistilled water, degreased in ethanol and dried at room temperature before use. They were also degreased with acetone and rinsed with distilled water two times and finally dried.

2.2. Weight loss measurements

The rectangular specimens of carbon steel (6 cm × 3 cm × 0.5 cm) were accurately weighed and then immersed for up to 24 h in a solution containing different concentrations of peracetic acid solution with and without different concentrations of tartaric acid and trisodium citrate. Afterwards, the steel sheets were taken out, rinsed thoroughly with distilled water, dried, and accurately weighed.

2.3. Potentiodynamic polarization measurements

Potentiodynamic polarization experiments were carried out using a conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as a reference electrode. The working electrode (WE) was a carbon steel rod embedded in PVC holder using epoxy resin, so that the circular surface (0.34 cm^2) was the working area. Before each measurement, the electrode was immersed in a test solution at open circuit potential (OCP) for 30 min, until a steady state was reached. All polarization curves were recorded by a Voltalab 40 Potentiostat PGZ 402 and a personal computer was used with Voltamaster 4 software at 25 ^{o}C. Each experiment was repeated at least three times to check the reproducibility. The potentiodynamic polarization measurements were obtained by changing the electrode potential automatically from -900 to -200 mV vs. Ag/AgCl at open circuit potential with a scan rate 0.2 mV s^{-1} at 25 ^{o}C.

3. Results and discussion

3.1. Potentiodynamic polarization curves

The potentiodynamic polarization curves for carbon steel in 0.015, 0.0375 and 0.075% of PAA solutions without and with different concentrations tartaric acid after 30 min immersion at 25 ^{o}C are shown in Figs. 1-3. As can be seen from Figs. 1-3, the corrosion potentials in the presence of tartaric acid comparing with that in PAA without tartaric acid are shifted to more negative direction, the cathodic branches are shifted to negative potential direction and the anodic branches are shifted to negative potential direction, which reveal that tartaric acid acts as a mixed type inhibitor [14-17]. Accordingly, the cathodic and anodic current density also decreases with increasing of tartaric acid, suggesting that tartaric acid inhibit both the anodic and cathodic reactions. Furthermore, we can be seen from Figs. 1-3, corrosion current density values increases with increasing the concentration of PAA suggesting that PAA accelerate both the anodic and cathodic reactions which indicates that the maximum acceleration of the anodic reaction occurs in PAA at 0.075 %. The potentiodynamic polarization curves for carbon steel in 0.015, 0.0375 and

0.075% PAA solutions without and with different concentrations trisodium citrate after 30 min immersion at 25 °C are shown in Figs. 4-6. Figs. 4-6 show that the corrosion potentials in the presence of trisodium citrate in PAA are slightly shifted to more negative direction and this indicating that trisodium citrate act as a mixed type inhibitor [18-20]. In addition, the cathodic and anodic current density also decreases with increasing of trisodium citrate, suggesting that trisodium citrate inhibit both the anodic and cathodic reactions.

The corrosion inhibition efficiency (*IE*) was calculated using the following equation [21-24]:

$$IE = \left(\frac{i^o_{corr} - i_{corr}}{i^o_{corr}} \right) \times 100 \qquad (1)$$

where i^o_{corr} and i_{corr} are the corrosion current density values without and with different concentrations of inhibitors, respectively.

The values of anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were calculated and listed in Tables 1&2. The results in Tables 1&2 show that the corrosion inhibition efficiency of trisodium citrate is better than tartaric acid and this is due to acidity of tartaric acid.

3.2. Weight loss results

The effect of food grade organic compounds, tartaric acid and trisodium citrate, on the corrosion of carbon steel in environmental corrosive media like as peracetic acid solution (PAA) was investigated by weight loss at 25 °C. The corrosion rate (*k*) was calculated by the following equation [25, 26]:

$$k = \frac{\Delta W}{S.t} \qquad (2)$$

where ΔW is the average weight loss of three carbon steel sheets, S is the total area of one carbon steel specimen, and t is the immersion time.

The inhibition efficiency (IE) was calculated as follows [27-30]:

$$IE = \left(1 - \frac{W^o_{corr}}{W_{corr}} \right) \times 100 \qquad (3)$$

where W^o_{corr} and W_{corr} are the weight loss of carbon steel in the absence and presence of the inhibitor, respectively.

Weight loss data of carbon steel in PAA in the absence and presence of different concentrations of tartaric acid and trisodium citrate at 25 °C are listed in Table 3. It indicates that the corrosion inhibition efficiency of both tartaric acid

and trisodium citrate increases with increasing the concentration. This behavior may be attributed to adsorption of tartaric acid and trisodium citrate molecules on the metal surface.

3.3. Adsorption Isotherm

Basic information on the interaction between the inhibitor molecules and metal surfaces was provided by the adsorption isotherms. The values of surface coverage (θ) were calculated from the following equation [31] and obtained from weight loss measurements at 25 °C.

$$\theta = 1 - \left(\frac{W_{corr}}{W^o_{corr}} \right) \qquad (4)$$

where $W°$ and W are the weight loss in the absence and presence of inhibitors, respectively.

A correlation between θ and inhibitor concentration in the corrosive medium was represented by the Langmuir adsorption isotherm [32-34]:

$$\frac{C}{\theta} = \left(\frac{1}{K_{ads}} \right) + C \qquad (5)$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process and C is the inhibitor concentration. Plotting of C/θ versus C yielded a straight line (Figs. 7&8) with slope close to 1.

K_{ads} values could be calculated from the intercepts of the straight lines on the C/θ -axis, the K_{ads} was related to the standard free energy of adsorption, ΔG^o_{ads}, according to the following equation:

$$\Delta G^o_{ads} = -RT \ln (55.5 \, K_{ads}) \qquad (6)$$

The value 55.5 in the above equation is the molar concentration of water in solution in mol dm^{-3} [34].

The thermodynamics parameters derived from Langmuir adsorption isotherms for the studied compounds, are given in Table 4. The negative values of ΔG^o_{ads} along with the high K_{ads} indicate a spontaneous adsorption process [35, 36]. Generally, the energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption. While, those of -40 kJ mol^{-1} or more negative were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond [37, 38]. The values of ΔG^o_{ads} in our measurements suggested that the adsorption of these products involves two types of interaction physisorption and chemisorption.

3. Tables, Figures

Table 1

Potentiodynamic polarization parameters for carbon steel in various concentrations of PAA solution in the absence and presence of different concentrations of TA at 25 ^{o}C

Conc.	E_{corr} (mV vs Ag/AgCl)	i_{corr} (µA cm^{-2})	β_a (mV dec^{-1})	β_c (mV dec^{-1})	IE (%)
0.015 % PAA	-630	213.4	156.9	-178.3	-
5.0x10^{-4} M	-675	105.28	157.9	-177.0	50.66
7.5x10^{-4} M	-670	76.17	153.5	-185.7	64.31
1.0x10^{-3} M	-640	64.63	165.9	-198.3	69.71
2.5x10^{-3} M	-636	53.60	143.0	-197.9	74.88
5.0x10^{-3} M	-654	42.13	167.4	-180.0	80.13
0.0375 % PAA	-582	288.4	147.8	-180.5	-
5.0x10^{-4} M	-628	133.85	149.4	-171.4	63.24
7.5x10^{-4} M	-589	99.27	162.7	-197.2	65.58
1.0x10^{-3} M	-619	74.12	155.0	-174.3	74.3
2.5x10^{-3} M	-613	68.05	177.4	-169.0	76.40
5.0x10^{-3} M	-597	49.21	145.0	-167.8	82.94
0.075 % PAA	-561	497.3	145.6	-181.3	-
5.0x10^{-4} M	-612	174.32	166.1	-183.6	64.95
7.5x10^{-4} M	-608	159.83	161.0	-184.9	67.86
1.0x10^{-3} M	-606	102.42	187.7	-193.2	79.40
2.5x10^{-3} M	-583	85.79	141.8	-197.2	82.75
5.0x10^{-3} M	-606	61.88	175.1	-200.9	87.56

Table 2

Potentiodynamic polarization parameters for carbon steel in various concentrations of PAA solution in the absence and presence of different concentrations of TSC at 25 ^{o}C

| Conc.	E_{corr} (mV vs Ag/AgCl)	i_{corr} (µA cm^{-2})	β_a (mV dec^{-1})	β_c (mV dec^{-1})	IE (%)
0.015 % PAA	-630	213.4	156.9	-178.3	-
5.0x10^{-4} M	-642	105.28	157.9	-177.0	50.66
7.5x10^{-4} M	-643	76.17	173.5	-175.7	64.31
1.0x10^{-3} M	-645	64.63	164.9	-199.3	69.71
2.5x10^{-3} M	-654	53.60	166.0	-181.9	74.88
5.0x10^{-3} M	-625.5	42.13	137.4	-197.0	80.13
0.0375 % PAA	-582	288.4	147.8	-180.5	-
5.0x10^{-4} M	-603	133.85	157.4	-191.4	63.24
7.5x10^{-4} M	-634.5	99.27	174.7	-201.2	65.58
1.0x10^{-3} M	-616	74.12	175.0	-199.3	74.3
2.5x10^{-3} M	-625.5	68.05	141.4	-172.0	76.40
5.0x10^{-3} M	-597	49.21	123.0	-171.8	82.94
0.075 % PAA	-561	497.3	145.6	-181.3	-
5.0x10^{-4} M	-607.5	174.32	156.1	-185.6	64.95
7.5x10^{-4} M	-619.5	159.83	161.0	-189.9	67.86
1.0x10^{-3} M	-621	102.42	165.7	-199.2	79.40
2.5x10^{-3} M	-627	85.79	167.8	-197.2	82.75
5.0x10^{-3} M	-559.5	61.88	138.1	-205.9	87.56
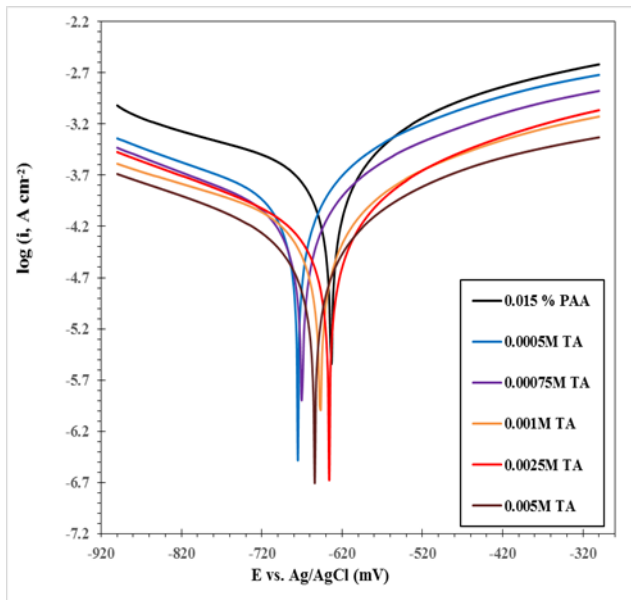
Fig. 1. Potentiodynamic polarization curves for carbon steel in 0.015 % PAA solution in the absence and presence of different concentrations of TA at 25 ^{o}C.
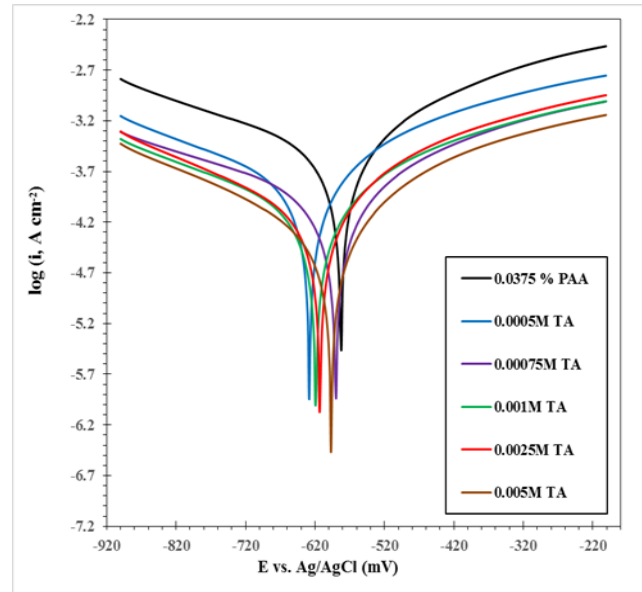

Fig. 2. Potentiodynamic polarization curves for carbon steel in 0.0375 % PAA solution in the absence and presence of different concentrations of TA at 25 ^{o}C.
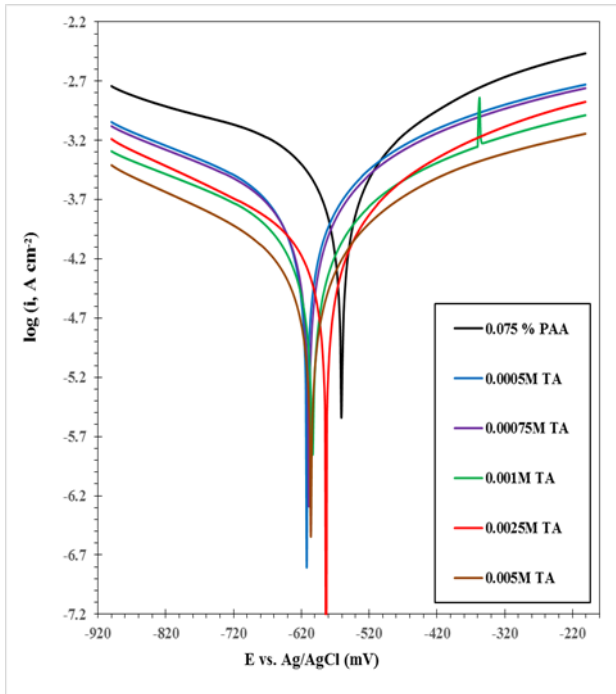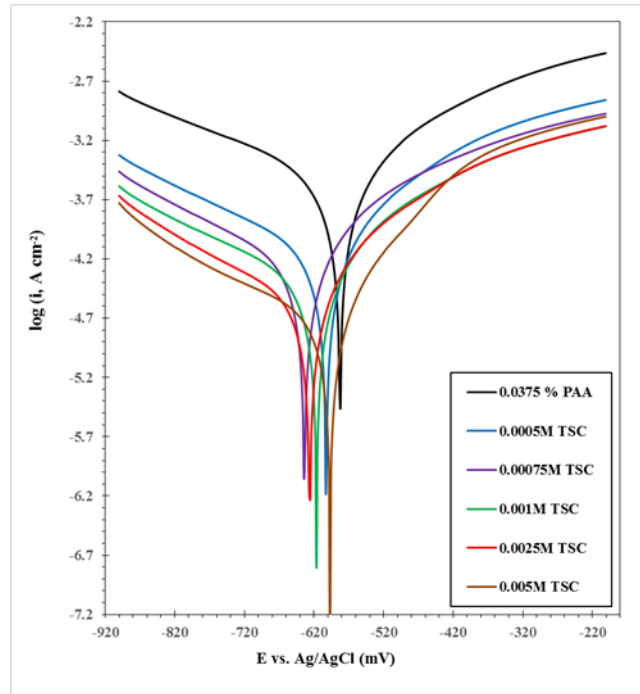
Fig. 3. Potentiodynamic polarization curves for carbon steel in 0.075 % PAA solution in the absence and presence of different concentrations of TA at 25 ^{o}C.

Fig. 5. Potentiodynamic polarization curves for carbon steel in 0.0375 % PAA solution in the absence and presence of different concentrations of TSC at 25 ^{o}C.
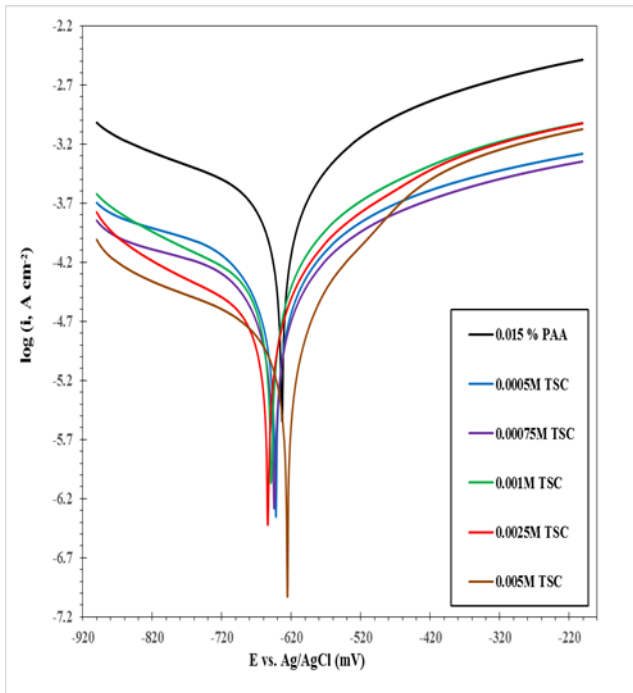

Fig. 4. Potentiodynamic polarization curves for carbon steel in 0.015 % PAA solution in the absence and presence of different concentrations of TSC at 25 ^{o}C
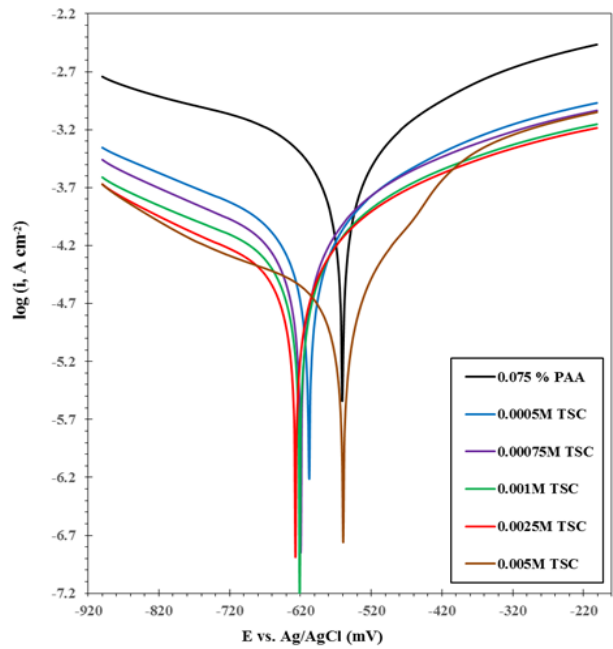

Fig. 6. Potentiodynamic polarization curves for carbon steel in 0.075 % PAA solution in the absence and presence of different concentrations of TSC at 25 ^{o}C.

Table 3

Weight loss data for carbon steel in different concentrations of peracetic acid in the absence and presence of various concentrations of tartaric acid and trisodium citrate at 25 °C

| Inhibitor name	Inhibitor conc. (M)	Peracetic acid (PAA)								
		0.015 %			0.0375 %			0.075 %		
		k (mg cm^{-2} h^{-1})	Θ	IE (%)	k (mg cm^{-2} h^{-1})	Θ	IE (%)	k (mg cm^{-2} h^{-1})	Θ	IE (%)
Absence	0.00	210.49	-	-	285.32	-	-	492.51	-	-
TA	5.0×10^{-4}	100.86	0.52	52.08	102.39	0.64	64.11	171.24	0.65	65.23
	7.5×10^{-4}	72.79	0.65	65.42	96.16	0.66	66.30	159.17	0.68	67.68
	1.0×10^{-3}	64.41	0.69	69.40	72.28	0.75	74.67	101.37	0.79	79.42
	2.5×10^{-3}	53.10	0.75	74.77	60.09	0.79	78.94	84.60	0.83	82.82
	5.0×10^{-3}	37.09	0.82	82.38	46.49	0.84	83.70	51.45	0.90	89.55
TSC	5.0×10^{-4}	58.69	0.72	72.12	60.72	0.79	78.72	82.57	0.83	83.23
	7.5×10^{-4}	37.22	0.82	82.32	47.38	0.83	83.39	51.58	0.90	89.53
	1.0×10^{-3}	30.11	0.86	85.70	36.71	0.87	87.13	36.84	0.93	92.52
	2.5×10^{-3}	19.44	0.91	90.77	22.99	0.92	91.94	26.30	0.95	94.66
	5.0×10^{-3}	13.59	0.94	93.54	16.64	0.94	94.17	13.47	0.97	97.27
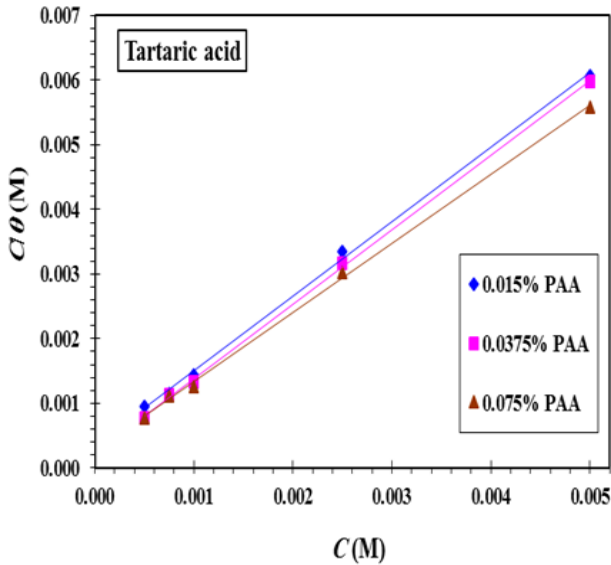
Fig. 7: The Langmuir isotherm adsorption plot for carbon steel in different concentrations of PAA containing different concentration of the TA at 25 °C.
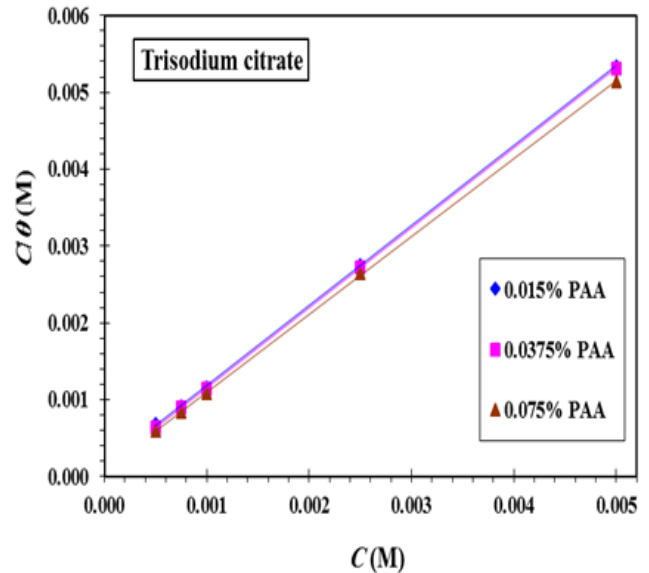

Fig. 8: The Langmuir isotherm adsorption plot for carbon steel in different concentrations of PAA containing different concentration of the TSC at 25 °C.

Table 4

Thermodynamic parameters of adsorption on carbon steel surface in different concentrations of Peracetic acid in the absence and presence of various concentrations of tartaric acid and trisodium citrate at 25 ^{o}C

Inhibitor Name	K_{ads} x10^{-4} (M^{-1})	ΔG^{o}_{ads} (kJ mol^{-1})
Tartaric acid	0.29	-29.73
	0.44	-32.77
	0.39	-34.50
Trisodium citrate	0.68	-31.83
	0.86	-34.58
	1.17	-37.61

4. Conclusion

- The effect of food grade organic compounds, tartaric acid and trisodium citrate, on the corrosion of carbon steel in environmental corrosive media like as peracetic acid solution (PAA) was investigated by weight loss and potentiodynamic polarization curves at 25 ^{o}C.

- Weight loss and Tafel results show that corrosion rate of carbon steel decreases with increasing the concentration of both tartaric acid and trisodium citrate.

- Tafel curves reveal that both tartaric acid and trisodium citrate act as a mixed type inhibitor.

- The results show that both tartaric acid and trisodium citrate as regard effective corrosion inhibitor for carbon steel in different concentrations of peracetic acid solution (PAA). But trisodium citrate is better than tartaric acid as corrosion inhibitor for carbon steel in peracetic acid solution (PAA).

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