Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(12):1179-1194

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Anti-corrosive effect of olive oil mill wastewaters C38 steel in acid HCl

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ABSTRACT

The need arises to adopt more economically and environmentally sustainable solutions for OMW disposal such as the corrosion. The possibility of recycling a given process residue would reduce the environmental impact of this effluent. Therefore, recycling any material, rejected as a by-product of a process, would reduce environmental pollution and cost production. Considering the problem of the corrosion, the conception of reuse the OMW such as inhibitor of the corrosion would be a partial solution to the olive oil processing wastewater. The effect of olive oil mill wastewater (OMW) as a corrosion inhibitor on the corrosion rate of the steel alloy in 1M HCl acid was investigated using the gravimetric method. The corrosion rates were studied in different concentrations of vegetables (0.6, 1, 1.6, 2 and 2.6 g / v) at temperatures of 30, 40, 50, 60 and 70° C. The results showed that the OMW decreased the corrosion rate at different concentrations considered. The minimum efficiency of inhibition was obtained at 80%, while the maximum efficiency of 92% inhibition was obtained with the inhibitor concentration of 2.6 g / v at 30°C, the vegetable is as effective corrosion inhibitor in the range of temperature and concentration studied. The results showed that OMW adsorbed on the surface of the steel alloy and obeys Langmuir adsorption isotherm.

Keywords: Corrosion, Carbon Steel X70, Olive Oil Mill Wastewater, Inhibition, Adsorption, HCl.

INTRODUCTION

The Corrosion affects most of the industrial sector and may cost billions of dollars each year for preventing, replacement and maintenance [1]. In industrialized countries the costs of corrosion are three to four percent of gross national product. Corrosion is not only wasteful of raw materials and energy, plus it can cause accidents with serious consequences and, in some cases, contribute to pollution of the natural environment [2]. From 25 to 30% of the total economic losses in the oil and gas industry [3-5] is due to failures of pipes and other plants systems resulting from metallic corrosion. Among the methods of protection, used inhibitors, By definition, a corrosion inhibitor is a chemical substance that when added in small concentration to an environment, effectively decreases the corrosion rate by forming a protective films which give the surface a certain level of protection [6]. The inhibitors play an important in the fight against corrosion, in the protection and mitigation strategies for retarding corrosion [7], to reduce the rate of dissolution of metals, that is to say, reduce the rate of either anodic oxidation or cathodic reduction or both, Most well-known acid inhibitors are organic compounds containing N, O, and S atoms [8-9], Adsorption of organic compounds containing functional group containing hetero atoms (N, O, P or S) of the density and high electron long hydrophobic alkyl chains are effective corrosion inhibitors for corrosion of various metals in acidic medium [10-14]. Inhibiting process involves chemisorption of the nucleophilic heteroatom on the metal surface, which in turn is protected by the hydrophobic groups of hostile aqueous medium [15-17]. However, some synthetic corrosion inhibitors have been identified to be toxic and non eco-friendly [18-19], due to the several negative effects they have caused in the environment [20]. The toxic effect does not only affect living organisms but also poisons the environment [21]. Thus, search for an eco-friendly and non-toxic corrosion inhibitors of natural source has been considered to be more important and desirable [22].The use of plant extract and oils; otherwise known as green corrosion inhibitors has gained recognition due to their availability, non toxicity and renewable source of materials for wide range of corrosion control [23-24]. Olive Mill Wastewaters seem to be ideal candidates to replace traditional toxic corrosion inhibitors. some kinds of organic compounds to have been used as inhibitors of steel corrosion in HCL solution, such as plant extract [25- 26], The encouraging results of the anticorrosion effect obtained from extracts and oil of natural products as corrosion inhibitor for steel in acidic solutions by several authors (jojoba oil [27], Solanum trilobatum [28], Garcinia kola extract [29]. Artemisia oil [30], pennyroyal oil from Mentha pulegium [31], Eucalyptus oil [32], Azadiracta indica [33], Cedre oil [34], Black pepper [35], Atractylis serratuloides extract [36], fenugreek extracts [37], Hibiscus sabdariffa extract [38], Adathoda vasica [39], and thymus oil [40], encourage us to test in liquid products mills (waters) in the study of corrosion There is no report to our knowledge of the effect of the addition of Olive Mill Wastewarter on the corrosion of C38 steel alloy in HCl solution.

Olive Mill Wastewaters (OMW)

Although the process of the production of olive oil is a seasonal process, and in general all that begins in September and ends in the month of February at the latest [41], Olive oil industries are of fundamental economic and social importance for many Mediterranean countries responsible for 98% of the entire worldwide olive oil production such as Spain, Italy, Greece, Turkey, Tunisia and Morocco [42-44]. Olive oil production involves one of the following extraction processes batch (press olive oil extraction) or continuous Methods (three and two-phase centrifugal olive oil extraction [45-46]. In batch (traditional) system, oil is extracted by applying pressure [47]. Continuous system is a modernized method and based on centrifugal separation. Olive oil extraction processes generate three phases: olive oil, solid residue and aqueous liquor (OMW) which averagely represents 20, 30 and 50% respectively of the total weight of the processed olives [48]. An amount of water is added in the conventional traditional process, this amount is relatively low (approximately 40%), but in the continuous system three phase; it varies from 70 to 110% [49]. After the process, three “phases” are produced; oil, wastewater and olive pomace. In two phase application, no process water is added and only two phases are produced: oil and olive pomace with moisture [46; 50]. The extraction of oil from the olives generates large quantities of liquid by-products [51-52]. The wastewater arising from the milling process amounts to 0.5– 1.5 m3 per 1000 kg of olives depending on the applied process [53]. The volume of OMW produced in traditional presses and in three-phase extraction systems amounts to about 600 and 1000 l per ton of processed olives, respectively, while it is much lower in the two-phase process [54]. The Olive oil Mill Wastewater (OMW) is the liquid by-product generated during olive oil production [55], this effluent are brown to reddish brown, with cloudiness [56-60].This black liquid wastewater is composed of the olive fruit vegetation water, the water used for washing and treatment and a portion of the olive pulp and residual oil [61]. They hold olive pulp, mucilage, pectin, oil, etc., suspended in a relatively stable emulsion [62-63]. Several factors can affect the quality and physicochemical composition of olives and their by-products extraction, especially liquid waste "oil mill wastewaters", during extraction and after discharge into the milieu receiver, including: cultivation practices such as fertilization [64], the irrigation management [65], and agronomic practices adopted in the field [66]. The quality and quantity of olive mill wastewater depend on cultivation parameters, milling method applied for oil extraction technology [67- 69], the operation of extracting olive oil, the variety of olives, the harvest season, the rate of fruit ripening and climatic conditions [70], growing techniques, and especially the technology used for oil extraction [42]. The volume of this liquid waste varies from (per 100 kg of olives): 40–60 l for pressing method to 80–100 l for three-phase centrifugation technique [71]; age of growth, yearly changes, [72], use of pesticides and fertilizers, [73], operation conditions [74], The storage time and conditions [75-82]. During the seasonal extraction of olive oil, the quantities of olive mill wastewater (OMW) produced more than 30 million m3 per year In the Mediterranean (Spain, Italy, Greece, Turkey, Syria, Tunisia, Morocco) [63,76,77,83-85], The annual production of olive mill wastewater (OMW) in Morocco exceeds 250.000m3 [86],the olive mill wastewaters are 100–400 times higher heavily loaded with pollutants than more than ordinary domestic wastewater [45,87].

The by-product (Olive Mill Wastewater) is characterized a low pH (3.5–5.5) and a high salinity depending essentially on olive oil extraction process [88], it is containing many dissolved and suspended substances organic and minerals, Typically, the composition of OMW is 83–92% water, 4–16% organics and 0.4–2.5% mineral salts [89-93].The organic load reflected in the high BOD (up to 100 g/1) and COD (up to 200 g/1) concentrations [94], The organic fraction is composed of sugars (1–8%), N-compounds (especially amino acids) (0.5–2.4%), organic acids (0.5–1.5%), fats (0.02–1%) as well as phenols and pectins (1–1.5%) [93, 95-97], More than 50 phenolic compounds, many alcohols, aldehydes and other low molecular weight compounds have been reported in the literature [98], Oils (1–14%), polysaccharides (13–53%), proteins (8–16%), polyalcohols (3–10%) and polyphenols (2–15%) [99], tannins, pectins, carotenoids, and almost all of the water soluble constituents of the olives [100-101]. OMW are characterized by the great variety of pollutants contained, including aromatics (such as cathecol, p-coumaric acid, 4-methylcathecol, benzene-acetaldehyde, phenyl ethyl alcohol, benzofurane, and tyrosol) and also aliphatic compounds (such as hexane, octane, nonanol nonanoic acid, decanoic acid, dichloropropene, pentadecene, and hexadecane) [102], Mineral salts of OMW are mainly carbonates (21%), phosphates (14%), potassium (47%) and sodium (7%) [99]. OMW contain also, other inorganic compounds such as chloride, sulfate and phosphoric salts of potassium as well as calcium, iron, magnesium, sodium, copper and traces of other elements [103-104]. Total suspended solid (TSS) is principally derived from the olive pulp and contains mainly cellulose and pectins [105].

No chemical or biological effective treatments are available to deal with these wastewaters and mitigate their impact on receiving systems [106], because one hand due to its high content in highly toxic and recalcitrant organic compounds and high COD levels, and on the other hand, The current technologies used to reduce the large load of potentially toxic organic substances present in OMW are expensive and/or unreliable [54]. Therefore, the disposal of olive oil mill wastewater (OMW) represents a major social, economic, and environmental problem in Mediterranean olive oil producing countries [107-108]. Therefore, the need arises to adopt more economically and environmentally sustainable solutions for OMW disposal such as the corrosion. The possibility of recycling a given process residue would reduce the environmental impact of this effluent. Therefore, recycling any material, rejected as a by-product of a process, would reduce environmental pollution and cost production. Considering the problem of the corrosion, the conception of reuse the OMW such as inhibitor of the corrosion would be a partial solution to the olive oil processing wastewater.

My objective of this research is exploring the possibility of reuse Olive oil Mill Wastewaters (OMW) as a corrosion inhibition of steel in an acidic medium (HCL 1M), and compared the inhibitory effect of Olive oil Mill Wastewaters (OOMW) samples collected from three extraction process of olive oil (traditional, semi-modern and continuous) in the eastern region of Morocco. The electrochemical behavior of the C38 steel in HCl medium in the absence and presence OMW's was studied by gravimetric and electrochemical techniques such as potentiodynamic polarization, linear polarization and impedance spectroscopy (EIS). The effect of temperature is also studied. It was also the aim of this study to test the experimental data with several adsorption isotherms at different temperatures to determine the standard free energy of adsorption process and get more information on the adsorption mode of inhibitor on the surface of the electrode.

EXPERIMENTAL SECTION

Samples and materials

The aggressive solution (1M HCl) was prepared by dilution of analytical grad 37% HCl with bi-distilled water. Steel sample containing 0.09%P; 0.38%Si; 0.01%Al; 0.05%Mn; 0.21%C; 0.05%S and the remainder iron. Prior to all measurements, the steel samples are polished with different emery paper up to 1200 grade, washed thoroughly with bi-distilled water degreased and dried with ethanol, acetone.

Olive Oil Mill Wastewaters(OOMW) samples were collected from three different units for each type of process; three units for continuous [OMW_{19}, OMW_{20}, OMW_{21}], three for semi-modern[OMW_{8}, OMW_{11}, OMW_{14}] and three for traditional processes[OMW_{1}, OMW_{2}, OMW_{3}] in the area of Oujda(Oujda, Berkane, Nador, Taourirt, and Jerada).

Gravimetric and polarization measurements

Gravimetric measurements were carried out in double walled glass cell equipped with a thermostatic-cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2.5cm x 2.4cm x 0.07cm). The immersion time for the weight loss is 6 h at 308±1K.

Electrochemical measurements were carried out in a conventional three electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) had the form of a disc cut from the steel sheet. The area exposed to the corrosion solution was 1 cm2. A saturated calomel electrode (SCE) and disc platinum electrode were used as reference and auxiliary electrode, respectively. The temperature was thermostatically controlled at 308 ±1K.

The polarization curves are recorded with a potentiostat type EG&G and G 273, at a scan rate of 30mV/min. The steel electrode was maintained at corrosion potential for 30 min and there after pre-polarized at − 800 mV for 10 min in order to move oxide film from the electrode. The potential was swept to anodic potentials. The test solution is de-aerated for 30 min in the cell with pure nitrogen which is maintained throughout the experiments.

Weight loss measurements

Weight loss measured on sheets of pure steel of apparent surface area of 6 cm2. These sheets were abraded successively with fine emergy paper. The sheets were then rinsed with distilled water, degreased and dried before being weighed and immersed in the corrosive medium. The immersion time for the weight loss was from 6h to study the effect of the concentration of the samples and 1h at different temperatures (35, 40, 50, 60.70 ° C) for the temperature effect.

RESULTS AND DISCUSSION

Effect of concentration

Weight loss measurements

Table 1 resumes the results of the corrosion rate obtained in 1M HCl (W°_{corr}) and at various contents of samples of oil mill wastewaters (W_{corr}) determined at 308K after 6h of immersion rate and inhibition efficiencies (E_w%) is determined by the relation (1):

$$Ew\% = 100 \times \left(1 - \frac{W_{Corr}}{W^{\circ}_{Corr}}\right) \qquad (1)$$

W_{corr} and W°_{corr} are the corrosion rates of steel with and without samples of Olive Mill Wastewaters, respectively.

Table 1 : Gravimetric results of steel corrosion in 1M HCl without and with addition of the Olive Mill Wastewaters obtained from each process (the traditional press process, the semi- modern process and the continuous process) at various concentrations studied at 308K after 6h of immersion period

process	samples	Concentration (ppm)	W ($mg.cm^{-2}.h^{-1}$)	E_w %
		Blank 1M HCL	0.93	*
Traditional press process	OMW_1	O,6	0.69	86.67
		1	1.15	86.9
		1.6	1.82	87.99
		2	2.26	88.46
		2.6	2.93	88.7
	OMW_2	O,6	0.69	87.06
		1	1.14	87.96
		1.6	1.81	88.38
		2	2.24	89.4
		2.6	2.9	89.76
	OMW_3	O,6	0.79	87.79
		1	1.3	88.20
		1.6	2.04	88.93
		2	2.51	89.94
		2.6	3.17	92.46
Semi- modern process	OMW_8	O,6	0.67	88.93
		1	1.12	89.12
		1.6	1.79	89.33
		2	2.23	89.68
		2.6	2.86	90.77
	OMW_{11}	O,6	0.67	88.93
		1	1.12	89.485
		1.6	1.77	90.31
		2	2.21	90.67
		2.6	2.84	91.49
	OMW_{14}	O,6	0.68	88.35
		1	1.12	89.05
		1.6	1.79	89.42
		2	2.22	89.9
		2.6	2.87	90.71
Continuous process	OMW_{19}	O,6	0.68	88.34
		1	1.12	88.93
		1.6	1.79	89.62
		2	2.22	90.03
		2.6	2.88	90.39
	OMW_{20}	O,6	0.69	86.66
		1	1.15	86.83
		1.6	1.82	87.9
		2	2.26	88.59
		2.6	2.92	89.12
	OMW_{21}	O,6	0.69	87.17
		1	1.14	88.04
		1.6	1.81	88.49
		2	2.26	88.69
		2.6	2.92	89.15

It is clear that for each sample of olive mill wastewater tested, the steel corrosion rate values decreases when the concentration of inhibitors increases. It is important to note that the inhibitory effect increases with the increase of Olive Mill Wastewaters concentration and reaches a maximum at 2.6M , all the samples of the Olive Mill Wastewaters reduce the rate of corrosion in HCl solution with an efficiency percentage of over 89%, but a small percentage of efficacies were recorded between samples of each extraction processes; average efficiencies of 90 %, 91 % and 89 % for the three types processes extraction (traditional, semi-modern and modern), respectively , however, we can classify the samples according to the inhibition efficiency as follows: $OMW_3 > OMW_{11} > OMW_8 > OMW_{14} > OMW_{19} > OMW_2 > OMW_{21} > OMW_{20} > OMW_1$, The efficiency reaches a maximum of 92 %, 91%, and 90% samples of the traditional press process, the semi- modern process and the continuous process, respectively, at a concentration of 2.6 ppm.

We can conclude that the OMW oil mills are good inhibitors of corrosion of steel in 1M HCl solution, this difference in the inhibition efficiency between samples is attributed to the difference in the composition and extraction processes of olive mill wastewaters.

Electrochemical polarization measurements:

The cathodic and anodic polarization curves of C38 steel in 1M HCl in the absence and presence of olive mill wastewaters (OMW) at different concentrations at 298 K are presented in Figs. 1, 2 and 3, respectively. Values of the associated electrochemical parameters are given in Table 2.

The Table 2 gives values of corrosion current (I_{corr}), corrosion potential (E_{corr}), Cathodic Tafel slope (β_c) for all samples of olive mill wastewaters in 1M HCl. In the case of polarisation method, the relation (2) determines the inhibition efficiency (E %):

$$E\% = 100\times\left(1-\frac{I_{Corr}}{I^{\circ}_{Corr}}\right) \qquad (2)$$

Where I°_{corr} and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential (E_{corr}).

Polarisation behaviour of steel in 1M HCl in the presence and absence of inhibitors is shown in [Fig. 1-3].

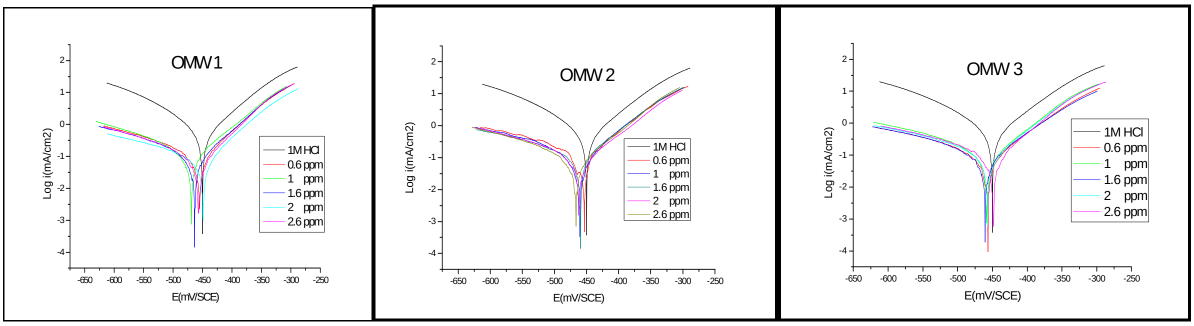

Fig 1 : Typical polarization curves of steel in 1MHCL for various concentrations of oil mill wastewater (OMW) from the traditional process (OMW_1, OMW_2 and OMW_3)

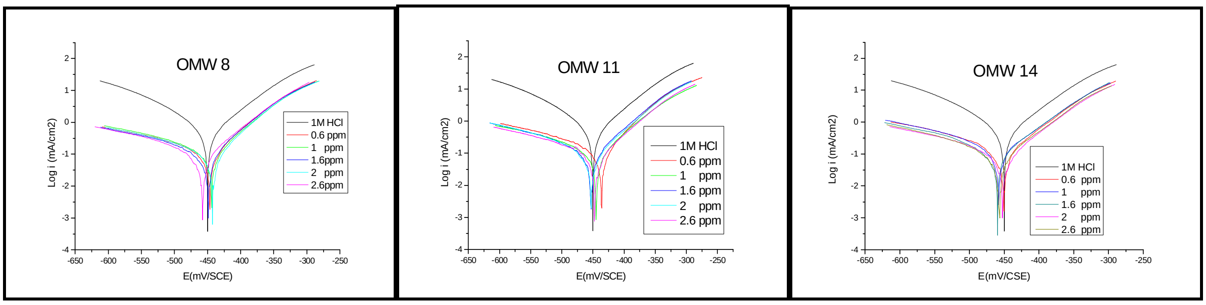

Fig 2 : Typical polarization curves of steel in 1MHCL for various concentrations of oil mill wastewater (OMW) from the semi-modern process (OMW_8, OMW_{11} and OMW_{14})

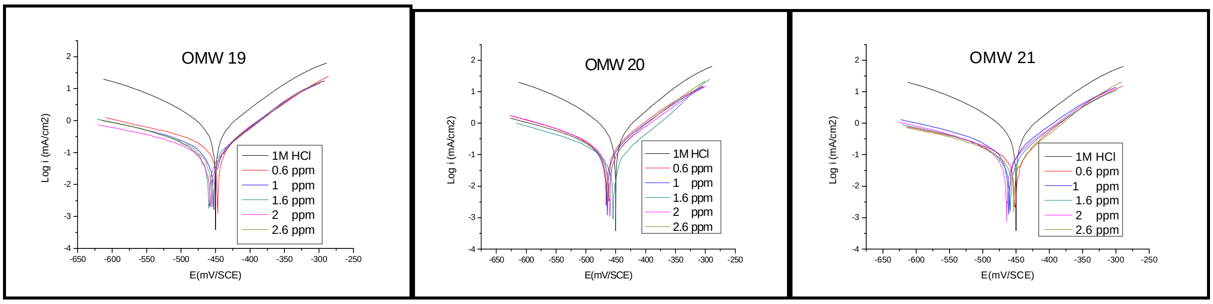

Fig 3 : Typical polarization curves of steel in 1MHCL for various concentrations of oil mill wastewater (OMW) from the modern process (OMW_{19}, OMW_{20} and $OMW_{2}1$)

Table 2 : results of Tafel plots of a mild steel sample in various solutions containing the inhibitors of OMWs

Process	Samples	Concentration ppm	Tafel plots				
			E_{corr} (mV/SEC)	β_a (mV/dec)	$-\beta_c$ (mv/dec)	I_{corr} (mA/cm^2)	E (%)
	Blank	1M HCl	-450	63	87.4	0.3765	-
Traditional press process	OMW_1	0.6	-454.6	60.6	163.2	0.0759	79.84
		1	-469	66.8	137.7	0.0748	80.13
		1.6	-463.3	61.9	144.5	0.0609	83.82
		2	-448.6	61.3	190.7	0.0607	83.88
		2.6	-456.7	55.2	138.1	0.0478	87.3
	OMW_2	0.6	-453.6	65.4	135.5	0.1007	73.25
		1	-459.7	65.8	174.5	0.0874	76.79
		1.6	-458.7	63.8	150.8	0.0822	78.17
		2	-462.6	64.2	142.8	0.0525	86.06
		2.6	-467.1	60.1	121.3	0.0453	87.97
	OMW_3	0.6	-456.1	64.9	157.0	0.0668	82.26
		1	-458.1	59.2	130.5	0.0660	82.47
		1.6	-460.7	68.5	139.9	0.0646	82.84
		2	-456.8	59.5	150.3	0.0644	82.9
		2.6	-448.9	55.1	147.2	0.0616	83.64
Semi- modern press process	OMW_8	0.6	-446.3	62.3	244.1	0.1551	58.8
		1	-441.7	60	196.2	0.1007	73.25
		1.6	-445.5	60	219.7	0.0973	74.16
		2	-441.2	57.1	185.2	0.0854	77.32
		2.6	-457.2	62.3	154.9	0.0752	80.03
	OMW_{11}	0.6	-436.5	53	168.3	0.0858	77.21
		1	-444.7	63.9	160.8	0.0828	78.01
		1.6	-452.9	60.2	132	0.0762	79.76
		2	-452.6	60.2	139.8	0.0679	81.97
		2.6	446.9	60.5	164.3	0.0626	83.37
	OMW_{14}	0.6	-450.6	63.6	158.1	0.0976	74.08
		1	-457.9	63.9	141.8	0.0844	77.58
		1.6	-459.6	64.7	123.6	0.0819	78.25
		2	-451.5	61.8	168.3	0.0667	82.28
		2.6	-457.4	62.8	141.1	0.0604	83.96
Continuous process	OMW_{19}	0.6	-446.8	69.2	194	0.1395	62.95
		1	-453.3	60.2	139.2	0.0798	78.8
		1.6	-459	63	128	0.0678	81.99
		2	-465.9	61.5	155.2	0.0677	82.02
		2.6	-454.7	58.5	133.4	0.0645	82.87
	OMW_{20}	0.6	-465.9	88.1	184.4	0.02361	93.73
		1	-464.4	75	166.1	0.1338	64.46
		1.6	-453.3	64.4	181.7	0.1275	66.14
		2	-460.3	74.3	141	0.1206	67.97
		2.6	-461.8	68.2	149.8	0.1120	70.25
	OMW_{21}	0.6	-451.2	69.4	221.1	0.1429	62.05
		1	-460.9	69.2	152.3	0.1073	71.5
		1.6	-458.9	68.4	163.5	0.0826	78.06
		2	-464.2	66	136.8	0.0704	81.3
		2.6	-453.1	58	151.5	0.0554	85.29

The recording of the anodic and cathodic polarization curves has been conducted to obtain information about the action of inhibitor on the partial corrosion processes. It is clear from Fig.1-3 and Table 2, that the tested Olive Mill Wastewaters reduces the corrosion rate by affecting both steel dissolution (anodic reaction) and the hydrogen reduction (cathodic reaction). The addition of the different samples of Olive Mill Wastewaters caused a decrease of the current density. That the inhibiting action is more pronounced with flowing order: OMW_{20}< OMW_8< OMW_{19}< OMW_{11}< OMW_3< OMW_{14}< OMW_{21}< OMW_1< OMW_2. In the cathodic domain, the curves rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activation controlled. This result shows that the addition of the samples of Olive Mill Wastewater does not affect the mechanism of the processes [109]. Values of the corrosion potential do not change in the presence of Olive Mill Wastewaters. The values of corrosion potential (E_{corr}) and cathodic Tafel slope (βc) slightly change when the concentration increases. These results demonstrated that the reduction of hydrogen was inhibited and that the inhibition efficiency increased with inhibitor concentration. E% increases with the concentration of Olive Mill Wastewaters and reaches a maximum value of the traditional process, the semi-modern and the modern process: 87.97%, 83.96% and 85.29%, respectively, at the concentration 2.6ppm; In the anodic range, the polarization curves of steel in molar HCl with and without the Olive Mill Wastewaters show that the addition of the inhibitor decreases the anodic current densities in the studied domain of potential. It could be concluded that the presence of the OMW affects the anodic dissolution of steel as well as the cathodic reduction of hydrogen ions. This fact means that the inhibition mode of Olive Mill Wastewaters does not depend on the electrode potential; therefore, Olive Mill Wastewater adsorbs onto both anodic and cathodic sites of the steel surface. This behavior indicates that the OMW acts as a mixed inhibitor.

Table 3 : Impedance parameters of steel in acid at various samples of OMWs

Process	Samples	Concentration ppm	Rp ($\Omega.cm^2$)	F_{max} (Hz)	C_{dl} ($\mu F/cm^2$)	E% Polarisation	E% Impedance (EIS)	E% gravimetric
	Blank	1M	23.45	125	4602.06	*	*	*
Traditional press process	OMW_1	0.6	134.2	20	4213.88	79.84	82.53	86.669
		1	156.7	25	6150.48	80.13	85.04	86.8965
		1.6	206.5	10	3242.05	83.82	88.64	87.9995
		2	217.2	15.823	5395.71	83.88	89.2	88.461
		2.6	268.1	15.823	6660.17	87.3	91.25	88.7
	OMW_2	0.6	157.8	25	6193.65	73.25	85.14	87.0635
		1	173.8	15.823	4317.56	76.79	86.51	87.9635
		1.6	195	15.823	4844.21	78.17	87.97	88.376
		2	228	15.823	5664	86.06	89.71	89.392
		2.6	239	10	3752.3	87.97	90.19	89.7645
	OMW_3	0.6	148.9	15.823	3698.99	82.26	84.25	87.794
		1	167.2	15.823	4153.6	82.47	85.97	88.2035
		1.6	195.9	15.823	4866.57	82.84	88.03	88.9335
		2	211.9	15.823	5264.04	82.9	88.93	89.94
		2.6	217.1	10	3408.47	83.64	89.2	92.4585
Semi- modern press process	OMW_8	0.6	150.4	20	4722.56	58.8	84.41	88.925
		1	163.3	20	5127.62	73.25	85.64	89.115
		1.6	170	15.823	4223.16	74.16	86.21	89.33
		2	195.2	15.823	4849.18	77.32	87.99	89.68
		2.6	205.5	15.823	5105.05	80.03	88.59	90.77
	OMW_{11}	0.6	162.7	20	5108.78	77.21	85.59	88.925
		1	166.3	20	5221.82	78.01	85.9	89.485
		1.6	184.2	15.823	4575.92	79.76	87.27	90.305
		2	203.8	7.9365	2539.41	81.97	88.49	90.665
		2.6	272.7	15.823	6774.44	83.37	91.4	91.495
	OMW_{14}	0.6	155	25	6083.75	74.08	84.87	88.345
		1	167.8	25	6586.15	77.58	86.03	89.05
		1.6	168.6	15.823	4188.38	78.25	86.09	89.42
		2	176.5	15.823	4384.63	82.28	86.71	89.895
		2.6	201.1	15.823	4995.75	83.96	88.34	90.71
Continuous process	OMW_{19}	0.6	145.9	20	4581.26	62.95	83.93	88.3355
		1	178	15.823	4421.9	78.8	86.83	88.925
		1.6	185	12.5	3630.63	81.99	87.32	89.623
		2	186.2	15.823	4625.6	82.02	87.41	90.029
		2.6	224.9	15.823	5586.99	82.87	89.57	90.3895
	OMW_{20}	0.6	95.37	31.646	4738.38	37.29	75.41	86.66
		1	99.69	40	6260.53	64.46	76.48	86.825
		1.6	105.9	31.646	5261.56	66.14	77.86	87.9
		2	116.2	31.646	5773.31	67.97	79.82	88.585
		2.6	163	15.823	4049.26	70.25	85.61	89.12
	OMW_{21}	0.6	103.5	31.646	5142.32	62.05	77.34	87.165
		1	156.2	15.823	3880.34	71.5	84.99	88.044
		1.6	177	15.823	4397.05	78.06	86.75	88.493
		2	193.8	15.823	4814.4	81.3	87.9	88.69
		2.6	206.7	15.823	5134.86	85.29	88.66	89.1545

Electrochemical impedance spectroscopy measurements (EIS)

The corrosion behavior of steel, in acidic solution 1M HCl in the absence and presence of the different samples of Olive Mill Wastewater, was also investigated by (EIS) method at 298 K after 30 min of immersion [Fig. 4, 5 and 6]. The inhibition efficiency can be calculated by the following formula (3):

$$E_{Rt}\% = 100 \times \left(1 - \frac{R^{\circ}t}{Rt}\right) \qquad (3)$$

Here R_t and R°_{t} are the charge transfer resistances in inhibited and uninhibited solutions, respectively.

The values of the polarization resistance were calculated by subtracting the high frequency intersection from the low frequency intersection [110]. Double layer capacitance values were obtained at maximum frequency (fm), at which the imaginary component of the Nyquist plot is a maximum, and calculated using the following equation (4).

$$C_{dl} = \frac{1}{2\pi fmRt} \qquad (4)$$

With C_{dl} Double layer capacitance ($\mu F.cm^{-2}$); f_m: maximum frequency (Hz) and R_t: charge transfer resistance ($\Omega.cm^2$).

The impedance parameters derived from these investigations are listed in Table (3).

It is visible from the Fig.4, 5 and 6, that the obtained impedance diagrams for all samples of Olive Mill Wastewaters are a semi-circular appearance, indicates that a charge transfer process mainly controls the corrosion of steel [111].

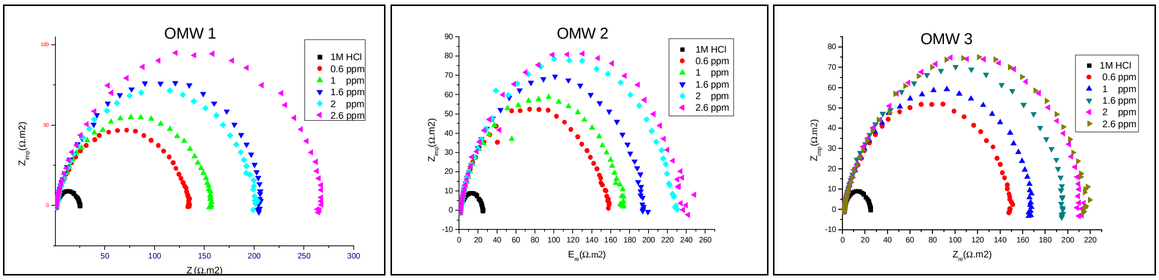

Fig4 : Nyquist diagrams for steel electrode with and without at various samples of OMWs from the processes traditional after 30 min of immersion (OMW_1, OMW_2, and OMW_3)

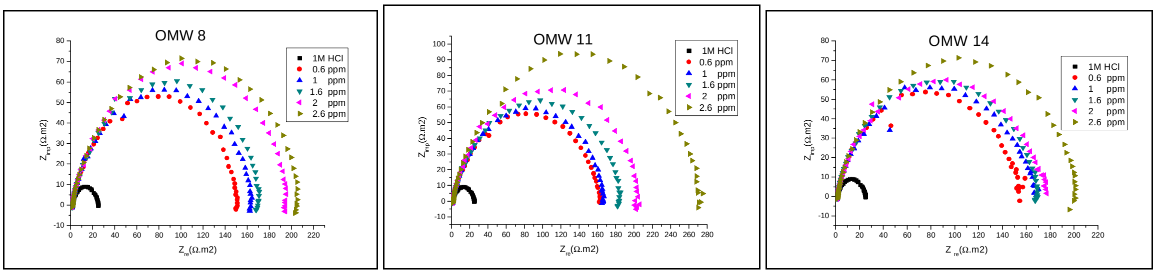

Fig 5 : Nyquist diagrams for steel electrode with and without at various samples of OMWs from the processes semi-modern after 30 min of immersion (OMW_8, OMW_{11}, and OMW_{14})

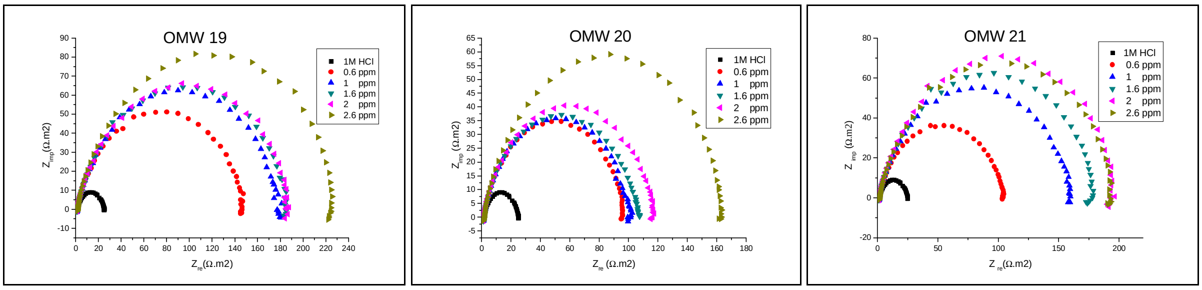

Fig 6 : Nyquist diagrams for steel electrode with and without at various samples of OMWs from the processes modern after 30 min of immersion (OMW_{19}, OMW_{20}, and OMW_{21})

The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole concentration, indicating that almost no change in the corrosion mechanism occurred due to the inhibitor addition [112]. The R_t values increased with the increase of the concentration of Olive Mill Wastewaters. The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS). Also, Inhibition efficiency values obtained from the gravimetric method agree with those obtained from the Tafel extrapolation.

The impedance diagrams show perfect semi-circles indicating a charge-transfer process mainly controlling the corrosion of steel. In fact, the presence of OMW enhances the value of the transfer resistance in acidic solution. EIS study shows that the OMW tested is an efficient inhibitor.

Effect of temperature

Weight loss, corrosion rates and inhibition efficiency

The composition of the medium and its temperature are essential parameters affecting the phenomenon of the corrosion. The effect of temperature in the range 303–343 K on the electrochemical parameters of steel are in the absence and presence of Olive Mill Wastewaters from the different processes extraction at a concentration of [2.6 ppm] shown in Table 4.

To determine the action energy of the corrosion process, gravimetric measurements are taken at various temperatures (303–343 K) in the presence and absence of 2.6 ppm of the samples of Olive Mill Wastewaters at 1 h of immersion. The inhibition efficiency E_w (%) is calculated as follows equation (5):

$$E\% = 100 \times \left(1 - \frac{W_{Corr}}{W^{\circ}{}_{Corr}}\right) \tag{5}$$

where W_{corr} and $W°_{corr}$ are the corrosion rate of steel in 1 M HCl in the absence and presence of the inhibitor, respectively.

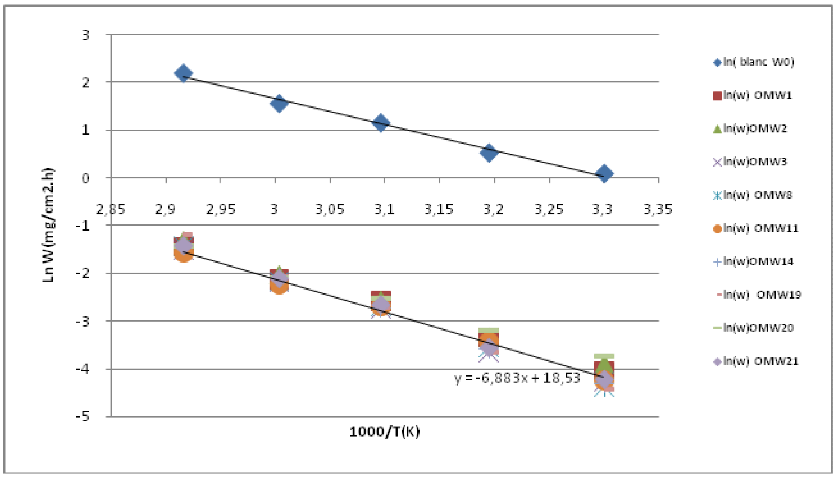

Fig 7 : Typical Arrhenius plots of steel in 1M HCl without and with the different samples of Olive Mill Wastewaters at concentration 2.6ppm

Results in Table 4 shows that the corrosion rates of steel in 1MHCl are lower in the presence of the samples of Olive Mill Wastewaters compared to the blank acid solution. also shows that corrosion rate increases with increase in temperature with the highest values obtained at 343 K. E% is still significant even at high temperature (97% at 343K), Inhibition efficiency values also presented in Table 4 reveals a decreasing trend with increasing experimental temperatures for all the samples of Olive Mill Wastewaters from the different extraction processes studied, indicating that at higher temperatures, dissolution of steel predominates on inhibitor adsorption. This suggests possible desorption of some of the adsorbed inhibitors from the metal surface at higher temperatures. Such behavior shows that the additive was physically adsorbed on the metal surface [112].

Table 4 : Effect of temperature on the corrosion rate of steel at concentration 2.6 ppm of all samples of OMW

inhibitors	Tp(K)	W (Mg.cm-2.h-1)	E %	ϴ
Blank (HCl)	303	1.1	*	*
	313	1.7	*	*
	323	3.2	*	*
	333	4.8	*	*
	343	9.1	*	*
OMW$_1$	303	0.0176	98.4	0.984
	313	0.0354	97.9	0.979
	323	0.076	97.6	0.976
	333	0.1204	97.5	0.975
	343	0.2375	97.4	0.974
OMW$_2$	303	0.0203	98.1	0.984
	313	0.0356	97.9	0.979
	323	0.0775	97.6	0.976
	333	0.1327	97.2	0.975
	343	0.2724	97	0.974
OMW$_3$	303	0.0141	98.7	0.981
	313	0.0264	98.5	0.979
	323	0.0651	98	0.976
	333	0.1121	97.7	0.972
	343	0.2239	97.5	0.97
OMW$_8$	303	0.0125	98.9	0.987
	313	0.0287	98.3	0.985
	323	0.0685	97.9	0.98
	333	0.1159	97.6	0.977
	343	0.2438	97.3	0.975
OMW$_{11}$	303	0.0144	98.7	0.989
	313	0.0328	98.1	0.983
	323	0.0693	97.8	0.979
	333	0.1094	97.7	0.976
	343	0.2148	97.6	0.973
OMW$_{14}$	303	0.0135	98.8	0.987
	313	0.0275	98.4	0.981
	323	0.0656	98	0.978
	333	0.122	97.5	0.977
	343	0.2482	97.3	0.976
OMW$_{19}$	303	0.0121	98.9	0.988
	313	0.0264	98.5	0.984
	323	0.0656	98	0.98
	333	0.1268	97.4	0.975
	343	0.3036	96.7	0.973
OMW$_{20}$	303	0.0243	97.8	0.989
	313	0.0418	97.6	0.985
	323	0.082	97.4	0.98
	333	0.1262	97.4	0.974
	343	0.2433	97.3	0.967
OMW$_{21}$	303	0.0146	98.7	0.978
	313	0.0285	98.3	0.976
	323	0.0698	97.8	0.974
	333	0.1211	97.5	0.974
	343	0.2408	97.4	0.973

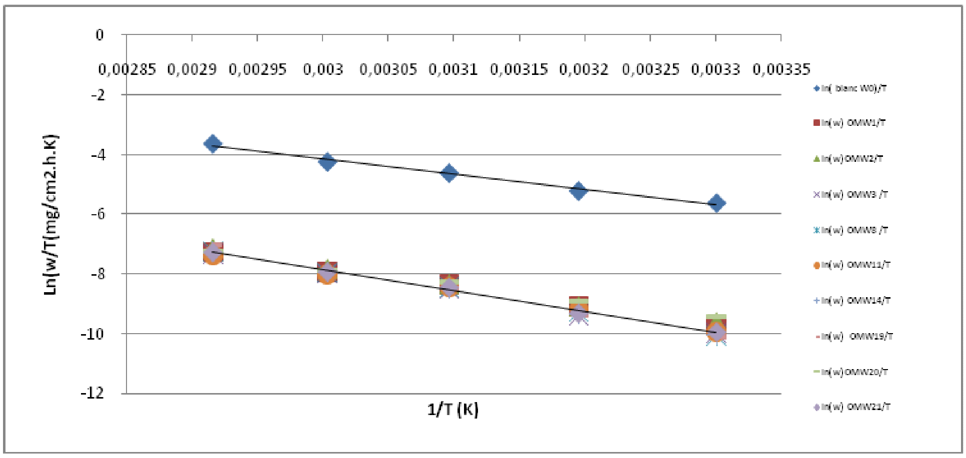

Fig. 8 : The relation between log (w/T) vs. 1/T for steel at different concentration of all samples of OMWs

Thermodynamic parameters:
In order to calculate activation thermodynamic parameters of the corrosion process for steel corrosion rate for both blank and inhibitor solutions, The activation energy E_a is calculated from the slope of the plots of Log (W_{corr}) vs. 1000 / T [Fig.7].

The activation energies can be estimated from the slopes of the lines of the Arrhenius Equation (6) and transition state Equation (7) [113-114] were used:

$$W = K \exp\left(- \frac{E_a}{RT} \right)$$

(6)

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^o}{R} \right) \exp\left(- \frac{\Delta H_a^o}{RT} \right) \qquad (7)$$

where : E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is Plank's constant, N is Avogadro's number, ΔS°ads is the entropy of activation and ΔH°ads is the enthalpy of activation.

The decrease of the samples of OMWs efficiencies with temperature rise leads to a higher value of Ea, when compared to that in an uninhibited acid, is interpreted as an indication for an electrostatic character of the inhibitor's adsorption [115]. The positive values of ΔH°ads mean that the dissolution reaction is an exothermic process and that the dissolution of steel is difficult [116]. Practically Ea and ΔH°ads are the same order. Also, the entropy ΔS°ads increase positively with the presence of the inhibitor than the non-inhibited one. The negative value of ΔG°ads reveals the spontaneity of the adsorption process and is characteristic of strong interaction and stability of the adsorbed layer with the steel surface [117]. This reflects the formation of an ordered stable layer of inhibitor on the steel surface [118]. From the previous data, we can conclude that OMW is an effective inhibitor. This phenomenon is often interpreted with physical character and formation of an adsorption film of electrostatic character [119].

Adsorption isotherm
Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Frumkin, Temkin, Flory–Huggins, Dhar–Flory–Huggins, Bockris–Swinkels . . .

The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clues to the nature of the metal–inhibitor interaction .

In order to obtain the adsorption isotherm, the degree of surface coverage (θ) for various concentrations of the OMW has been calculated at 308 K from the weight loss measurements by the ratio E (%)/ 100. The results obtained for OMW in 1M HCl solution fit well Langmuir adsorption isotherm given by Equation. (8).

$$\frac{C(inh)}{\theta} = \frac{1}{K(ads)} + C(inh) \qquad (8)$$

Table 5 : Activation parameters of the dissolution of steel in 1M HCl in the absence and presence of different samples of OMWs

inhibitors	T(K)	Ea (kJ/mol)	ΔH°add (kJ/mol)	ΔSadd (kJ/mol)	Ea-ΔH°a (kJ/mol)
Blank (HCl)	303	45.4	42.72	1.26	2.68
	313				
	323				
	333				
	343				
OMW_1	303	55.6	52.92	1.26	2.68
	313				
	323				
	333				
	343				
OMW_2	303	56.18	53.5	1.26	2.68
	313				
	323				
	333				
	343				
OMW_3	303	60.29	57.61	1.27	2.68
	313				
	323				
	333				
	343				
OMW_8	303	63.49	60.81	1.28	2.68
	313				
	323				
	333				
	343				
OMW_{11}	303	57.23	54.55	1.26	2.68
	313				
	323				
	333				
	343				
OMW_{14}	303	63.21	60.53	1.28	2.68
	313				
	323				
	333				
	343				
OMW_{19}	303	69.21	66.53	1.3	2.68
	313				
	323				
	333				
	343				
OMW_{20}	303	49.33	46.65	1.24	2.68
	313				
	323				
	333				
	343				
OMW_{21}	303	60.97	58.29	1.27	2.68
	313				
	323				
	333				
	343				

Fig.9-11. shows the linear dependence of $\theta / 1 - \theta$ as a function of concentration C of inhibitors where θ is the surface coverage determined by the ratio E% / 100. Inhibitor adsorbs on the steel surface according to the Langmuir kind isotherm model which obeys the relation:

$$\frac{\theta}{1-\theta} = KC$$

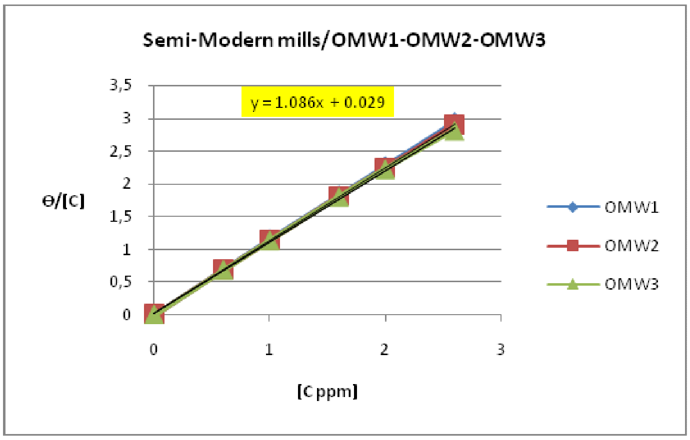

Fig 9 : Plot of Langmuir isotherm adsorption of the samples of OMWs from the processes traditional on the steel surface in HCl 1M at 303K

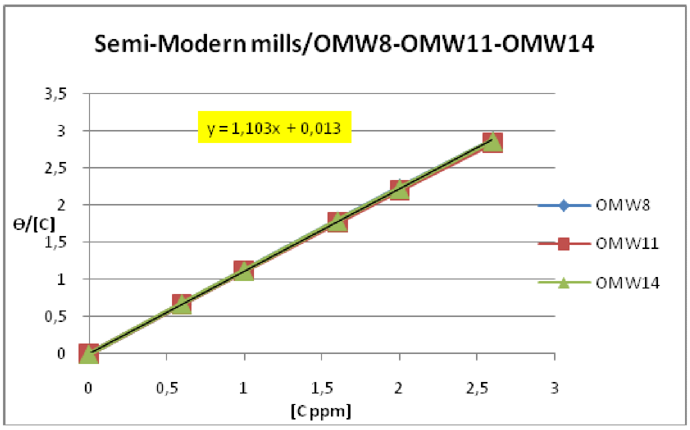

Fig. 10 : Plot of Langmuir isotherm adsorption of the samples of OMWs from the processes semi-modern on the steel surface in HCl 1M at 303K

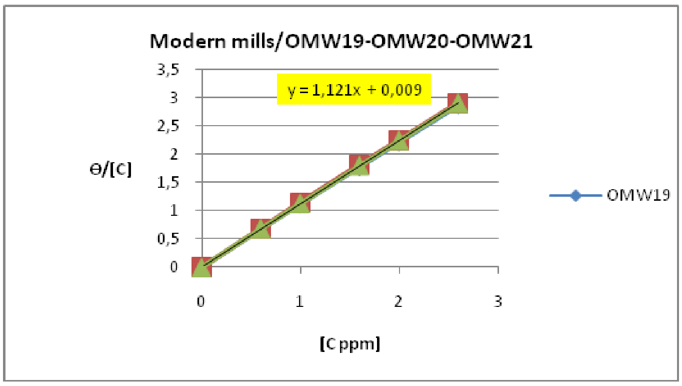

Fig. 11 : Plot of Langmuir isotherm adsorption of the samples of OMWs from the processes modern on the steel surface in HCl 1M at 303K

CONCLUSION

The lack of regulations governing the use and disposal of most organic inhibitors, which are, according to the literature, are harmful to the environment, it is best to search for inhibitors of the problem of corrosion from natural resources such as plant extracts or reuse of effluent from industrial units of mills as in our case study, to reduce the organic load on the one hand and on the other hand, enhance the main constituents of these by-products:

From the overall studies, the following conclusions could be deduced:

- The inhibition efficiency increases with increased Olive Mill Wastewaters concentration to attain a maximum value of 92% at 2.6 M for all samples with small differences between the samples;
- The inhibition efficiency of Olive Mill Wastewaters decreases with the rise of temperature;
- The inhibition efficiency of OMW varies slowly with the temperature;
- The Olive Mill Wastewaters acts as a mixed inhibitor without modifying the hydrogen reduction mechanism;
- Adsorption of inhibitor tested follows Langmuir adsorption isotherm;
- The presence of Olive Mill Wastewaters increases the activation energy of the corrosion process;
- The inhibitor was physically adsorbed on the steel surface;
- Therefore, there is a need for guidelines to manage these wastes through technologies that minimize their environmental impact and lead to a sustainable use of resources;
- the acidity, the high organic load, and the phototoxic material (high phenol, lipid and organic acid concentrations) of the wastewater present no problems for such application such as the corrosion;
- Although the above utilization of olive mill waste is technically feasible, it is too early to achieve large-scale application such as in industrial areas.
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