

Comparative Study of Corrosion Inhibition on Mild Steel in HCl Medium by Three Green Compounds: *Argania spinosa* Press Cake, Kernels and Hulls Extracts

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Abstract *Argania spinosa* press cake, kernels and hulls extracts are excellent corrosion inhibitors for steel. In this work electrochemical methods are used to study the inhibition of corrosion on steel in 1 M HCl. It has shown that Argan press cake, kernels and hulls extracts suppress both the anodic and cathodic process and they behave as mixed-type inhibitors. The inhibition efficiency was found to increase with inhibitors content. Data obtained from EIS measurements, were analyzed to model the corrosion inhibition process through appropriate equivalent circuit model; a constant phase element has been used. The values of the inhibition efficiency calculated from these techniques are in reasonably good agreement. The adsorption isotherm of natural compounds on the steel surface was found to obey Langmuir's adsorption isotherm.

Keywords Corrosion · Steel · Inhibition · *Argania spinosa* extracts

1 Introduction

Hydrochloric acid is widely used for the removal of rust and scale in several industrial processes. The corrosion of steel and ferrous alloys in such environments and its inhibition constitute a complex problem of process. HCl is one of the most important pickling acids. Various types of organic compounds are widely used as corrosion inhibitors for protection materials against deterioration from corrosion. These compounds adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion process [1–7]. However, study on the inhibition efficiency of natural products for mild steel in acidic medium is still lacking. Aiming to find cheap, environmentally benign, non-toxic natural compound that could be used for acidization and acid pickling of metals in acid medium. Numerous studies had been conducted to examine extracts from naturally materials as corrosion inhibitors: *Aloe vera* extract [8], *Gossypium hirsutum* [9], *Cocos nucifera* [10], lawsonia [11], *Azadirachta indica* [12], *Salvia aucheri mesatlantica* [13], olive leaves extract [14], Pennyroyal Mint oil [15], Argan oil [16], *Argania* plant extract [17], *Argania spinosa* Kernels Extract and Cosmetic Oil [18], Argan Hulls Extract [19], henna extract [20], Eucalyptus oil [21], Jojoba oil [22], Rosemary oil [23–25], Artemisia oil [25–27], Lavender oil [28], Menthol derivatives [29], Eugenol and Acetyleneugenol [30], Pulegone [31] and Limonene [32]. It has been found to be very efficient corrosion inhibitors for steel in acid media. However, the constituents that provide inhibitive action, the mechanisms and the best condition for inhibition are still unclear.

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The Argan tree, called *Argania spinosa* (L.) Skeels, is a tropical plant, which belongs to the Sapotaceae family. Populations of Morocco traditionally use the fruits of *A. spinosa* to prepare edible oil [33]. It represents the only endemic species of the genus *Argania*. As an important traditional alimentary medicine, *A. spinosa* is a valuable potential for Moroccan. Traditionally, the Argan tree is used for many purposes. In cosmetics, Argan oil is advocated as moisturizing oil, against acne juvenile and flaking of the skin as well as for nourishing the hair [34].

The aim of the present work is to compare the effect of *A. spinosa* extracts: press cake, kernels and hulls bean as inhibitors for the acidic corrosion of steel by electrochemical techniques and to discuss their inhibition mechanism.

2 Experimental Setup

2.1 Electrochemical Tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was C38 steel that had the following chemical composition (wt%): 0.179 % C, 0.165 % Si, 0.439 % Mn, 0.203 % Cu, 0.034 % S and Fe balance. For electrochemical tests, the commercial C38 steel samples are in the form of a surface parallelepiped of 0.056 cm² used as a work electrode that is mechanically abraded with 180, 320, 800 grades of emery papers, rinsed with distilled water then with ethanol before plunging the electrode in the solution. Anodic and cathodic potentiodynamic polarization curves were plotted separately at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from –800 to –400 mV at 298 K. The solution test is there after de-aerated by bubbling nitrogen. Gas pebbling is maintained prior and through the experiments. The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 h of

exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

2.2 Solutions Preparation

Sample of leaves and fruits of *A. spinosa* plant was collected from the area of Biougra located at Chtouka Ait Baha (Morocco) at December month. Dried and pulping fruits were crushed. Stock solution of the extracts was prepared by stirring cold weighed amounts of the ground press cake, leaves or hulls of *Argania spinosa* plant for 24 h in 1 M HCl solution (The solution 1 M HCl was prepared by dilution of analytical grade 37 % HCl with double distilled water). The resulting solution was filtered. These extracts were used to study the corrosion inhibition properties and to prepare the required concentrations of as. The solution tests are freshly prepared before each experiment.

3 Result and Discussion

3.1 Polarization Curves

Typical potentiodynamic polarization curves for steel in 1 M HCl in the presence and absence of the tested inhibitors are shown in Figs. 1, 2 and 3. The corrosion parameters including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic slope (β_a) and inhibition efficiency (E %) are listed in Table 1.

The percentage of inhibition efficiency (E %) was calculated from polarization measurements using the relation:

$$E \% = \left(1 - \frac{I'_{\text{corr}}}{I_{\text{corr}}}\right) \times 100, \quad (1)$$

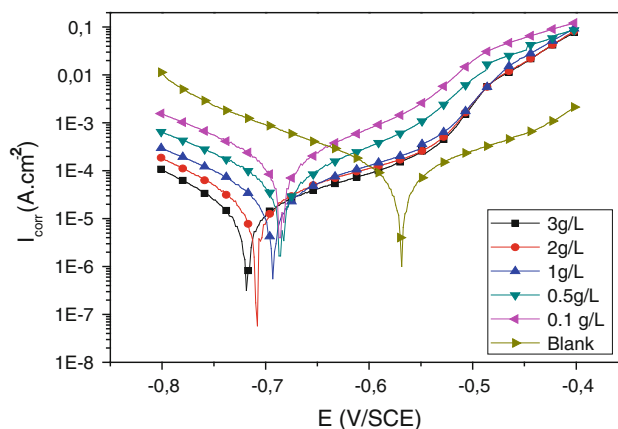


Fig. 1 Potentiodynamic polarisation curves of C38 steel in 1 M HCl in the presence of different concentrations of Argan press cake extract (APCE)

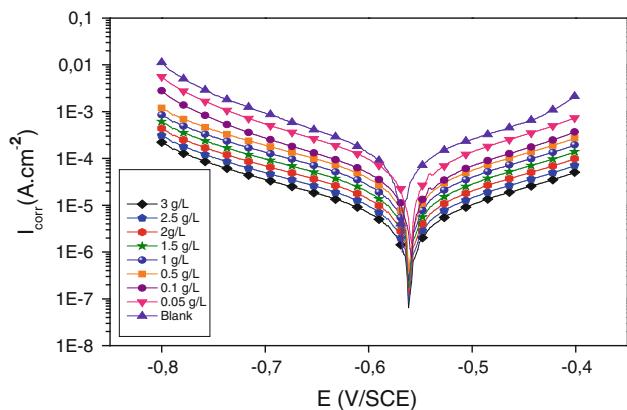


Fig. 2 Potentiodynamic polarisation curves of C38 steel in 1 M HCl in the presence of different concentrations of Argan kernels extract (AKE)

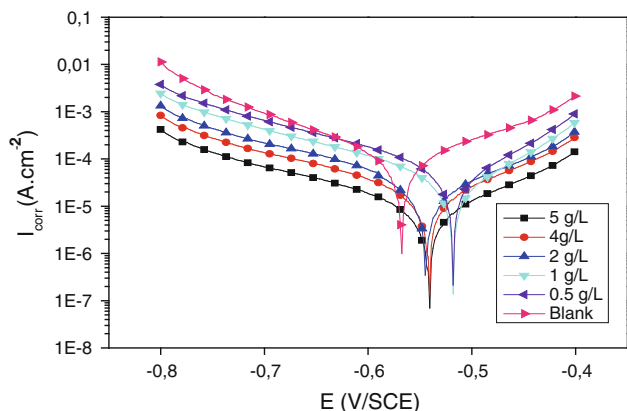


Fig. 3 Potentiodynamic polarisation curves of C38 steel in 1 M HCl in the presence of different concentrations of Argan hulls extract (AHE)

where I_{corr} and I'_{corr} are, respectively, the uninhibited and inhibited current density respectively.

The corrosion current density was calculated from the intersection of cathodic and anodic Tafel line.

Inspection of the Figs. 1, 2 and 3 reveals that the polarization curves are shifted toward less current density upon addition of Argan extracts. This result confirms the presence of the Argan extracts inhibits the acid corrosion of steel [35]. Addition of AKE and AHE affects both anodic dissolution of steel and cathodic reduction reactions indicating that the two compounds could be classified as mixed-type inhibitors. Moreover, the presence of APCE affects both the anodic and cathodic reactions with a huge displacement of E_{corr} towards cathodic potentials; the curves must be compared with $E-E_{corr}$. The nature of chemical composition of this kind of extract reveals that it is different of the two others. APCE may be also classified as a mixed type inhibitor with predominance in cathodic branche.

Table 1 Electrochemical parameters of C38 steel at various concentrations of different extracts in 1 M HCl and corresponding inhibition efficiency

Inhibitors	Concentrations (g/l)	E_{corr} (mV/SCE)	I_{corr} (μ A/ cm^2)	$-\beta_c$ (mV/dec)	β_a (mV/dec)	E (%)
Blank	0	-567	94	136	108	-
Argan press cake extract	0.1	-686	86	80	84	08.5
	0.5	-680	60	91	99	36.2
	1.0	-694	29	82	117	69.1
	2.0	-709	18	79	89	80.9
	3.0	-718	11	69	111	88.3
Argan kernels extract	0.05	-559	59	126	123	37.2
	0.1	-560	30	103	107	68.1
	0.5	-562	27	122	118	71.3
	1.0	-560	18	137	128	80.9
	1.5	-558	13	122	119	86.2
	2.0	-561	10	138	128	89.4
Argan hulls extract	2.5	-561	7	119	117	92.6
	3.0	-559	3	134	128	96.8
	0.5	-518	58	155	76	38.3
	1.0	-516	37	162	71	60.6
	2.0	-545	29	146	97	69.1
	4.0	-540	19	171	86	79.8
	5.0	-541	9	155	97	90.4

The anodic and cathodic Tafel slopes (β_a and β_c) are affected in the presence of extracts suggesting that the inhibiting action occurred by modification of the mechanism of this process [36].

From electrochemical polarisation measurements, it is clear that the addition of the different inhibitors leads to a decrease in the cathodic current densities. Examination of the IE values given in Table 1 reveals that inhibition efficiency increases with an increase in the concentration of additives. The increase in inhibition efficiency observed at higher inhibitors concentration indicates that more inhibitors molecules are adsorbed on the metal surface thus providing wider surface coverage and these compounds are acting as adsorption inhibitors. We remark that the corrosion current densities were more significantly reduced in the presence of different extracts in the following order : AKE then APCE and finally AHE, and became only 10, 18 and 29 μ A/ cm^2 at 2 g/L respectively. The maximum of inhibition (96.8 %) was obtained at 3 g/L AKE extract.

3.2 Electrochemical Impedance Spectroscopy Measurements

The Nyquist impedance plots for the steel in 1 M HCl solution in the presence and absence of the different

inhibitors are shown in Figs. 4, 5 and 6. The impedance parameters derived from these investigations are mentioned in Table 2.

The inhibition efficiencies obtained from the EIS measurements are calculated by the relation:

$$E_{Rt} \% = \frac{(R_t - R_t^0)}{R_t} \times 100, \quad (2)$$

where R_t and R_t^0 are the charge transfer resistances in inhibited and uninhibited solutions respectively.

Fig. 4 Nyquist diagrams for C38 steel electrode with and without Argan press cake extract

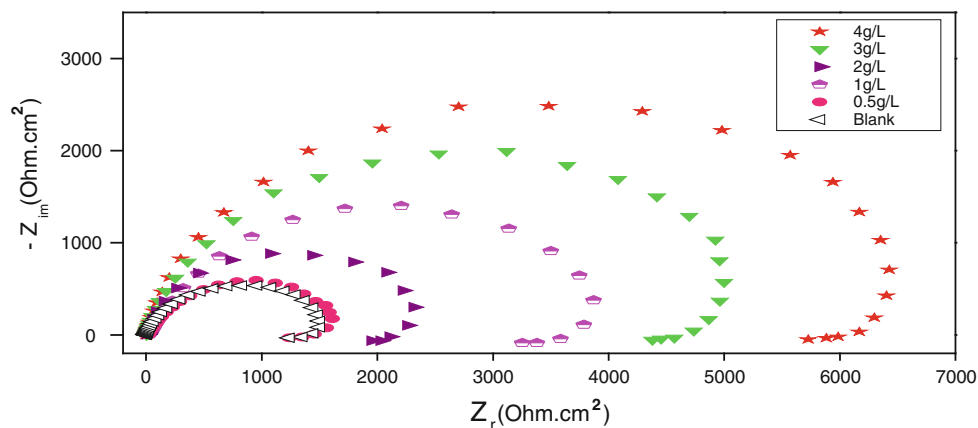


Fig. 5 Nyquist diagrams for steel electrode with and without Argan kernels extract

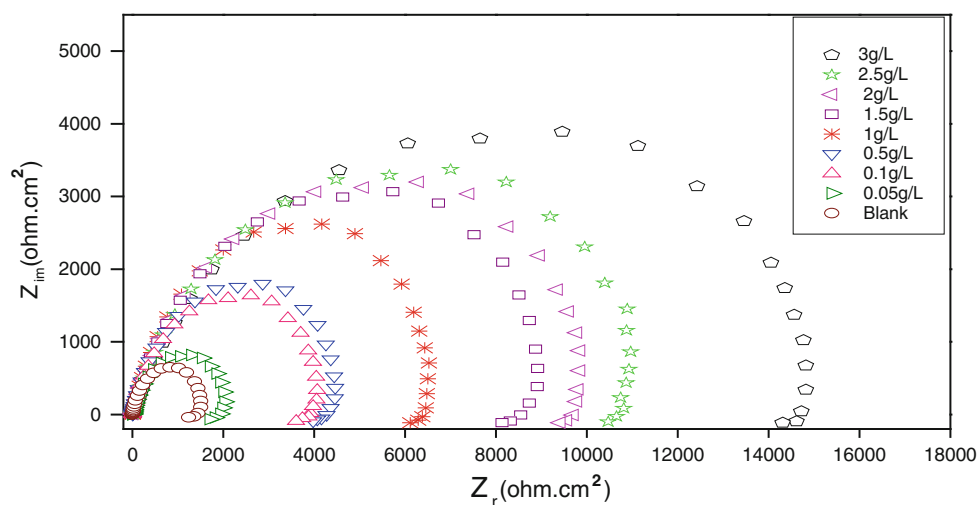


Fig. 6 Nyquist diagrams for C38 steel electrode with and without Argan hulls extract

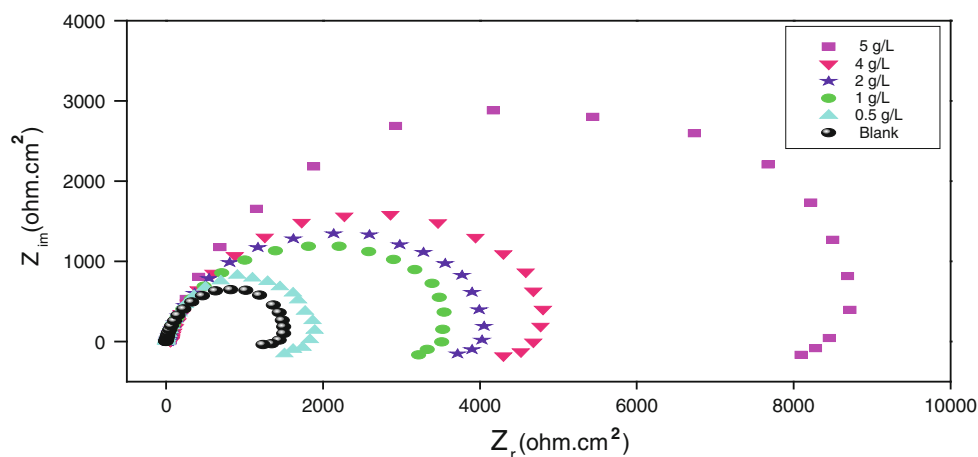


Table 2 Impedance parameters for corrosion of steel in acid at various contents of different extracts

Inhibitors	Concentrations (g/L)	R_t ($\Omega \cdot \text{cm}^2$)	f_{max} (Hz)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	E_{RT} (%)
Blank	0.0	21	59	126	–
Argan press cake extract	0.1	24	56	118	11.1
	0.5	36	40	117	40.0
	1.0	70	35	65	69.4
	2.0	90	34	52	76.3
	3.0	117	30	45	81.7
Argan kernels extract	0.05	35	58	78	38.5
	0.1	71	50	45	70.0
	0.5	78	49	42	72.4
	1.0	115	42	33	81.4
	1.5	157	33	30	86.4
	2.0	175	31	29	87.8
	2.5	223	29	25	90.4
Argan hulls extract	3.0	286	28	20	92.5
	0.5	33	58	83	35.1
	1.0	60	40	66	64.4
	2.0	73	37	59	70.7
	4.0	96	32	52	77.8
	5.0	159	28	36	86.5

The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [37]. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{\text{max}}$) are found as represented in equation:

$$C_{\text{dl}} = \left(\frac{1}{\omega \cdot R_t} \right) \tag{3}$$

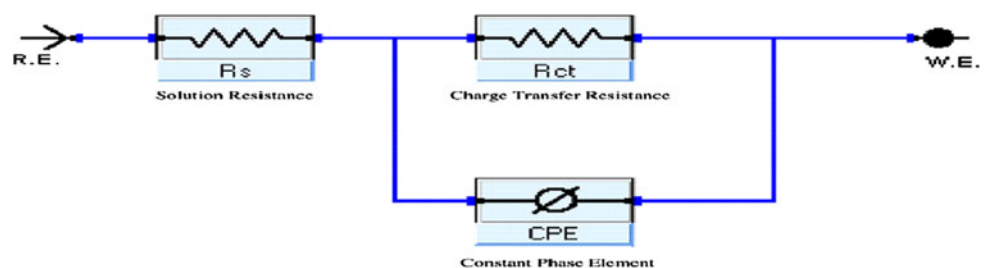
where $\omega = 2\pi f_{\text{max}}$ With C_{dl} : Double layer capacitance ($\mu\text{F cm}^{-2}$); f_{max} : maximum frequency (Hz) and R_t : Charge transfer resistance ($\Omega \text{ cm}^2$)

As we notice, Figs. 4, 5 and 6, impedance diagrams almost a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of steel [38]. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [39, 40].

When a non-ideal frequency response is present, it is commonly accepted to employ distributed circuit elements in an equivalent circuit. The most widely used is the constant phase element (CPE), which has a non-integer power dependence on the frequency [41]. Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system. Fig. 7 shows the electrical equivalent circuit employed to analyze the impedance spectra with one capacitive loop [42, 43].

Excellent fit with this model was obtained with our experimental data. It is observed that the fitted data match the experimental, with an average error inferior to 0.1%. R_t values were simultaneously determined by analysis of the complex-plane impedance plots and the equivalent circuit model and the result are very similar with insignificant changes. According to the equivalent circuit, it was found that R_t values increased with increasing inhibitors concentration, this result indicated that charge transfer process mainly controls the corrosion process.

Fig. 7 Electrochemical equivalent circuit used to fit the impedance spectra for the tree extracts



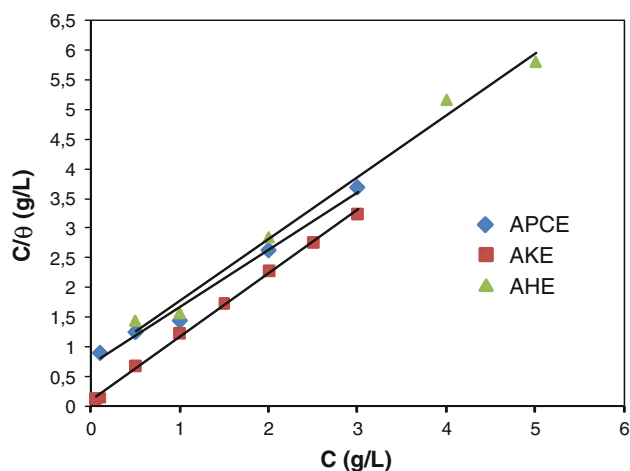


Fig. 8 Plots of Langmuir adsorption isotherm of APCE, AKE and AHE on the steel surface at 298 K

The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole concentrations, indicating that almost no change in the corrosion mechanism occurred due to the inhibitors addition [44]. From the impedance data given in Table 2, we note that the value of R_t increases with increase in the concentration of the different inhibitors. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitors and the decrease in the values of C_{dl} follows the order similar to that obtained for I_{corr} in this study. It has been reported that the adsorption process on the metal surface is characterized by a decrease in C_{dl} [37]. The best efficiencies obtained in the presence of APCE, AKE and AHE respectively are 81.7 % at 3 g/L, 92.5 % at 3 g/L and 86.5 % at 5 g/L. The results obtained from the polarization technique were in good agreement with those obtained from the EIS for the tree compounds.

3.3 Adsorption Isotherm

Additional information about the properties of the tested compounds may be provided from the kind of adsorption isotherm. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to provide best description of the adsorption behaviour of the investigated inhibitor. The Langmuir isotherm is given by the equation [45]:

$$\frac{C}{\theta} = \frac{1}{K} + C, \quad (4)$$

where C is the inhibitor concentration, θ the fraction of the surface covered determined by $E/100$, k the equilibrium constant.

Fig. 8 shows the dependence of the ratio C/θ as function of C for different extracts.

The data fit straight line, with slope nearly equal unity, indicating that these compounds adsorbed according to Langmuir adsorption isotherm.

4 Conclusion

The following results can be drawn from this study:

- APCE, AKE and AHE act as mixed type inhibitors.
- The inhibition efficiency of APCE, AKE and AHE extracts increases with the rise of inhibitors concentration.
- The data obtained from the different methods: potentiodynamic polarization and EIS are in good agreement.
- APCE, AKE and AHE extracts are excellent inhibitors for steel in acidic medium at 298 K.
- APCE, AKE and AHE extracts being natural and environmentally benign products they can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.

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