UTILIZATION OF *Ammi majus* L. FRUITS EXTRACTS AS INHIBITORS FOR MILD STEEL CORROSION IN ACID MEDIA

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ABSTRACT

The inhibition effect of *Ammi majus* L. fruit extracts, alcoholic extract (A), aqueous extract (B) and defatting extract (C), on the corrosion of mild steel in 2.0M H₂SO₄ containing 10% EtOH at 30°C was investigated using chemical, electrochemical and scanning microscopy measurements. It was found that as the concentration of extracts increases, the rate of mild steel corrosion is decreased, which indicates that an inhibition of the corrosion process takes place. The decrease of the inhibition efficiency of the extracts was given as: B > C > A, the electrochemical results showed that the extracts A, B and C, act as mixed inhibitors and the corrosion inhibition of mild steel occurred mainly by charge transfer mechanism. The scanning electron microscopy results showed that the changes (pits) on the mild steel surface is due to the effect of acid corrosion became less, the steel surface appears to be unchanged, by the extracts addition.

The experimental results fit Langmuir isotherm. Values of equilibrium constant of adsorption $K_{ads}$ and the standard free energies of adsorption $\Delta G^{ads}$ for the extracts, were calculated.

The effect of two coumarin compounds was studied by chemical methods in 2.0M H₂SO₄ containing 10% EtOH separately and in mixture of them. The results showed that:

- As the concentration of studied compounds (Xabithotoxin(I), Imperatorin (II) increases, the rate of mild steel corrosion was decreased.
- The inhibition efficiency obtained from the mixture was very high and nearly the same as when the extract was used which supported that the inhibition of *A. majus* extract is due to the presence of coumarin compounds.

Keywords: *Ammi majus*, fruit extracts, mild steel corrosion & acid media.

INTRODUCTION

Steel is considered to be the main constructing material in industry. There is a great need to protect it from dissolution by using corrosion inhibitors¹.

Inhibitors can offer a cheap, easy to apply and highly effective method of corrosion control when certain considerations are observed.

The most commercial acid corrosion inhibitors are highly toxic and very hazardous products, dangerous to eyes and skin. Some may affect lungs, the central nervous system, visual ability and may lead to death upon high direct contact².

Numerous additives have been used to control corrosion, of these, certain inorganic / organic compounds such as chromate which were widely used as corrosion inhibitors. Because the environmental threat of the high chromate concentration does, chromate have been recently replaced by other environmentally safe inhibitors, such as zinc salts, calcium polyphosphates and phosphorates.

Extract of some herbs have been found to inhibit corrosion of steel in different solutions³-⁷. Natural products are promising as corrosion inhibitors⁸, they usually used as medicament for several sickness and have been selected due to both:

1. containing organic compounds which have lone pairs of electrons and/or multiple
double bonds\(^8\), (e.g. coumarin compounds)  
2. replacements of toxic chemical widely used in industry as corrosion inhibitors.

Extracts from plant origin have been proved to be good inhibitors for the corrosion of metals. The use of these extracts offers main advantage, since they can be easily obtained from cheap plants, or wastes remaining in canning - industry, also they includes new compounds which have the ability of anti-corrosion activity, also they are safe for the environment\(^9-12\).

*Ammi majus* L. plant belongs to family Umbellifreae which is rich with coumarin compounds, since they have high ability to be adsorbed on metal surfaces and good inhibition efficiency for metal corrosion is expected\(^8\).

In the present investigation, the inhibitive action of extracts of *Ammi majus* L. fruits on the corrosion of mild steel in 2.0M sulphuric acid (H\(_2\)SO\(_4\)) solution containing 10% ethyl alchohol have been studied.

**EXPERIMENTAL**

The effect of *Ammi majus* L. plant extracts on the corrosion of mild steel sample in 2.0M H\(_2\)SO\(_4\) solution was studied using chemical (hydrogen evolution (HE) and mass loss (ML)) methods. Electrochemical (polarization (p) and impedance (EIS) and sacaning electron microscopy (SEM) measurements at 30°C were carried out.

The chemical composition of the studied mild steel specimen is given as:

| Element | Fe | C  | Si | Mn | Ni | P  | S  | V  | Cu | Cr | Mo |
|---------|----|----|----|----|----|----|----|----|----|----|----|
| Amount %| 98.52 | 0.31 | 0.21 | 0.81 | 0.02 | 0.01 | 0.01 | 0.002 | 0.06 | 0.02 | 0.02 |

The sample was polished first with a series of emery papers of type (231 Qwedordry Imperial Paple Aesco), starting with a coarse one and proceeding in steps to finer grades. Then, the sample was throughly washed with deionized water and with acetone (A.R.) and dried by a steam and air. The sample, then was immediately immersed in the test solution.

The solution which is used in the study was 2.0M H\(_2\)SO\(_4\) containing 10% EtOH. All solutions were prepared with analytical grade reagents (A.R.).

The chemical study was carried out using a vessel which has the same form as that described by Mylius\(^13\). The electrochemical measurements (polarization and impedance) were carried out using (ACM Gill AC) connected to a Samsung computer (Bridge DVD ASUS 8X max)\(^14\). Scanning electron microscopy analysis was carried out using Leitz METALLUX3 scanning microscope\(^11\).

The preparation of *Ammi majus* plant extracts were carried, as follows:

(i) The dried powdered fruits (2.0 kg) of *Ammi majus* were extracted with:
   1) ethyl alcohol (95%) (A).
   2) water extract (B) and
   3) defatting extract(C).

(ii) The extraction was repeated several times then, collected and dried under vacuum and weighed.

(iii) Purification and identification of compounds using spectroscopic methods (IR, Mass, NMR and UV), was done and were compared with suggested pure compounds using thin layer chromatography (TLC) and benzene / ethyl acetate 4:1 as eluent. The purified spots were flashed under Ultraviolet rays (UV) and the reagent Iodide – Potassium iodied. The compound under investigation (xanthotoxoxin, imperatorin, bergapten and marmesin) were isolated and identified.

**RESULTS AND DISCUSSION**

The chemical study was applied by using: hydrogen evolution (HE) and mass loss (ML), while the electrochemical study consists of potentiodynamic polarization and impedance (R\(_{ct}\) and C\(_{dl}\)) techniques.

The study of mild steel corrosion in 2.0M H\(_2\)SO\(_4\) containing 10% ETOH in absence and presence of three extracts A,B and C at 30°C was carried out.

The percentage of inhibition efficiency was calculated from HE (Inh\(_{HE}\)%, ML (Inh\(_{ML}\)%), (Inh\(_{p}\)%),
(Inh_{R}%, \text{ and } (\text{Inh}_{C}d\%) \text{ using the following equations})^{15-24}:

\[
\text{Inh}_{R} = 100(1-R/Ro) \quad (1)
\]
\[
\text{Inh}_{M} = 100(1-R/Ro) \quad (2)
\]
\[
\text{Inh}_{P} = 100(1-I_{corr}/I^{*}_{corr}) \quad (3)
\]
\[
\text{Inh}_{Rct} = 100(R^{-1}_{cto}-R^{-1}_{ct})/R^{-1}_{cto} \quad (4)
\]
\[
\text{Inh}_{Cdl} = 100(C_{dl}-C_{dl0})/C_{dl0} \quad (5)
\]

Where \( R_{o}, R, R_{cto} \text{ and } R \) represents the rates of corrosion from HE and ML in absence and presence of a specific concentration of the extracts respectively. \( I^{*}_{corr} \text{ and } I_{corr} \) are the corrosion current density values without and with the extracts and \( R_{cto}, R_{ct}, C_{dl0} \text{ and } C_{dl} \) are the values of charge transfer resistance and the double electric capacity for mild steel sample in 2.0M H_{2}SO_{4} solutions without and with the three extracts respectively.

The results also show that the alcoholic extract gives more inhibition efficiency than the aqueous and defatting extracts. The inhibition efficiency gets to 100% at the concentration 3.5 \times 10^{-3} \text{ w/v}, the inhibition activity of extracts follows the order:

Aqueous extract (B) < Defatting extract (C) < Alcoholic extract (A)

Also, the table shows that the values of inhibition efficiency calculated from HE confirms well with the values calculated from ML, but the inhibition percentage calculated from electrochemical measurements are always different from chemical measurements. This difference can be attributed to the fact that chemical methods give average corrosion rates, whereas electrochemical methods give instantaneous corrosion rates^{25,26}.

Table -1 shows the inhibition efficiency obtained from the studied methods. It is clear that as the concentration of extracts increases the inhibition percentage is increased.

![Table 1: Inhibition percentages for corrosion of mild steel in 2.0M H_{2}SO_{4} solution containing 10% EtOH in presence of different concentrations of the studied extracts at 30°C](image)

| C/(w/v) | Inh_{R} % | Inh_{M} % | Inh_{P} % | Inh_{Rct} % | Inh_{Cdl} % |
|--------|------------|------------|------------|-------------|-------------|
| 3.0 \times 10^{-5} | 15.76 | 15.24 | 33.83 | 20.73 | 12.28 |
| 5.0 \times 10^{-4} | 26.73 | 23.43 | 48.48 | 74.37 | 65.41 |
| 1.0 \times 10^{-4} | 29.86 | 29.99 | 60.14 | 93.54 | 87.62 |
| 3.0 \times 10^{-4} | 53.88 | 51.12 | 68.47 | 97.80 | 88.34 |
| 5.0 \times 10^{-4} | 73.10 | 73.64 | 70.32 | 98.46 | 88.69 |
| 7.0 \times 10^{-4} | 86.27 | 82.90 | 74.65 | 98.56 | 89.02 |
| 1.0 \times 10^{-3} | 100.00 | 97.04 | 83.54 | 99.31 | 92.21 |
| 2.5 \times 10^{-3} | 100.00 | 98.07 | 88.30 | 99.45 | 92.54 |
| 3.0 \times 10^{-5} | 21.13 | 22.42 | 21.17 | 30.00 | 21.23 |
| 1.0 \times 10^{-4} | 34.16 | 37.39 | 32.97 | 37.04 | 21.28 |
| 3.0 \times 10^{-4} | 60.00 | 62.55 | 61.25 | 55.26 | 48.76 |
| 5.0 \times 10^{-4} | 73.55 | 73.21 | 63.61 | 81.35 | 81.47 |
| 7.0 \times 10^{-4} | 76.94 | 77.88 | 67.31 | 81.76 | 82.57 |
| 1.0 \times 10^{-3} | 84.86 | 82.52 | 70.54 | 90.81 | 84.68 |
| 2.5 \times 10^{-3} | 90.63 | 88.23 | 76.06 | 93.05 | 84.87 |
| 3.5 \times 10^{-3} | 90.70 | 91.33 | 82.00 | 94.86 | 85.23 |
| 3.0 \times 10^{-5} | 15.68 | 19.02 | 37.89 | 57.50 | 60.65 |
| 1.0 \times 10^{-4} | 29.54 | 33.59 | 47.44 | 71.05 | 66.16 |
| 3.0 \times 10^{-4} | 53.93 | 55.46 | 60.58 | 90.81 | 84.68 |
| 5.0 \times 10^{-4} | 58.96 | 63.89 | 74.19 | 96.91 | 85.79 |
| 7.0 \times 10^{-4} | 84.64 | 81.96 | 78.68 | 98.06 | 86.30 |
| 1.0 \times 10^{-3} | 94.17 | 93.90 | 80.86 | 98.53 | 87.61 |
| 2.5 \times 10^{-3} | 100.00 | 97.65 | 81.16 | 98.68 | 87.81 |
| 3.5 \times 10^{-3} | 100.00 | 98.08 | 82.59 | 98.80 | 88.44 |
extract (A), aqueous extract (B) and defatting extract (C)) at 30°C respectively. This figure shows that all the extracts impede both anodic and cathodic processes (metal dissolving and hydrogen evolution), this appears in the displacement of Tafel lines (anodic and cathodic), i.e., these extracts act as mixed type inhibitors.

Nyquist plots Fig. -2 (a, b & c) were obtained after immersing the mild steel sample in 2.0M H$_2$SO$_4$ containing 10% EtOH without and with different concentrations of the studied extracts at 30°C, and the measurements was carried out by using EIS in open circle conditions (ocp) between (0.5Hz-3000Hz).

It can be seen from the figure that the difference has attributed to frequency dispersion and the half circule indicates that the corrosion of mild steel is mainly controlled by the charge transfer process and the presence of extracts in solution does not affect the mechanism of dissolution of mild steel$^{27,28}$.

The electrochemical parameters, corrosion current (I$_{corr}$), corrosion potential (E$_{corr}$), anodic and cathodic Tafel slopes (b$_a$ and b$_c$), the charge transfer resistance (R$_{ct}$) and the double electric capacity (C$_{dl}$) are calculated for all extracts and recorded in Table - 2.

Table - 2 : Electrochemical parameters for corrosion of mild EtOH in 2.0M H$_2$SO$_4$ containing 10% EtOH in absence and presence of different concentrations of the studied extracts (A, B and C) at 30°C

| C$_{wv}$ | E$_{corr}$(mv) | I$_{corr}$(ma.cm$^{-2}$) | b$_a$(Vdec$^{-1}$) | b$_c$(Vdec$^{-1}$) | R$_{ct}$(Ωcm$^2$) | C$_{dl}$(µf) |
|---------|---------------|-------------------------|-------------------|-------------------|-----------------|-------------|
| 0.0     | 513.17        | 7.13                    | 0.0914            | 0.0870            | 12.20           | 154.6       |
| 3.0x10$^{-5}$ | 488.00        | 4.72                    | 0.0654            | 0.0753            | 15.38           | 135.6       |
| 5.0x10$^{-5}$ | 504.26        | 3.67                    | 0.0658            | 0.0815            | 16.54           | 53.47       |
| 1.0x10$^{-4}$ | 498.00        | 2.84                    | 0.0910            | 0.1309            | 18.88           | 19.14       |
| 3.0x10$^{-4}$ | 490.27        | 2.25                    | 0.0647            | 0.1490            | 54.28           | 18.02       |
| 5.0x10$^{-4}$ | 474.80        | 2.11                    | 0.0571            | 0.1033            | 79.24           | 17.48       |
| 7.0x10$^{-4}$ | 462.33        | 1.79                    | 0.0457            | 0.1018            | 84.97           | 16.98       |
| 1.0x10$^{-3}$ | 458.40        | 1.74                    | 0.0369            | 0.0986            | 175.8           | 12.14       |
| 2.5x10$^{-3}$ | 458.24        | 0.843                   | 0.0339            | 0.0844            | 223.6           | 11.54       |
| 3.0x10$^{-5}$ | 478.78        | 5.62                    | 0.0749            | 0.0873            | 17.37           | 135.7       |
| 1.0x10$^{-5}$ | 487.30        | 4.78                    | 0.0770            | 0.0977            | 19.37           | 121.7       |
| 3.0x10$^{-5}$ | 470.93        | 2.76                    | 0.0643            | 0.0883            | 27.62           | 79.21       |
| 5.0x10$^{-5}$ | 482.84        | 2.62                    | 0.0652            | 0.0829            | 65.39           | 28.64       |
| 7.0x10$^{-5}$ | 484.50        | 2.33                    | 0.0612            | 0.0905            | 66.85           | 26.94       |
| 1.0x10$^{-4}$ | 476.47        | 2.10                    | 0.0592            | 0.0911            | 134.6           | 23.68       |
| 2.5x10$^{-3}$ | 471.19        | 1.71                    | 0.0567            | 0.1103            | 175.5           | 23.39       |
| 3.5x10$^{-3}$ | 464.69        | 1.28                    | 0.0589            | 0.0807            | 237.3           | 22.84       |
| 3.0x10$^{-5}$ | 509.11        | 4.43                    | 0.0914            | 0.1030            | 18.23           | 107.2       |
| 1.0x10$^{-5}$ | 447.79        | 3.75                    | 0.0722            | 0.1318            | 42.12           | 52.31       |
| 3.0x10$^{-5}$ | 483.03        | 2.81                    | 0.0645            | 0.1263            | 124.90          | 23.68       |
| 5.0x10$^{-5}$ | 462.36        | 1.84                    | 0.0621            | 0.1343            | 395.0           | 21.97       |
| 7.0x10$^{-5}$ | 462.67        | 1.52                    | 0.0504            | 0.1684            | 628.9           | 21.19       |
| 1.0x10$^{-4}$ | 469.74        | 1.37                    | 0.0442            | 0.1077            | 83.38           | 19.16       |
| 2.5x10$^{-3}$ | 470.21        | 1.34                    | 0.0396            | 0.0874            | 92.45           | 18.84       |
| 3.5x10$^{-3}$ | 469.27        | 1.24                    | 0.0557            | 0.0823            | 101.9           | 17.76       |

This table shows that both anodic and cathodic Tafel slopes (b$_a$ and b$_c$) values for the corrosion of mild steel sample in 2.0M H$_2$SO$_4$ containing 10% EtOH are: b$_a$=0.1 Vdec$^{-1}$, b$_c$ = 0.1 Vdec$^{-1}$, which are in good agreement with those recorded in previous studies$^{29-32}$. Also, it is clear from Table -2 that slopes b$_a$ and b$_c$ have not been noticeably affected which indicates that the addition of the studied inhibitors did not changed the mechanism of anodic and cathodic reactions.
Figure 1 (a, b & c): Polarization curves of mild steel sample in 2.0 M H₂SO₄ containing 10% EtOH in absence and presence of different concentrations of:

a) extract (A), b) extract (B) and extract (C) at 30°C
Figure - 2 (a, b & c): Nyquist Plots for mild steel sample corrosion in 2.0M H2SO4 containing 10% EtOH in absence and presence of different concentrations of: a) extract (A), b) extract (B) and extract (C) at 30°C.
Figure - 3 : SEM photographs for mild steel sample after polishing

Figure - 4 : SEM photographs for mild steel sample in 2.0M $\text{H}_2\text{SO}_4 + 10\% \text{EtOH}$ solution at 30°C
Figure 5 (a, b, & c): SEM photographs for mild steel sample in 2.0M H2SO4 + 10% EtOH in presence of 2.5 x 10^-3 w/v of: a) extract (A), b) extract (B) and extract (C) at 30°C.
As can be seen that there is irregular displacement in the corrosion potential ($E_{corr}$) values for the extracts under study to less negative values (more positive) with regard to the standard solution (blank). This displacement was clear in alcholonic extract.

The values of charge transfer resistance ($R_{ct}$) were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsura et al. The double electric capacity ($C_{dl}$) has been obtained from the highest value of the imaginary part of impedance $Z_{max}^{'}$ by applying the following equation:

$$C_{dl} = \frac{1}{2\pi R_{ct} f(Z_{max}^{'})}$$  \hfill (6)

The values of $R_{ct}$ and $C_{dl}$ established from Nyquist diagram obtained without and with different concentrations of the extracts in 2.0M H$_2$SO$_4$ containing 10% EtOH are listed in Table -2. As can be observed the charge transfer resistance ($R_{ct}$) and the double electric capacity ($C_{dl}$) increases along with the increase of the extract concentration, and consequently the rate of corrosion of mild steel sample in 2.0M H$_2$SO$_4$ decreases and the increase in $C_{dl}$ values due to the effect of the extract adsorption on the mild steel surface.

Table - 3 : Inhibition percentages of steel corrosion in 2.0 M H$_2$SO$_4$ containing 10% EtOH in Presence of Xanthotoxin (I) and Imperatorin (II)

| C(M)     | Xanthotoxin (I) | Imperatorin (II) |
|----------|-----------------|------------------|
|          | Inh. M% | Inh. H% | Inh. M% | Inh. H% |
| 0.5x10^{-3} | 37.39 | 34.16 | 36.43 | 34.30 |
| 1.0x10^{-3} | 47.23 | 49.81 | 48.11 | 46.08 |
| 2.0x10^{-3} | 55.46 | 53.93 | 51.88 | 53.71 |

As can be observed the charge transfer resistance ($R_{ct}$) and the double electric capacity ($C_{dl}$) increases along with the increase of the extract concentration, and consequently the rate of corrosion of mild steel sample in 2.0M H$_2$SO$_4$ decreases and the increase in $C_{dl}$ values due to the effect of the extract adsorption on the mild steel surface.

Figure - 3 reveals the microstructure of polished mild steel sample before polishing it, the scan shows a solid and homogeneous surface.

Figures - 4, 5 (a, b & c) illustrates the effect of 2.0M H$_2$SO$_4$ containing 10% EtOH on the mild steel sample at 30°C after 70 minutes immersion in absence and presence of 2.5x10^{-3} w/v of the extracts A, B and C. It appears from Fig. - 4 that the presence of a large number of vacules and inhomogenous metal surface. Fig. - 5 shows the disappearance of vacules especially in the case of extract (A), this is probably explained by the formation of an adsorbed film of the extract particles which was more effective in the case of extract (A). This confirms with the previous results obtained from chemical and electrochemical studies.

The effect of two coumarin compounds was studied by chemical methods in 2.0M H$_2$SO$_4$ containing 10% EtOH separately and in mixture of them. The results showed that as the concentration of the studied compounds (xanthotoxin , Imperation) increased, the rate of steel corrosion was decreased, and the inhibition efficiency obtained from the mixture was very high and nearly the same as when the extract was used which supported that the inhibition of Ammi majus extract is due to the coumarin compound presence, Table -3.

Adsorption Isotherms:

The decrease in the corrosion rate by the addition of the three extracts of Ammi majus is attributed to either adsorption of these extract molecules on the metal surface or to the formation of barrier film separating between the metal surface and the corrosion medium. The process of adsorption can be described by two main type of interactions: physical adsorption and chemical adsorption. These are influenced by the nature and charge of the metal, extract composition and the type of electrolyte.

Figure - 6 shows the relationship between Inh. % and logarithm of concentration (log C) of the investigated extracts in 2.0M H$_2$SO$_4$ contain 10% EtOH from chemical and electrochemical methods. It is clear that good agreement between results is found. As can be readily seen, all plots have the form of S-shaped adsorption isotherm. This indicates that corrosion inhibition process occurs by adsorption.
It has been proposed that adsorption is a process of exchange between the extract molecules and the water molecules on the metal surface as follows\textsuperscript{36,37}:

$$\text{Ex}_{(\text{sol.})} + X\text{H}_2\text{O}_{(\text{ads.})} \rightleftharpoons \text{Ex}_{(\text{ads.})} + \text{H}_2\text{O}_{(\text{sol.})}$$  \hspace{1cm} (7)

Where $\text{Ex}_{(\text{sol.})}$ and $\text{Ex}_{(\text{ads.})}$ refer to the metal surface, successively and $\text{H}_2\text{O}_{(\text{ads.})}$ refers to water molecule in solution which are adsorbed on the metal surface, and $X$ to the number of water molecules exchange for one extract molecule. To know the mechanism of electrochemical reaction, it is necessary to select the appropriate curve. It is found from the results that the adsorption of extract confirms the Langmiur isotherm using the following two equations\textsuperscript{33,38}:

$$\Theta = \frac{KC_{\text{inh.}}}{1+KC_{\text{inh.}}}$$  \hspace{1cm} (8)

$$\frac{C}{\Theta} = \frac{1}{K} + C$$ \hspace{1cm} (9)

Where $C$ is the extract concentration, $K$ is adsorption constant and $\Theta$ is degree of surface coverage.

**Figure - 6**: The variation of inhibition efficiency (Inh, %) against $\log C$ of extracts (A, B & C) for mild steel in 2.0M $\text{H}_2\text{SO}_4$ + 10% EtOH at 30°C. 

It is clear from Fig. 7 a straight lines are found when drowing $C/\theta$ vs. $C$ which means the application of Langmuir model at 30°C.

Table 4 gives the adsorption constant ($K_{ads}$) and the standard free energy of adsorption ($\Delta G_{ads}$). The value of constant $K_{ads}$ is related to the standard and free energy of adsorption $\Delta G^o_{ads}$ by the following relation:

$$K = \frac{1}{55.5 \exp \left(-\frac{\Delta G_{ads}}{RT}\right)}$$

(10)

The value 55.5 is the concentration of water in solution in mole/L.

As can be seen from Table 4, negative values of $\Delta G_{ads}$ are a characteristic feature of strong adsorption for all extracts which also reflect the high values of inhibition.

**Table 4**: The adsorption constants ($K_{ads}$ and $\Delta G_{ads}$) obtained from Langmuir isotherm for the three extracts in 2.0M H$_2$SO$_4$ containing 10% EtOH

| Extracts            | $K_{ads}$ (mol$^{-1}$) | Slope | $\Delta G^o_{ads}$ (K.J.mol$^{-1}$) | C.C% |
|---------------------|------------------------|-------|------------------------------------|------|
| Alcoholic extract   | 4713.20                | 0.93  | 31.43                              | 99   |
| Water extract       | 7461.61                | 1.07  | 32.59                              | 99   |
| Defatting extract   | 4885.19                | 0.95  | 31.52                              | 99   |
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