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Kinetics and Thermodynamics of Oil Extraction from Olive Cake

Smail Meziane · Hocine Kadi

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Abstract The kinetics of oil extraction from olive cake by using ethanol 96% was studied for different solvent-to-solids ratios and temperatures. The thermodynamic aspect of the extraction process was also examined. In the kinetic study, the results produced by the model of So and Macdonald (a model involving two main mechanisms of oil extraction: a washing process and a diffusion process with two stages) were found to be in good agreement with the experimental data. The yield of oil in the extract increased with increasing contact time, solvent-to-solids ratio and extraction temperature. The calculated values of the mass transfer coefficients of various stages of the extraction were found to increase linearly with solvent-to-solids ratio and temperature. In all cases, the predominant mechanism in the extraction was the washing of the oil occurring on the particle surface. The values of the activation energy were 8.56 kJ mol^{-1} for the washing stage, 9.88 kJ mol^{-1} for the first stage of diffusion and 17.55 kJ mol^{-1} for the second stage of diffusion by changing temperature from 20 to 50 °C. Further, the results obtained from thermodynamic study of extraction process gave positive values of enthalpy and entropy changes and negative values of change in free energy. Under the equilibrium conditions, the temperature coefficient was found to be 1.02.

Keywords Oil of olive cake · Solvent extraction · Kinetics · Arrhenius equation parameters · Thermodynamic parameters

Introduction

Olive culture and the olive oil industry are economically important for Mediterranean countries. Spain, Italy, Greece, Turkey and Maghrebian countries are the principal olive oil producers and this represents about 97% of olive oil production in the world. Olive cake is an important by-product of the mechanical processing of olives in the production of virgin olive oil. It constitutes more than 80% by weight of the processed olives and consists of pieces of pulp, pit and skin of the olive fruit, and has a significant oil content (4–12% depending on the extraction technology).

The International Olive Oil Council estimated that in 1987, Algerian olive oil mills (traditional pressing systems in the main) produced 17,500 tons of olive cake, which is currently evaluated at more than 150,000 tons per year. Its principal use is for fuel in olive oil mills or in brick manufacture after sun drying, whereas the residual oil that it contains could be economically recovered by solvent extraction processes. The oil extraction is carried out after reducing the moisture content of olive cake to between 5 and 10%. The extracted oil known as “crude pomace oil” is considered an inferior grade and it used as a raw material for soap making or industrial purposes. It can be also used for human consumption after refining but only if it is mixed with a certain amount of virgin olive oil.

The application of the kinetic models of Patricelli et al. [1] (model involving two main mechanisms of oil extraction: a washing process and a diffusion process) and of So and Macdonald [2] (model involving two main mechanisms of oil extraction: a washing process and a diffusion process with two stages) to the oil extraction of olive cake had been previously investigated [3]. The effects of the size

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S. Meziane (✉) · H. Kadi
Laboratoire de Chimie Appliquée et de Génie Chimique,
Faculté des Sciences, Université Mouloud Mammeri,
15000 Tizi-Ouzou, Algeria
e-mail: smmeziane@yahoo.fr

of particles and nature of the solvent on the kinetics of the extraction showed that the model of So and Macdonald [2] appears to be the best adapted to this extraction. In this work, we applied this model to our experimental results obtained from the study of the effects of the solvent-to-solids ratio and temperature on the oil extraction. In addition, the energetic aspect of the extraction of vegetable oils is of a fundamental importance. However, to our knowledge the thermodynamic parameters of the oil extraction from olive cake are not to be found in the literature. We then determined the parameters of Arrhenius equation and the thermodynamic parameters of extraction process of the oil.

Materials and Methods

Raw Materials

Olive cake used was obtained from a local olive oil mill with a centrifugation system. It had an initial moisture content of 47.0 ± 0.2% (wet basis), which was reduced by drying to 8.35 ± 0.06% (wet basis). The moisture content was determined by drying in an oven at 103 ± 1 °C till the weight did not change any more. The average diameter of particles (d_{av}) of the sample was 1.65 ± 0.04 mm. It was determined by a weighted arithmetical average from sieving results of the sample, which was performed on a series of sieves with decreasing meshes.

$$d_{\mathrm{av}} = \frac{1}{\sum_{i=1}^{n} m_i} \sum_{i=1}^{n} (m_i \varnothing_i) \tag{1}$$

where i is the class of particles, m_i is the amount of particles in class i (g), and $\varnothing_{i,\mathrm{av}}$ is the median of class i (mm). The oil content of the sample determined by an exhaustive extraction with hexane was 11.07 ± 0.06%. The olives of the cake were the Chemlal variety. The values of the moisture content and the average diameter of the particles were obtained in triplicate. Each experiment for determining the oil content was repeated five times.

Extractions

Batch extractions were performed in an isothermal cylindrical reactor of 600 ml equipped with a mechanical agitator. A condenser was fitted to avoid solvent losses. For each experiment, the sample was heated to the extraction temperature before adding solvent also heated to the same temperature. After extraction, the solid–liquid separation was performed by means of vacuum filtration in a Buchner funnel using Whatman filter paper no.3. The miscella was distilled under reduced pressure by means of a rotary-evaporator apparatus. The remaining traces of solvent were removed by placing the flask containing the extract in an oven at 103 ± 1 °C. After 15 min, the flask was removed from the oven and cooled to room temperature in a desiccator. After weighing, the procedure was repeated until the difference between two consecutive weighings was smaller than 15 mg.

The parameters studied were (a) extraction temperature (*T*): 20, 25, 40 and 50 (°C); (b) solvent-to-solids ratio (*L*/*S*): 3, 4 and 5 (ml solvent/g solids); and (c) contact time (*t*): from 0 to 60 min for the kinetic study and 150 h for the equilibrium study. The stirring velocity (v_a) was kept constant at 800 rpm for all the extraction experiments. Each extraction was carried out with 50 g of the sample. The solvent used was chemical grade 96.0% ethyl alcohol. It is a Prolabo (Fontenay S/Bois, France) product, with an average density of 0.806 g ml^{-1}. Each result represented the average of three replicates for the kinetic study and five for the equilibrium study.

The total oil content of the sample was determined by Soxhlet apparatus (250 ml), using the norm NF V03-924 [4]. The weight of cake submitted to the extraction was always 20 g.

Kinetic Model

The oil extraction from cakes and oleaginous seeds, based on the solubilization of fat matter by solvent, is mainly controlled by diffusion. The mathematical model of So and Macdonald [2] considers that this extraction occurs according to two simultaneous processes: (a) oil occurring on the seed surface is quickly removed by simple washing with the solvent at the beginning of the extraction process; and (b) the extraction of any remaining oil in the broken or unbroken cells is governed by a diffusion process in two steps occurring inside the seed: slow, unhindered diffusion of oil held in the broken cells of the seed (diffusion 1) and a very slow, hindered diffusion of oil held in the unbroken cells of the seed (diffusion 2). The concentration (C_t) at any time (t) of oil in the solvent is given by the following equation:

$$\begin{aligned} C_t = {} & \left(C_{\mathrm{e}}^{\mathrm{w}}\right)\left(1 - \mathrm{e}^{-k_{\mathrm{w}} t}\right) + \left(C_{\mathrm{e}}^{\mathrm{d1}}\right)\left(1 - \mathrm{e}^{-k_{\mathrm{d1}} t}\right) \\ & + \left(C_{\mathrm{e}}^{\mathrm{d2}}\right)\left(1 - \mathrm{e}^{-k_{\mathrm{d2}} t}\right) \end{aligned} \tag{2}$$

where $C_{\mathrm{e}}^{\mathrm{w}}$ and $C_{\mathrm{e}}^{\mathrm{d}}$ represent the oil concentrations (g oil/100 g solvent) at equilibrium in the solvent of the washing and diffusion steps, respectively, k_{w} and k_{d} represent the mass transfer coefficients of the washing and diffusion steps (min^{-1}), and the numbers 1 and 2 represent the relative indexes to the first and the second diffusion. The final oil concentration in the miscella at time equal to infinity is:

$$C_e = C_e^w + C_e^{d1} + C_e^{d2} \quad (3)$$

In this work, we studied the oil yield of the extraction according to time for different solvent-to-solids ratios and temperatures. This yield (noted ρ_t) can be expressed by the following equation:

$$\rho_t = \rho_e - (\rho_e^w)e^{-k_w t} - (\rho_e^{d1})e^{-k_{d1} t} - (\rho_e^{d2})e^{-k_{d2} t} \quad (4)$$

with

$$\rho_e = \rho_e^w + \rho_e^{d1} + \rho_e^{d2} \quad (5)$$

where ρ_e is the oil yield of the extraction at equilibrium (g oil/100 g solids), and ρ_e^w and ρ_e^d are the oil yields at equilibrium of the washing and diffusion steps (g oil/100 g solids).

The yield at any time (ρ_t) and the yield at equilibrium (ρ_e), calculated on dry weight basis, were defined as follows:

$$\text{Percentage extracted oil (w/w)} = \frac{m}{M} \times 100 \quad (6)$$

where m is the extracted oil mass (g), and M is the mass of the sample (g).

Values of the mass transfer coefficients k_w, k_{d1} and k_{d2} as well as the oil yields at equilibrium ρ_e^w, ρ_e^{d1} and ρ_e^{d2} have been calculated numerically with a non-linear least squares fitting method using the program “Origin 7.0” (OriginLab Corporation, Northampton, USA).

Results and Discussion

Kinetic Study

Experimental data given in Figs. 1 and 2 were fitted with the mathematical model of So and Macdonald. Very good fits are observed as shown by the high values of the coefficients of determination ($0.9980 < r^2 < 1.000$) given in Tables 1 and 2. For both parameters examined, the profile of the graphs clearly shows that the yield of oil rises rapidly with time at first, then less and less quickly with the progress of extraction. These observations are in agreement with those reported in a previous study [3] and recently with that of oil extraction from tobacco *(Nicotiana tabacum L.)* seeds [5]. With a ratio of 4 and at 25 °C, the oil yield increased approximately from 50 to 80% of the value at equilibrium as the time of extraction was increased from 4 to 60 min.

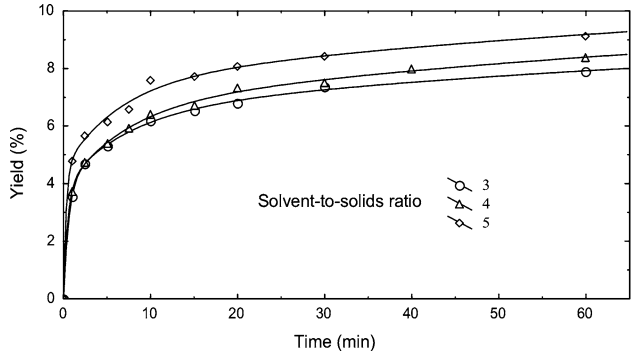

Fig. 1 Plot of extraction yield versus contact time showing the effect of solvent-to-solids ratio (temperature = 25 °C; stirring speed = 800 rpm)

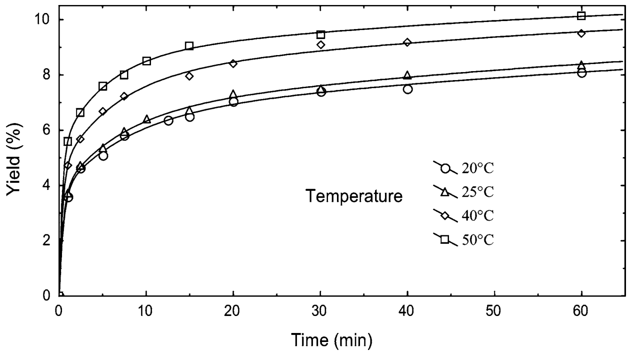

Fig. 2 Plot of extraction yield versus contact time showing the effect of temperature (solvent-to-solids ratio = 4 ml/g; stirring speed = 800 rpm)

Effect of the Solvent-to-Solids Ratio

The results obtained, represented in Fig. 1, show that the amount of extracted oil increases with the solvent-to-solids ratio. This effect was expected, since the concentration driving force increases at higher *L/S* values. Table 1 gives the calculated values of mass transfer coefficients for the various steps. They show the prevalence of the washing process on that of diffusion 1 and diffusion 2. Indeed, for a ratio *L/S* varying from 3 to 5, the washing coefficients are 12–21 times greater than those of the diffusion 1 and 175 to about 310 times greater than those of the diffusion 2. Also, the coefficients of diffusion 1 are on average 14 times greater than those of the diffusion 2. Further, it can be seen that the solvent-to-solids ratio influences all the coefficients of mass transfer positively. For each step, the plot of the mass transfer coefficient versus the solvent-to-solid ratio was carried out and was found to be linear resulting in determination coefficient values (r^2) greater than 0.96. In the range of ratio studied *L/S*, the increase in the coefficients is about 98.0% for the washing, 16.0% for diffusion 1 and 12.0% for diffusion 2. The effect of the solvent-to-solids ratio on the extraction process would thus favor the oil extraction being on the particle surface.

Under the equilibrium conditions, the change in yield of oil is relatively weak. In the range 3–5 (ml/g), it is approximately 13.3%. The value corresponding to the solvent-to-solids ratio 5 represents about 92.1% of the oil content of the sample.

Table 1 Effect of solvent-to-solids ratio on the mass transfer coefficients and the yields at equilibrium

L/S (ml/g)	Coefficients of mass transfer (min^{-1})			Yields at equilibrium (%)				Coefficients of determination, r^2
	k_w	k_{d1}	k_{d2}	ρ_e^w	ρ_e^{d1}	ρ_e^{d2}	ρ_e	
3	1.66	0.135	0.0095	3.95	2.53	3.32	9.80 ± 0.06	0.9995
4	2.19	0.144	0.0101	3.74	2.90	3.86	10.50 ± 0.06	0.9989
5	3.29	0.156	0.0106	4.50	2.98	3.62	11.10 ± 0.08	0.9957

Table 2 Effect of temperature on the mass transfer coefficients and the yields at equilibrium

T (°C)	Coefficients of mass transfer (min^{-1})			Yields at equilibrium (%)				Coefficients of determination, r^2
	k_w	k_{d1}	k_{d2}	ρ_e^w	ρ_e^{d1}	ρ_e^{d2}	ρ_e	
20	2.01	0.128	0.0086	3.74	2.80	3.88	10.42 ± 0.04	0.9985
25	2.19	0.144	0.0101	3.74	2.90	3.86	10.50 ± 0.06	0.9989
40	2.53	0.161	0.0145	4.54	3.32	2.93	10.79 ± 0.06	0.9985
50	2.82	0.194	0.0167	5.29	3.31	2.40	11.00 ± 0.07	0.9995

Effect of Temperature

The effect of temperature on the oil extraction kinetics was studied from 20 to 50 °C and the results are shown in Fig. 2. As expected, the increase in temperature results in an increase in oil yield in the extract. The change in yield can be explained by the fact that the rise in temperature increases the solubility and the facility of diffusion of the oil while decreasing viscosity. Table 2 gives the calculated values of the mass transfer coefficients and the yields of oil at equilibrium for the different steps. They show the predominance of the washing stage on both diffusion stages. The washing coefficients are on average 15 times greater than those of diffusion 1 and 169–310 times greater than those of diffusion 2. Also, the coefficients of diffusion 1 are 11–15 times greater than those of diffusion 2. It can be also seen that all these coefficients increase with raising the temperature of extraction. For each step, a plot of the mass transfer coefficient (k) against temperature (T) was carried out and was found to be linear with r^2 values ranging between 0.9521 and 0.9953. Under the conditions studied, the increase in coefficients is about 40.3% for the washing, 51.6% for diffusion 1 and 94.2% for diffusion 2. The temperature would thus affect much more the coefficients of mass transfer of the diffusion steps.

As can be seen in Table 2, there is a weak change in yield of the extracted oil at equilibrium, which is only 5.6%.

Parameters of the Arrhenius Equation

The temperature dependence of mass transfer coefficients given in Table 2 is described by an Arrhenius type relationship:

$$k = A\mathrm{e}^{-E_\mathrm{a}/RT} \tag{7}$$

where k is the coefficient of mass transfer (min^{-1}), A the frequency factor (min^{-1}), E_a is the activation energy (kJ mol^{-1}), R the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), and T is the absolute temperature (K).

For each step of the process, the Arrhenius plot (natural logarithm of mass transfer coefficient against reciprocal of absolute temperature) appeared linear where the logarithm of k decreased linearly with increasing $1/T$ resulting in r^2 values greater than 0.95 (Table 3). The values of the Arrhenius equation parameters were obtained from the slope and intercept of each curve (Table 3). The values of the activation energy are low. The activation energy of the step of diffusion 2 is relatively most important. All these values are characteristic of an extraction process of a physical nature. The results also give a value of frequency factor of the washing step approximately nine times greater than that of diffusion 1 and six times greater than that of diffusion 2.

Thermodynamic Study

The yields of oil at equilibrium given in Table 2 have been used to calculate the thermodynamic parameters of the extraction process of the oil.

Enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of extraction process were calculated using the Van't Hoff equation:

Table 3 Arrhenius parameters for the oil extraction kinetics

Parameters	Step		
	Washing	Diffusion 1	Diffusion 2
E_a (kJ mol^{-1})	8.56	9.88	17.55
A (min^{-1})	68.4	7.8	12.0
r^2	0.9940	0.9572	0.9890

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{8}$$

where R is the universal gas constant (kJ mol^{-1} K^{-1}), T is the absolute temperature (K), and K is the constant at equilibrium defined as:

$$K = \frac{(\rho_e)_{\text{miscella}}}{(\rho_e)_{\text{solid}}} \tag{9}$$

with $(\rho_e)_{\text{miscella}}$ is the oil yield in the extract at equilibrium at temperature T (K), and $(\rho_e)_{\text{solid}}$ is the equilibrium unextracted oil at temperature T (K), calculated from oil content of the sample (12.05 ± 0.05%) determined by an exhaustive extraction with ethanol 96%. The plot of the natural logarithm of the equilibrium constant versus the reciprocal of the absolute temperature was found to be linear resulting in an r^2 value of 0.9889. The values of ΔH° and ΔS° were obtained from the slope and intercept of the plot. Values of ΔG° were deduced then by applying the Gibb's free energy expression.

$$\Delta G^{\circ} = \Delta H^{\circ} - \mathrm{T}\Delta S^{\circ} \tag{10}$$

The values of equilibrium constant and thermodynamic parameters for the oil extraction process are given in Table 4.

The enthalpy change was found to be positive, indicating the endothermic nature of the oil extraction process. The value obtained is in the range (4–13.5 kJ mol^{-1}) obtained by Ibemesi and Attah [6] for the extraction of melon and rubber oil by different solvents at different temperatures. It is also comparable with the reported value of Topallar and Geçgel [7] for the oil extraction from sunflower seeds with 10% H_2SO_4 (11.2 kJ mol^{-1}).

A negative change of free energy was also obtained in this study, indicating the feasibility and spontaneous nature of the oil extraction process. This spontaneity was favoured with an increase in temperature. The ΔG° values lie within the reported values of Topallar and Geçgel (−0.90 kJ mol^{-1} at 313 K and −0.99 kJ mol^{-1} at 323 K) [7].

The system in the initial state includes the oily oil cake in aqueous ethanol solution. During extraction, the oil molecules are extracted from the solid phase thus increasing the entropy of the mixture. The change in entropy then takes a positive value (59.33 J mol^{-1} K^{-1}), which is in agreement with that obtained by Topallar and Geçgel.

The temperature coefficient (γ) is given by the following relation [6]:

$$\rho_T = \rho_{T_0}\gamma^{T/10} \tag{11}$$

where ρ_T is the oil yield at equilibrium at temperature T (°C), and ρ_{T_0} is the oil yield at equilibrium at 0 °C. The plot of the natural logarithm of the oil yield at equilibrium against the inverse of the temperature was found to be linear ($r^2 = 0.9991$). The value of γ, obtained from the slope of the plot, was about 1.02. It indicates that the yield increased by a factor of about 1.02 for every 10 °C rise in temperature. This value is in the range (1.02–1.14) reported by the authors [6] for the extraction of melon and rubber oils by different solvents at different temperatures. The value of the extraction yield at 0 °C (ρ_{T_0}), calculated from ordinate to origin of the plot, was 10.04%. It represents 83.32% of the oil content of the sample. The same value of the temperature coefficient was found by using the modified form of Eq. 11:

$$\rho_T = \rho_{T'}\gamma^{(T-T')/10} \tag{12}$$

where ρ_T is the yield at equilibrium at temperature T (°C), and $\rho_{T'}$ is the yield at equilibrium at given temperature T'(°C).

The predicted value of the oil yield at equilibrium at the boiling point of the solvent was $\rho_{78} = 11.60\%$. It is approximately 96.3% of the oil content of the sample.

In conclusion, this study showed that the model of So and Macdonald gave excellent fits of the experimental data of oil extraction from olive cake using ethanol 96% as solvent. As expected, increases in both the solvent-to-solids ratio and temperature resulted in an increase in extraction yields and in the calculated values of mass transfer coefficients of the various stages. The most important and fastest mechanism in the extraction process was the washing of oil occurring on the particle surface. The solvent-to-solids ratio would influence greatly the washing of oil from the grain. On the other hand, the temperature would have a greater effect on the diffusion of oil in the broken or unbroken cells of the grain. The values of the activation energy of different stages and the change in enthalpy of the oil extraction process were typical of diffusion-controlled processes. The extraction process was found to be spontaneous and endothermic in nature. Under the equilibrium conditions, the yield of oil increased by a

Table 4 Equilibrium constant and thermodynamic parameters

T (K)	$(\rho_e)_{\text{miscella}}$ (%)	$(\rho_e)_{\text{solid}}$ (%)	K	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
293	10.42	1.63	6.39			−4.47
298	10.50	1.55	6.77	12.91	59.33	−4.77
313	10.79	1.26	8.56			−5.66
323	11.00	1.05	10.48			−6.25

factor of approximately 1.02 for every 10 °C rise in temperature.

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