The Removal of Metals from Edible Oil by a Membrane Extraction Procedure

J.T.F. Keurentjes*, Th.G.J. Bosklopper, L.J. van Dorp and **K. van 't Riet**
Wageningen Agricultural University, Department of Food Science, Food and Bioengineering Group, De Dreijen 12, 6703 BC Wageningen, The Netherlands

Edible oils may contain traces of metals. In oil refining procedures these metals have to be removed to guarantee oxidatively stable products. In this study we present a hollow fiber membrane extraction system for the removal of metals from an oil. Several extraction liquids were tested, of which an ammonia solution gives the best distribution coefficient (m=11.7). From mass transfer calculations it follows that the resistance to mass transfer in the extraction phase in the fiber wall can be neglected compared to the resistances in the oil phase inside the fibers and the extraction phase outside the fibers. A cost evaluation shows that such a membrane extraction can be profitable in conventional refining if more than 1.5% bleaching earth has to be added in surplus to remove metals.

Natural fats and oils may contain traces of heavy metals in various concentrations. They are already present in oil seeds, and therefore a background concentration cannot be avoided. These natural concentrations may range from 0.1-0.3 ppm for copper, 0.1-0.7 ppm for manganese and 1-5 ppm for iron (1,2). During handling and storage the amount of metals present in the oil may increase significantly. This effect is almost negligible for oils which are liquid at ambient temperatures, but fats which have to be kept at an elevated temperature (70°C) to facilitate pumping and transportation (e.g., palm oil) are much more susceptible. At these temperatures metals from piping and storage tanks are dissolved in the oil.

Traces of heavy metals catalyze oxidation reactions. Most of all, glycerides containing unsaturated fatty acids are susceptible to these kinds of reactions, causing rancidity (3). In order to obtain good oxidation-stable products minimal contents of these heavy metals are required, e.g., the copper concentration should not exceed 0.02 ppm (4).

Metals in oil can be present in several forms. First of all, they can be present as metal soaps or free ions, possibly surrounded by a water shell, or included in phospholipid vesicles (5,6). Metals may also be solubilized as small particles. In oil processing, metals present in a particulate form can be removed easily by means of filtration or a magnetic trap (7), although such a magnetic trap is not a part of the usual refinery equipment.

Metal ions are partially removed in the classical refining procedures. In the degumming step, a minor quantity is entrapped in the phosphatides. During deacidification and bleaching the remainder can be removed. In the final bleaching step the quantity of bleaching earth can be adjusted to the remaining metal concentration. At high metal contents, this can be a costly procedure. Other methods for the removal of these metal ions have been proposed by Vioque (8), using cation exchange resins, and by Beal (9), using an acid washing step followed by ion exchange treatment.

Using bleaching earth, crude oil is absorbed by the bleaching earth in considerable amounts—around 30% of the weight of the bleaching earth added (10). It is difficult to recover this absorbed oil. Therefore, this oil containing bleaching earth usually has to be disposed of. However, in the future environmental aspects may significantly influence the costs of disposal. These costs will become an important factor in the choice of refinery equipment.

In this study a system is investigated for the removal of trace metals from an oil by means of a membrane based extraction. Such a membrane extraction procedure can easily be applied, since no mixing of phases occurs, and, therefore, no phase separation is required afterwards. As a result, oil losses are absent in this type of process.

Theory. To facilitate reading, the symbols used are summarized at the end of the paper in Table 5. For the two phases, the mass balance equation for the oil phase is:

$$V_o.dC_o/dt = -K_o.A.(C_o-C_e/m) \qquad [1]$$

and for the extraction phase:

$$V_e.dC_e/dt = -K_o.A.(C_o-C_e/m) \qquad [2]$$

In these equations V_o and V_e are the volumes and C_o and C_e the concentrations of copper in the oil and extraction phase, respectively. The m is the distribution coefficient of copper over oil and the extraction phase, and is defined by $m = C_{e,eq}/C_{o,eq}$, where the $_{eq}$ indicates the equilibrium state. A is the contact area between the two phases, and K_o the overall mass transfer coefficient.

These two mass balance equations can be combined and linearized, resulting in equation [3]:

$$-\ln\{(C_{e,eq}-C_e)/C_{e,eq}\} = K_o.A.\{(V_e+V_o/m)/(V_e.V_o)\}.t \qquad [3]$$

For a hydrophilic membrane with the extraction phase in the membrane, the overall mass transfer can be written as (11):

$$K_o^{-1} = k_o^{-1} + (m.k_e)^{-1} + (m.k_m)^{-1} \qquad [4]$$

In this equation the overall mass transfer resistance (the reciprocal of the overall mass transfer coefficient, K_o) is the sum of the mass transfer resistance in the oil phase (k_o^{-1}), the mass transfer resistance in the extraction phase outside the fibers ($(m.k_e)^{-1}$) and the resistance of the extraction phase in the membrane wall ($(m.k_m)^{-1}$). Since the Reynolds number inside the fibers will be less than one, mass transfer in the fibers is given by equation [5] (12):

$$k_o.d_f/D_o = 1.64\ [(d_f^2.v)/(l_f.D_o)]^{1/3} \qquad [5]$$

in which d_f is the internal fiber diameter, l_f the fiber

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*To whom correspondence should be addressed.

length, D_0 the diffusion coefficient of the solute, and v the oil flow velocity. The resistance in the membrane wall is proportional with the membrane thickness, d_m, over the diffusivity, D_e, of the solute in the liquid filling the pores. With a correction for the effective diffusion distance by the tortuosity, τ, and a correction for the amount of pores by the surface porosity, ϵ, the resistance in the membrane is given by (13):

$$k_m = (D_e.\epsilon)/(d_m.\tau) \qquad [6]$$

The mass transfer resistance outside the fibers can now be calculated using equations [4], [5] and [6].

MATERIALS

Copper dissolved in soy bean oil was used as a model system. The preparation procedure was as follows: A 10 liter vessel was filled with soy bean oil of edible quality, and copper curls were added to it. This system was kept under nitrogen, heated at 70°C in a water bath, and stirred for six days. After cooling, the oil was stored at room temperature in plastic vessels.

The copper concentration in oil was determined on a Perkin Elmer 3030 Atomic Absorption Spectrometer using a graphite furnace atomizer. A three step procedure was used: 1) 900°C, 50 s ramp, 30 s hold, internal gas flow 300; 2) 2000°C, 0 s ramp, 5 s hold, maximum power; 3) 2700°C, 1 s ramp, 3 s hold, internal gas flow 50. In the extraction phase, copper was analyzed on a Perkin Elmer 2380 Atomic Absorption Spectrometer using an acetylene flame.

EXPERIMENTAL

Distribution coefficients were determined by mixing 50 ml copper-containing soy bean oil with 15 ml extractant for several days in order to obtain equilibrium. Afterwards the copper concentration was determined in both phases, and mass balances were made up to check the recovery.

Membrane extractions were carried out using a hollow fiber membrane module containing cellulose fibers (Cuprophan, ENKA-Membrana AG, Federal Republic of Germany) with an internal diameter of 0.2 mm and a wall thickness of 8 μm. The surface area in such a module is 0.77 m2. The experimental set-up is depicted in Figure 1. The oil phase was circulated inside and the extraction phase outside the fibers. The hydrophilic extraction phase wets the fiber wall. To avoid emulsion formation by extractant permeating into the oil phase, the oil phase was circulated at a static pressure of $2^{\cdot}10^5$ Nm^{-2}. The membranes were rinsed with demineralized water before use.

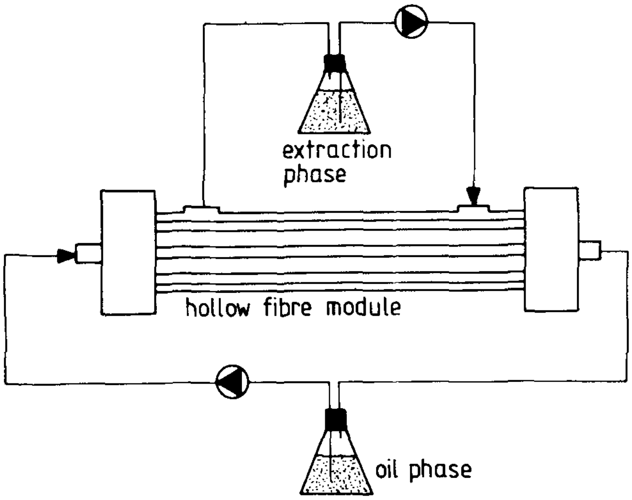

FIG. 1. Schematic respresentation of the membrane extraction experiments.

RESULTS

Distribution coefficients. In Table 1 the extractants used and the assumed extraction mechanism are shown. In this study only those extractants have been taken into consideration that do not form insoluble metal salts, since the application of such an extractant will cause a rapid clogging of the membrane. The distribution coefficients obtained are also given Table 1. The accuracy of the measurements is around 15%.

From these results it is evident that a lecithin solution gives the best distribution coefficient. However, in the absence of intensive mixing, the uptake of metals from the oil phase can merely take place by the lecithin adsorbed to the interface, and no real extraction takes place. In the case of intensive mixing a stable emulsion is formed which is very difficult to break. It can therefore be concluded that for a membrane based extraction the use of an ammonia solution will give the best results.

TABLE 1

Extractants and Corresponding Distribution Coefficients for Copper over the Extractant and Soy Bean Oil at 30°C

Extractant	Extraction mechanism	m
Water	solubility	3.1
Phosphoric acid (1 M)	complexation as $Cu(H_2PO_4)_2$ or $CuHPO_4$	6.7
Ammonia (0.9 M)	complexation as $Cu(NH_3)_4^{2+}$ (14)	11.7
Oxalic acid (0.3 M)	complexation	2.9
Citric acid (0.3 M)	complexation (15)	0.4
Lecithin (10 g/l)	inclusion	>50
Urea (3 M)	complexation	<1

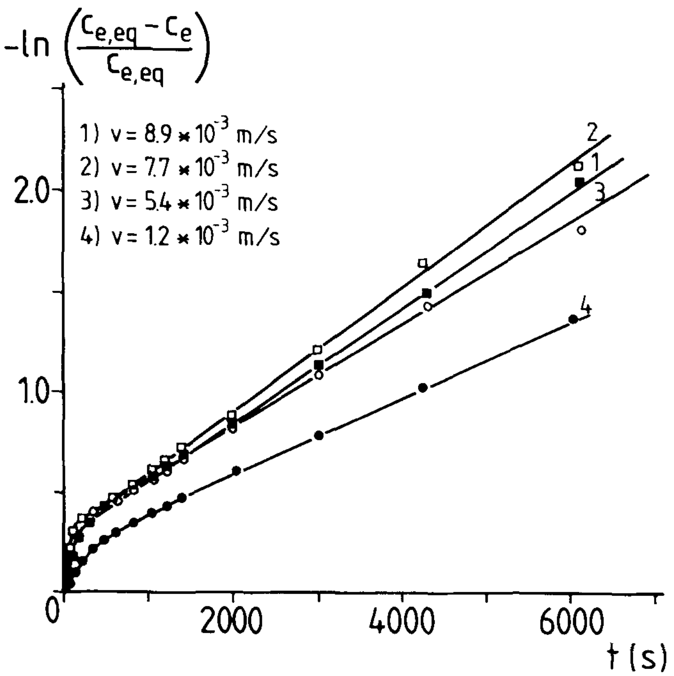

FIG. 2. Linearized copper concentration in the extraction phase at different oil phase velocities.

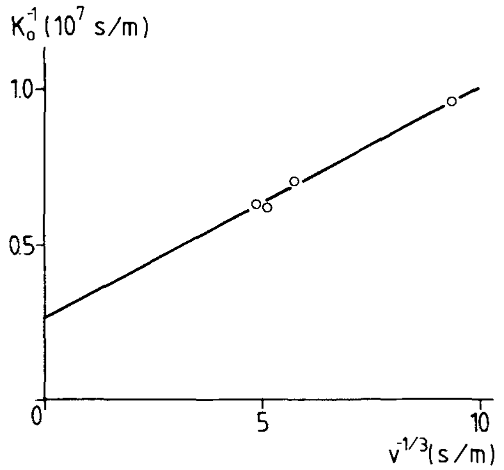

FIG. 3. K_o versus $v^{-1/3}$. The intercept represents the sum of the mass transfer resistances in the fibre wall and the extraction phase.

Membrane extraction. In Figure 2 the linearized results of extractions are depicted at several oil flow velocities at 40°C. In these experiments the flow of the ammonia phase is kept constant at 0.07 m/s. These lines are expected to be straight and to intersect the origin. However, in the first part of the experiments (the first few minutes) mass transfer occurs at a higher rate than in the second part. Mass transfer coefficients for the second part of the curves are calculated using equation [3] and are given in Table 2.

Plotting K_o^{-1} vs $v^{-1/3}$ (Fig. 3) the intercept gives the sum of the mass transfer resistances in the membrane and the extraction phase. This sum equals $0.25 \cdot 10^7$ s/m. The extrapolation needed in Figure 3 makes the accuracy of this number limited. For the calculation of the mass transfer coefficients in the oil, water and membrane, the diffusion coefficient of the copper-containing moiety has to be known. This diffusion coefficient can be estimated using the Wilke-Chang relation (16). It is not clear in which form the copper is present in the oil, therefore diffusion coefficients of the most probable forms are calculated. The results are given in Table 3.

The diffusion coefficients can be used for the calculation of k_o^{-1}, the mass transfer resistance in the oil phase inside the fibers, at a given flow velocity with equation [5]. k_o^{-1} can also be determined graphically from Figure 3. When the intercept is subtracted from the measured K_o^{-1} value, the residue equals k_o^{-1}. At $v=8.9 \cdot 10^{-3}$ m/s the graphically determined k_o^{-1} value is $3.5 \cdot 10^6$ s/m. This value indicates a diffusion coefficient of $1.1 \cdot 10^{-11}$ m²/s. Because of the extrapolation required in Figure 3, the accuracy of this value is limited, but is in the order of magnitude of the values given in Table 3. The difference between the calculated diffusion coefficient for the fatty acid bound copper and the measured value does not exclude this form, and directs us to this form as the most probable one.

TABLE 2

Overall Mass Transfer Coefficients for Different Flow Velocities Through the Fibers

v (10³ m/s)	K_o (10⁻⁷ m/s)
8.9	1.59
7.7	1.59
5.4	1.42
1.2	1.04

TABLE 3

Diffusion Coefficients of Different Copper Containing Moieties Calculated (16)

Appearing form	D (m²/s)	k_o^{-1} (s/m) at $v=8.9 \cdot 10^{-3}$ m/s
$Cu.FA_2$/oil	$4.1 \cdot 10^{-11}$	$1.4 \cdot 10^6$
$Cu.6H_2O$/oil	$1.3 \cdot 10^{-10}$	$6.7 \cdot 10^5$
Cu/oil	$3.0 \cdot 10^{-10}$	$3.8 \cdot 10^5$
$Cu(NH_3)_4^{2+}$/water	$7.9 \cdot 10^{-9}$	

The partial mass transfer resistance in the oil phase is also given for an oil flow of $8.9 \cdot 10^{-3}$ m/s (eq. 5).

Using equation [6], the resistance in the fiber wall can be estimated to be $3.2 \cdot 10^3$ s/m ($\epsilon=0.8$, $\tau=2.5$). Evidently, the resistance in the fiber wall can be neglected compared to the resistances inside the fibers and on the shell side of the fibers. With a negligible resistance in the membrane wall, the resistance at the shell side is surprisingly high. Formula for mass transfer outside fibers at the average flow velocity used (13) with the distribution coefficient of 11.7 predict a mass transfer resistance outside the fibers that should be negligible. The resistance is most probably due to channeling in the fiber bundle. This can result in local low velocities and large mass transfer boundary layer thickness, with a reduced mass transfer rate as a result. Channeling can be avoided by the use of spacered membrane modules. For theoretical reasons it is

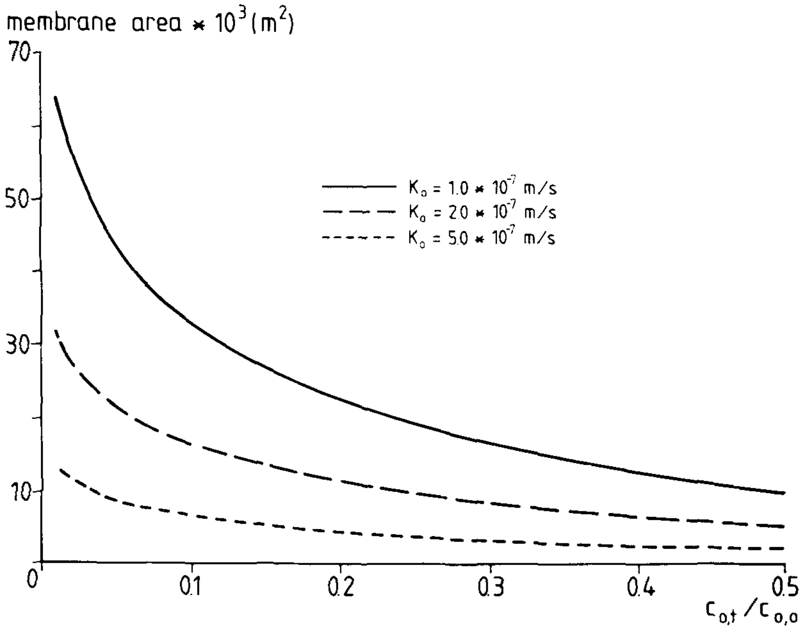

FIG. 4. Membrane surface area needed versus the removal efficiency at different overall mass transfer coefficients.

expected that in a well spacered module the resistance at the shell side will be negligible with respect to the resistance in the oil phase.

Costs evaluation. For an estimation of the costs of such a membrane system, a system with an oil flow of 5000 kg/h was chosen. To facilitate an estimation of the costs, the assumption was made that the metal concentration in the extraction phase equals zero. In practice, this can be achieved by placing an ion exchange resin in the system. Based on a maximum metal content of 50 mg/kg (with an average molecular weight of 50 g/mole and divalently charged) and an ion exchange capacity of 10 meq/g, 5 kg oil/g resin can be treated. At an oil flow of 5000 kg/hr, 1 kg resin is saturated per hour. Using two columns operated alternately for two days, 48 kg resin per column is needed. The costs of operating such an ion exchanger would be minor compared to the costs of the membrane system.

In the case of a zero concentration in the extraction phase, the decrease of the metal concentration is expressed by:

$$\ln(C_{o,t}/C_{o,o}) = -K_oAt/V_o \qquad [7]$$

where $C_{o,o}$ and $C_{o,t}$ are the metal concentrations in the feed and the treated stream, respectively. In Figure 4 the membrane surface area needed for different removal efficiencies at three mass transfer coefficients is depicted.

The major costs for a system of 10,000 m^2 are calculated according to Kloosterman (17) and are given in Table 4.

Related to the oil flow through the system (5000 kg/h, 8,500 h/year), the costs are 0.032 \$/kg. Figure 4 shows that for this system of 10,000 m^2 at an overall mass transfer coefficient of $2 \cdot 10^{-7}$ m/s, 75% of the metals can be removed for 0.032 \$/kg. Improving the mass transfer coefficient to $5 \cdot 10^{-7}$ m/s, the costs for the same 75% removal efficiency (based on 3,000 m^2) will be 0.012 \$/kg.

TABLE 4

Major Costs for a Membrane System of 10,000 m^2 for the Removal of Copper from an Oil

	$\cdot 10^3$ \$
Capital investment	1256
Costs of installment (2.5% of CI)	31
Automation (15% of CI)	188
Fixed capital investment	1475
Direct production costs	500[a]
Cost of membrane	
Membrane cleaning (10% of membrane cost)	50[b]
Electricity (0.1 kW/m^2 at 0.05 \$/kWh)	500
Maintainance (6% FCI)	89
Labor	30
Supervision/laboratory (20 %L)	6
	1175
Fixed charges	103
Depreciation (7% FCI)	
Insurance (1% FCI)	15
Overheads (40% TLSM)	50
	168
Annual production costs	1343

[a] The membrane lifetime is estimated to be 8,500 hours (1 year).

[b] Already partially refined oil will be circulated, and this will reduce cleaning costs.

Based on the mass transfer results, it can be expected that this mass transfer coefficient can be obtained after some optimization. An increase in removal efficiency from 75% to 95% at an overall mass transfer coefficient of $5{*}10^{-7}$ m/s results in a membrane area of 10,000 m^2, and the costs will be 0.032 $/kg. From these considerations it will be clear that K_o has to be optimized, then the efficiency needed has to be established, and then the membrane area needed can be calculated. Based on the above calculations, costs for such a system may be between 0.01 and 0.03 $/kg. The costs of the acid washing system [as proposed by Beal (9)] are estimated to be in the order of 0.01 $/kg. Depending on the removal rate required and the increase in mass transfer that can be obtained by optimization, membrane extraction can be competitive with such a wash procedure.

TABLE 5

List of Symbols

A	membrane surface area	[m^2]
C_e	metal concentration in the extraction phase	[kg/kg]
C_o	metal concentration in the oil phase	[kg/kg]
$C_{o,O}$	metal concentration in the oil feed	[kg/kg]
$C_{o,t}$	metal concentration in the oil leaving the system	[kg/kg]
D_e	diffusion coefficient in the extraction phase	[m^2/s]
d_f	internal fiber diameter	[m]
d_m	membrane thickness	[m]
D_o	diffusion coefficient in the oil phase	[m^2/s]
FA	fatty acid	
k_e	partial mass transfer coefficient for the extraction phase	[m/]
k_m	partial mass transfer coefficient for the membrane	[m/s]
k_o	partial mass transfer coefficient for the oil phase	[m/s]
K_o	overall mass transfer coefficient	[m/s]
l_f	fiber length	[m]
m	distribution coefficient	[-]
t	time	[s]
v	liquid velocity inside the fibers	[m/s]
V_c	volume of the extraction phase	[m^3]
V_o	volume of the oil phase	[m^3]
ϵ	porosity of the membrane material	[-]
τ	tortuosity of the membrane material	[-]

The costs of the membrane system must be compared with the costs of the addition of a surplus of bleaching earth. These consist of three different items: The amount of bleaching earth added, oil losses, and disposal costs. The first two can be estimated fairly easily—at an average bleaching earth price of 0.75 $/kg, an oil loss of 30% of the weight of the bleaching earth added and an oil price of $400/1000 kg, these costs will be 0.87 $/kg of bleaching earth added. However, disposal costs are difficult to estimate (and will increase significantly in the future). Therefore, disposal costs will influence the point where the membrane extraction system becomes feasible. In practice, a membrane extraction will likely be placed before the addition of bleaching earth to avoid the addition of a surplus of bleaching earth. Based on the above made considerations, it can be estimated that in cases where more than 1.5% of bleaching earth has to be added in surplus in order to remove the metals from an oil, the membrane system may be an economic alternative for the addition of bleaching earth.

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