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Solid–Liquid Extraction

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I. INTRODUCTION

Solid–liquid extraction or leaching is a separation process affected by a fluid involving the transfer of solutes from a solid matrix to a solvent. It is an extensively used unit operation to recover many important food components: sucrose in cane or beets, lipids from oilseeds, proteins in oilseed meals, phytochemicals from plants, and functional hydrocolloids from algae, among others. Solid–liquid extraction (or simply extraction) may also be used to remove undesirable contaminants and toxins present in foods and feeds.

"Solid–liquid" extraction may be a misnomer for it gives the impression that mass transfer occurs at a sharp interface between a "dry" solid and the liquid phase. In most food extractions, either the "solid" naturally contains a liquid phase or it becomes impregnated by the extraction liquid, so that liquid phase diffusion inside the solid is a major mass transfer mechanism during leaching.

A. Characteristics of Food Extraction

From an engineering viewpoint, solid–liquid extraction of foods is a multicomponent, multiphase, un-steady state mass transfer operation. It involves transfer of more than one chemical species—the solute—from a solid to a solvent. The solute is sometimes referred to as the extract, when the chemical species being recovered are ill defined, as occurs in the extraction of phytochemicals from plants. Commonly used solvents in extraction of food components are water,

ethanol (or ethanol-water mixtures), hexane, and carbon dioxide, but the trend is toward the use of natural chemicals.

During extraction, the concentration of solute inside the solid varies leading to the nonstationary or unsteady condition. A series of phenomenological steps have to occur during the period of interaction between the solute-containing particle and the solvent effecting the separation (1) as represented schematically in Fig. 1. These include:

1. Entrance of the solvent into the solid matrix
2. Solubilization and/or breakdown of components
3. Transport of the solute to the exterior of the solid matrix
4. Migration of the extracted solute from the external surface of the solid into the bulk solution
5. Movement of the extract with respect to the solid (i.e., extract displacement), and
6. Separation and discharge of the extract and solid

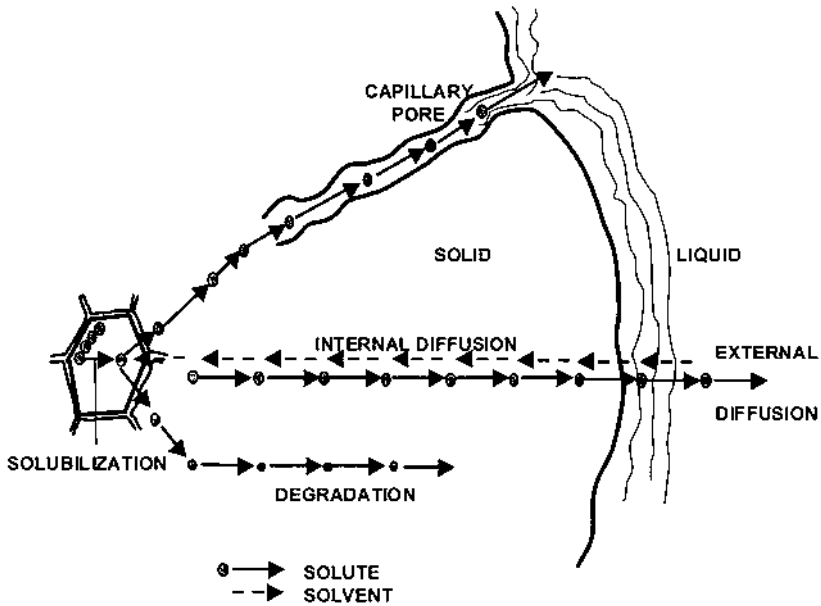

Figure 1 Scheme of the main steps in solvent extraction of solid food particles. Mass transfer of solute in liquid occupying pores is an important mechanism. External resistance is caused by the static liquid layer surrounding the particle.

As a result of these phenomena, extraction takes place at a rate expressed in terms of (mass of solute leached)/unit time or, more commonly, as change in solute concentration in the solid/unit time (*dc/dt* or *dx/dt*). In multicomponent extraction the relative rate at which different chemical species migrate through the solid may also be of concern. Since the aforementioned elementary steps occur at their own rate and in some cases sequentially, the overall rate of the extraction process is determined by the step having the slowest rate or the rate-controlling step. As discussed later, transport through the solid matrix is usually the rate-controlling step in food extractions.

Foods are unique in that the microstructure of the solid plays a major role in the rate and quality of the extraction process. To attain a fundamental understanding of the relationship between rate and food microstructure, it is necessary first to introduce some theoretical notions of mass transfer. A rigorous treatment on the subject may be found in the classical texts for chemical engineering. Gekkas (2) presents concepts of transport phenomena with applications to foods and biological materials. A recommended book on mass transfer for beginners and experts as well is that by Cussler (3).

B. Solvent Selection

Solvent selection is based on several properties:

1. Solubility of the specific compound (or compounds) in the solvent.
2. Recovery, since the solvent will be reused in subsequent extractions. If distillation or evaporation is used, the solvent should not form azeotropes and the latent heat of vaporization should be small. Removal of the solvent from the miscella (and from the spent solids) can pose serious problems if the residual level of the solvent must be minimized.
3. Interfacial tension and viscosity. The solvent should be capable of wetting the solid matrix and its viscosity should be sufficiently low so it can flow easily. Wettability is also important if the solvent must penetrate through pores and capillaries in the matrix.
4. Ideally, the solvent should be nontoxic, stable, nonreactive, nonflammable, harmless to the environment, and cheap.

Laws relating to extraction solvents for use in foods are concerned primarily with human health requirements. Accepted solvents for use in compliance with good manufacturing practice (GMP) provided the presence of residues are unavoidable are as follows: propane, butane, propyl acetate, ethyl acetate, ethanol, carbon dioxide, acetone and nitrous oxide. Substances that have been found acceptable by the Enzyme Commission (EC) when used under specific conditions are hexane, methyl acetate, ethylmethylketone, and dichloromethane.

II. EXAMPLE OF STRUCTURAL FEATURES OF A SOLID MATRIX: PLANT TISSUE

Food materials of plant origin have an intricate microstructure formed by cells, intercellular spaces, capillaries, and pores. There are four major types of mature plant tissue: (a) storage or parenchyma; (b) conducting or vascular, composed of phloem (transport of organic materials) and xylem (transport of water); (c) supporting: and (d) protecting tissue. Only two of these contribute to the microstructure of edible parts of plant foods: parenchyma cells and the conducting tissue forming an intricate network throughout. An excellent introduction to plant cells and microscopy techniques can be found at the web site http://www.rrz.uni-hamburg.de/biologie.

The desired solute in the tissue may be present inter- or intracellularly. In the first case, intact cell walls and adhering membranes constitute a major resistance to diffusion. They affect the permeability of solutes so that small molecules pass at a faster rate than larger ones, resulting in a selective transfer. The permeability of cell walls and membranes is increased and selectivity reduced by heat-induced denaturation. Moreover, cell walls forming most of the supporting tissues and certain types of conducting cells (tracheids, vessel elements) are lignified to a different extent, further reducing the passage of molecules.

During preparation for extraction the solid is reduced to small particles because, theoretically, extraction time varies inversely with the square of the characteristic dimension of the solid. As particle size decreases the ruptured outer cells constitute a larger proportion of the particle volume and extraction characteristics per unit mass of material change. Size reduction is limited because of pressure drop in the extractor, slow drainage rates, presence of fines in the extract, flow instability, and entrainment. It has to be kept in mind that extraction is just one of the unit operations in a separation process and downstream purification depends strongly on how "cleanly" the extract was obtained.

III. FUNDAMENTAL ASPECTS OF EXTRACTION

A. Extraction as a Diffusion Process

Molecular diffusion is the process by which molecules are transported from one part of the system to another by random movement as a result of a concentration gradient. In leaching of foods the interior of the solid cannot be agitated and turbulence is unlikely to occur in small capillaries and pores, leaving molecular diffusion as the main transport mechanism within the solid phase. Solvent extraction may be considered as a diffusion process in the liquid (fluid) state since

solute transfer, even inside a solid, exists as a dilute solution. In some cases, solvent influx may occur due to pressure gradients due to capillary forces or by mechanical relaxation of the cellular matrix.

Fick's laws provide the semiempirical bases for analysis of molecular diffusion. Fick's first law is useful for defining a diffusion coefficient or diffusivity (D). It simply establishes that under steady-state conditions (concentration does not change with time) the unidirectional flux of solute 1 (J_1, mol/s) in the r direction is directly proportional to the diffusivity of the solute, to the area traversed by the flux and to the gradient of solute concentration between two points, expressed in terms of absolute concentration (dc/dr) or molar fraction (dx/dr). Fick's first law describes diffusion referred to a fixed coordinate system and for the unidirectional case it takes the form:

$$j_1 = \frac{J_1}{A} - cD\frac{dx_1}{dr} = -\frac{Ddc_1}{dr} \tag{1}$$

where j_1 is the flux in moles per unit time and unit area, r is the direction of flow, A is the area across which diffusion occurs, and c is the total molar concentration (moles/volume). The minus sign gives a positive flux term since the gradient is negative (flow occurs down a concentration gradient, from high to low concentration). This equation can be regarded as a limit for long times, when transient conditions have disappeared and a linear gradient is established in the system. It can be applied without problems whenever the solute is in high dilution in the solvent; diffusion in concentrated systems involves convection and a more complex mathematical treatment (3).

In practical situations and for short times, unsteady or nonstationary conditions exist and the concentration of solute varies with time (t) and position (r) inside the solid. In such cases, Fick's second law (or the diffusion equation) applies and takes the general form:

$$\frac{\partial c_1}{\partial t} = \frac{1}{r^{\nu-1}} \frac{\partial\left(r^{\nu-1} D\dfrac{\partial c_1}{\partial r}\right)}{\partial r} \tag{2}$$

where the index ν equals 1 for an infinite slab, 2 for an infinite cylinder, and 3 for a sphere. It is easier to understand Fick's second law when Eq. (2) is written as:

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial r^2} = D\frac{\partial}{\partial r}\left(\frac{\partial c_1}{\partial r}\right) \tag{3}$$

for it says that the flow of solute is directly proportional to the change of the concentration gradient with position. So, when the gradient is constant (i.e.,

linear concentration profile), then $\partial c_1/\partial t = 0$, meaning that steady-state conditions exist and we are back to Eq. (1).

Analytical solutions for Eq. (3) under several simple initial and boundary conditions are found in many textbooks (4, 5); solutions to more complex situations and for different geometries are analyzed in the classical book by Crank (6). Schwartzberg and Chao (7) present a detailed analysis of the assumptions and conditions under which solutions to Eq. (3) can be applied to extraction in foods. In general, solutions relate the dimensionless extent of extraction of solute 1 as $X = (c - c_f)/(c_0 - c_f)$ with time in a series expression represented by Eq. (4), where c is the average solute concentration inside the solid at any time and c_0 and c_f are the initial and final equilibrium concentrations, respectively.

$$X = \Sigma\ B_n \exp\left(-\frac{q_n^2 Dt}{L^2}\right) \tag{4}$$

where X depends on $\alpha = mE/R$ (where m is the equilibrium distribution ratio between the solute concentration in the bulk solution and inside the solid, and E/R is the extract-to-solid volume ratio), and on Fick's dimensionless number Dt/L^2 (where L is a characteristic length, e.g., the particle size). Parameters B_n and q_n are functions of α. When only the first term of the series is considered (e.g., for $Dt/L^2 > 0.06$), plots of log X vs. t are straight lines with a slope equal to $-Dq_1^2/2.303L^2$, from which D can be obtained as an overall diffusion coefficient (effective or apparent diffusion coefficient).

The dimensionless number Dt/L^2 can be used as a criterion of closeness to the steady state. If it is much larger than unity (e.g., $Dt >> L^2$) an equilibrium or steady-state condition may be assumed. Also, two parameters may be established for un-steady-state conditions: a "velocity of diffusion," $\sqrt{D/\pi t}$ and a "penetration distance," $\sqrt{4Dt}$ (3). Note that both parameters involve the square root of time.

Solid–liquid extraction of various food materials is controlled by internal diffusion except in the case of very small particles, poor agitation, or presence of a skin (8–11). The extent of control between external and internal diffusion is indicated by the Sherwood number $N_{Sh} = k_c L/D$, where k_c is the liquid-phase mass transfer coefficient, L a characteristic dimension of the solid (e.g., particle size), and D the internal diffusion coefficient. If $N_{Sh} > 200$, internal control can be safely assumed (7).

B. Determination of Diffusion Coefficients

Data for diffusion coefficients are necessary to make calculations using the Fickean approach. Diffusivities may be determined experimentally or predicted. Experimental methods used for liquids are, among others, the diaphragm cell, the

rotating disk (used for drug dissolution), nuclear magnetic resonance (NMR) spin-echo techniques, and interferometer methods (Gouy interferometer). For details of these methods, see Cussler (3).

Orders of magnitude of these coefficients are important to remember (all units in cm^2/s): for gases, 10^{-1}; for liquids, around 10^{-5}; and for solids, between 10^{-8} and 10^{-30} (if m^2/s is used as unit, values must be divided by a factor of 10^4). Consequently, perfume in air diffuses 10,000 times faster than the tea extract in a cup of hot water! Diffusion coefficients of polymers in solvents under dilute conditions may be as low as 10^{-6} to 10^{-8} (cm^2/s) and of gases through synthetic membranes vary widely between 10^{-8} and 10^{-11} (cm^2/s).

Numerous attempts have been made to predict diffusivities in liquids. According to the Stokes-Einstein equation, the diffusion coefficient of large spherical solute species in a pure solvent of viscosity η is given by:

$$D = \frac{kT}{6\pi\eta r_s} \tag{5}$$

where k is the Boltzmann constant [gas constant divided by Avogadro's number (R/N_0)], T the absolute temperature, and r_s the effective radius of the diffusing molecule. This expression is misleading in the sense that in practice viscosity and solute radius effects are more important than those of temperature. Also, adaptations of Eq. (5) for dilute solutions of macromolecules must encompass consideration of their size and shape. Nevertheless, the Stokes-Einstein equation has provided the foundation for several useful semiempirical equations.

Most data for diffusion coefficients of liquids or gases (vapors) in solid foods come from solutions to the diffusion equation for standard geometries combined with experimental results, so they are "effective diffusion coefficients." The main problem is that all steps involved in the diffusion of a solute through a solid matrix are ignored and the process is characterized by a single coefficient that is highly dependent on experimental conditions, solid geometry, and microstructural arrangement. It is not surprising, then, that "diffusion coefficients" for solute extraction vary by several orders of magnitude, even for the same solute.

As explained before, effective or apparent diffusivities appear as a calculated value of D obtained from a transient diffusion experiment. Defining M as the total amount of solute that has diffused in (impregnation) or out (extraction) of a solid of regular geometry (slab, cylinder, or sphere) at any time and M_∞ as the amount transferred after equilibrium is reached, the ratio M/M_∞ may be calculated by integrating Fick's second law under appropriate boundary conditions. For a slab of thickness L when $1 - M/M_\infty$ is plotted against t, the slope is $-\pi^2 D_{app}/4L^2$ (the expression changes for other geometries) from which a value of D_{app} can be determined. The term "apparent" confirms that we do not know the exact mechanism of transport, which in most cases may be complex.

C. Diffusion Through the Solid Matrix

It should be evident from the previous analysis that microstructure influences molecular diffusion through its effect on the diffusion coefficient. Solute diffusivities can be defined in the liquid phase (D_L) or in the wet solid (D_S), and expressions for Fick's laws can be written accordingly. Differences between D_L and D_S can be attributed to factors such as membrane resistance, complexity of the diffusion path, sorption of the solute by the inert solid, etc. If all of these factors were accounted for, D_S could be related to D_L by an expression of the form:

$$D_S = F_m \times D_L \tag{6}$$

where F_m is a correction factor including all phenomena related to microstructure. Schwartzberg and Chao (7) have reviewed extensively the subject of solute diffusivities in foods. D_L values for various food solutes at infinite dilution in water at 25°C vary from 5.4×10^{-6} for sucrose to $1–7 \times 10^{-7}$ cm^2/s for some proteins. Selected D_S values listed in the literature where microstructural effects appear important are presented in Table 1. Extraction experiments from which these data were obtained do not lead to easy determination of a single, constant diffusion coefficient. Typical curves for hexane extraction of oil from soybean grits and flakes of different particle size and a theoretical curve are shown in Fig. 2 (12). The slope of the curves becomes less steep as extraction proceeds, meaning a decrease in the value of D_S so that usually an initial as well as a final diffusion coefficient has to be determined. The initial D_S may be influenced by the previously mentioned release of surface solute (washing); thus, it is not truly

Table 1 Diffusion Coefficients in Foods and Reference Values

Food material	Solute	Solvent	Temp. (°C)	$D_{AB} \times 10^6$ cm^2/s
Dilute solution	Sucrose	Water	25	5.4
Sugar cane (across grain)	Sucrose	Water	75	5.1
Sugar cane (with grain)	Sucrose	Water	75	3.0
Sugar beets	Sucrose	Water	24	1.6–2.5
Gelatin gel	Sucrose	Water	5	0.1–0.2
Dilute solution	NaCl	Water	25	16.1
Pickled cucumbers	NaCl	Water	25	5.3–11.0
Dilute solution	Lactose	Water	25	4.9
Small curds	Lactose	Water	25	3.0
Peanut slices	Oil	Hexane	25	0.007
Tungseed slices	Oil	Hexane	30	0.006
Dry solid matrix	Glyceride	—	50	5×10^{-4}

Source: Ref. 1.

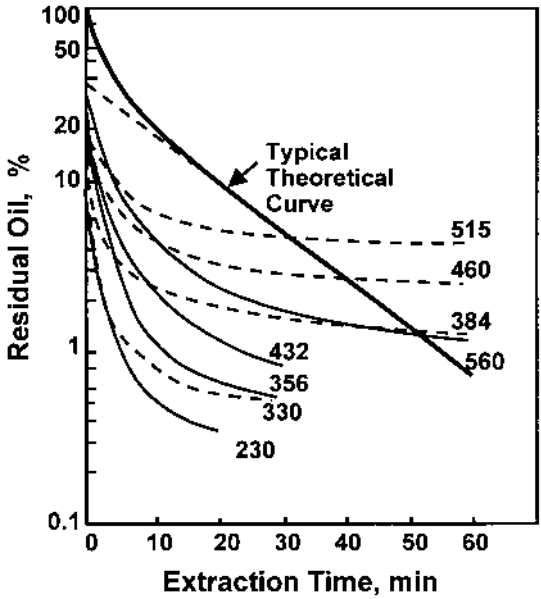

Figure 2 Kinetics of oil extraction from soybean flakes (------) and ground particles (————) and theoretical behavior. Numbers on curves are the thickness of flakes or particle size (in microns).

representative of diffusion of solute inside the solid. Consequently, data on solid diffusivities listed in Table 1 should be analyzed with caution, always referring to the original work if further conclusions are to be inferred.

D_L values from the literature and diffusivities calculated for extraction of the same component may be used to determine the order of magnitude of the correction factor F_m in Eq. (6). The D_L of caffeine in water is 6.9×10^{-6} cm^2/s whereas the diffusivity of coffee solubles during extraction from grinds is of the order of 1.1×10^{-6} cm^2/s (13). In sucrose extraction from beets the calculated diffusivities are one-half to one-third the D_L at the same temperature. Diffusivities of pure linoleic and oleic acid in hexane are 3.6×10^{-7} and 2.6×10^{-7} cm^2/s, respectively, while inside the seed they are reduced to $2.6–6.2 \times 10^{-8}$ cm^2/s (14). Hence, the correction factor in Eq. (6) appears to be of the order of 0.1–0.9 for small solutes, with higher values occurring when membranes have been denatured, as in sugar beet processing.

For macromolecules F_m is obviously larger. In fact, Schwartzberg and Chao (7) report that solutes exceeding a molecular weight of 2000 cannot diffuse into intact cells of coffee grounds. The reduction of the diffusion coefficient

for zein (corn protein) in dilute solution and inside the endosperm is about 1000-fold (15).

Sorption of solvent and/or solutes by the solid also retards diffusion. Microstructural entrapment seems to play a role at least as important as physicochemical sorption. Lignocellulosic materials are known to sorb water that is no longer available as solvent, particularly if ground into a fine powder. Sorption is critical when organic solvents must be removed from spent solids after extraction, in an operation known as desolventizing. Residual hexane left in rapeseed meals concentrates preferentially in the hulls, dissolved in the residual oil, entrapped inside thick-walled cells (16), or simply adsorbed. In this latter case, internal diffusion coefficients for hexane during adsorption into the solid matrix are very small (about 10^{-10} cm^2/s) and increase with hexane content, probably due to swelling of the structure.

IV. THE MICROSTRUCTURAL APPROACH

A. Simple Correction Factors

On examination of Eq. (3) and data previously presented it can be concluded that the influence of food microstructure on extraction rate is predominantly by its effect on the diffusion coefficient. Chemical engineers use the effective (or apparent) diffusion coefficient D_{eff} when dealing with impermeable porous solids with fluid-filled pores:

$$D_{eff} = D\frac{\varepsilon}{\tau} \tag{7}$$

where D is the diffusion coefficient of the solute in the fluid filling the pores, ε is the void fraction or porosity of the solid, and τ is the tortuosity of the pores, which attempts to account for the longer distance traversed by the solute along a sinuous path. Porosity may be very low in potato tissue (~2%) or high as in apples (~20%). For solid materials used in chemical engineering (adsorbents, porous catalysts) tortuosity varies between 2–6, and porosity between 0.3–0.8, thus D_{eff} may be 6 to 15 times lower than D.

When the size of the pore and the solute are of comparable magnitude (e.g., in some membranes), Eq. (7) is corrected by a factor λ that depends on the ratio of solute radius to pore radius. The restricted diffusion of spherical molecules within cylindrical pores (D_p) is usually modeled by the so-called Renkin equation (17):

$$D_p = D(1 - \lambda)^2 f(\lambda) \tag{8}$$

The squared term of the equation is a partition coefficient and accounts for steric hindrance at the pore entrance. The factor $f(\lambda)$ is a polynomial function

of λ and corrects for the friction between the diffusing molecule and the walls of the pore.

The previous results may be expressed in a more general form. For a two-phase composite where spherical particles of a material 1 are dispersed in a continuous phase 2, an effective diffusion coefficient may be obtained from the expression:

$$\frac{D_{\text{eff}} - D_1}{D_{\text{eff}} + 2D_1} = \phi\left(\frac{D_2 - D_1}{D_2 + 2D_1}\right) \tag{9}$$

where D_1 is the diffusion coefficient through the interstitial pores and D_2 is the diffusion coefficient through the particles.

So far we have assumed that pores are quite large. When the size of pores is of the order of magnitude of the distance between molecular collisions, Fick's laws no longer applies and the so-called Knudsen diffusion takes place in which molecules collide with the pore walls. We leave this section with the impression that a much better work in using Fick's laws could be made to predict extraction rates if we had an idea of the microstructural architecture of a solid food particle. Microscopy can assist in developing such structural models and in finding parameters such as tortuosity, porosity, and pore size.

B. Introducing Architectural Effects

Other correction factors where the diffusivity is corrected taking into account the architecture of the structure have been discussed by Cussler (3). A flake with uniformly distributed platelets impermeable to the solute, parallel or perpendicular to the diffusing stream where the volume fraction of the platelets is ϕ_F and their aspect ratio is α, results in an effective diffusivity given by the expression:

$$\frac{D_{\text{eff}}}{D} = \left(\frac{1}{1 + \alpha^2\phi_F^2/(1 - \phi_F)}\right) \tag{10}$$

A plot of D_{eff}/D vs. ϕ_F having α (long dimension divided by short dimension of platelets) as parameter is shown in Fig. 3.

When platelets are arranged parallel to the diffusion (segmented line), tortuosity is 1 and the effective diffusivity varies linearly with ϕ_F, underscoring the unidirectional nature of the diffusion. When platelets are arranged perpendicular to the diffusion D_{eff}/D depends strongly on α and a nonlinear dependence on ϕ_F is evident. For a constant value of α, D_{eff}/D becomes smaller as ϕ_F increases. It is also interesting to note that when α is very large, say $\alpha = 30$, even at low values of ϕ_F the ratio D_{eff}/D can become very small. Thus, this model shows an important effect of microstructure and architecture on the rate of trans-

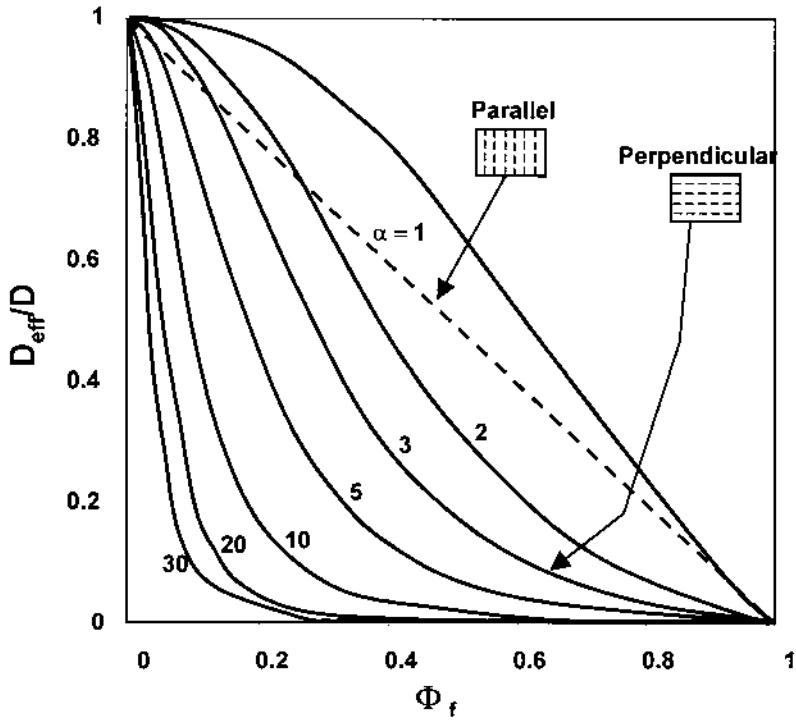

Figure 3 Curves showing the correlation between D_{eff}/D and volume fraction ϕ_F of impermeable platelets in a slab (ϕ_F) for different aspect ratios α of platelets. The effective diffusion coefficient varies sharply with ϕ_F when platelets are placed perpendicular to the diffusional flow.

fer of solute. However, it does not consider the possibility of nonuniform spatial distribution of the impermeable elements.

Another model that considers the situation of impermeable spheres occupying a volume fraction ϕ_S and uniformly distributed within the matrix giving rise to the expression of D_{eff}/D given by Cussler (3) is:

$$\frac{D_{eff}}{D} + \left[\frac{2(1-\phi_s)}{2+\phi_s}\right] \tag{11}$$

Evidently the size and distribution of the spheres is not considered in the model. In summary, although some expressions like (10) and (11) are available for

biphasic systems with uniformly distributed elements, they do not account for nonuniform architectural arrangements.

V. MATHEMATICAL MODEL FOR EXTRACTION FROM A TWO-DIMENSIONAL MATRIX

Fick's first law for the steady state and second law for the transient or unsteady state in two dimensions of a homogeneous and isotropic media are described by the following equations:

$$J = -D\left(\frac{\partial C}{\partial X} + \frac{\partial C}{\partial Y}\right) \tag{12}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X}\left(D\frac{\partial C}{\partial X}\right) + \frac{\partial}{\partial Y}\left(D\frac{\partial C}{\partial Y}\right) \tag{13}$$

Applying the precedent equations to a structure with two different phases A and B, continuity of mass flow must be observed at every boundary between the phases. Crank (6) proposed a discrete form (finite difference) for the unidirectional diffusional case of a two-phase compound:

$$\frac{1}{2}\{\Delta X_A + \Delta X_B\}\frac{C_{(i,n+1)} - C_{(i,n)}}{\Delta t} = \frac{D_B}{\Delta X_B}(C_{(i+1,n)} - C_{(i,n)}) - \frac{D_A}{\Delta X_A}(C_{(i,n)} - C_{(i-1,n)}) \tag{14}$$

where i is the position of the element or node and n the iteration index. Based on this equation and applying explicit finite difference discretization to the Fick's second law in two dimensions using $\Delta X = \Delta Y = \Delta L$ while taking into account the continuity between phases, equal distance increment in the phases (i.e., $\Delta X_A = \Delta X_B = \Delta X$) and constant diffusion coefficients at each point throughout the extraction process, the following expression is obtained:

$$\begin{aligned} C_{(i,j,n+1)} = C_{(i,j,n)} = \frac{\Delta t}{(\Delta L)^2} \times [&D_{(i+1,j,n)}(C_{(i+1,j,n)} - C_{(i,j,n)}) \\ &- D_{(i-1,j,n)}(C_{(i,j,n)} - C_{(i-1,j,n)}) \\ &+ D_{(i,j+1,n)}(C_{(i,j+1,n)} - C_{(i,j,n)}) \\ &- D_{i,j-1,n)}(C_{(i,j,n)} - C_{(i,j-1,n)})] \end{aligned} \tag{15}$$

which is based on the application of the Schmidt method of the finite difference approach to heterogeneous compounds (e.g., different diffusion coefficients at each specific spatial locations) as presented in Crank (6). The subindex (i,j,n) refers to the position (i,j) of an element in the matrix at the iteration step n, equivalent to a time $t = n \times \Delta t$.

Modeling extraction with Eq. (15) starts by defining a matrix of $M \times N$ elements representing the object being extracted bidirectionally and introducing the specific architectural elements in the form of pores, walls, or platelets. Geometrical arrangements of the structure are modeled assuming different diffusion coefficients for each phase or element.

The boundary condition for the model assumed that the object was surrounded by pure solvent at all times (bulk concentration of solute in solvent equal to zero or infinite volume of solvent). This is equivalent to saying that the internal resistance is controlling or the Biot number for mass transfer is infinite. The concentration at each point of the matrix and the corresponding diffusion coefficients at time 0 were the initial conditions for this model. Extraction was simulated for different architectures of the matrix. Extraction curves are semilog plots depicting variations in time of the ratio of the instant mass of solute remaining in the solid to the total initial mass (q/q_0).

A. Modeling Extraction from Cellular Material

An example of the previous approach has been applied to extraction from a cellular structure modified by various pretreatments (18). Figure 4 shows the architectural arrangements associated with four pretreatments. The basic structure considers that all cells are intact and completely surrounded by a thick cell wall (A). Enzymatic treatment with a cocktail of cell wall–degrading enzymes may pierce the wall of outer cells at different places, leaving openings that connect the cytoplasm directly to the solvent (B). A third situation may be that induced by blanching, resulting in degradation of the cell wall membrane (and possibly the cell wall itself), diminishing the overall internal resistance for transport of solute as most cells become interconnected (C). Another conceivable architecture is that of a totally connected cytoplasm and broken outer cells exposed to the solvent due to extensive physical destruction of the tissue (D). In all cases, the proportion of cell wall material to cytoplasm is the same.

The simulation used data obtained from Schwartzberg and Chao (7) for infusion of salt (NaCl) in pickled cucumbers and water. Data for the cell wall complex were $D_{cw} = 53\ \mu m^2/s$ and $C_{cw} = 1$ g/L, and for the cytoplasm $D = 219\ \mu m^2/s$ and $C = 3$ g/L. ΔL was 20 μm and Δt was 0.2 s. The overall size of the matrix was 380×380 μm in a grid of 19×19 elements.

The resulting extraction curves for the simulations are presented in Fig. 5. The fastest extraction rate corresponded to pieces having complete breakage of the cell wall and a layer of cytoplasm exposed directly to the solvent. Washing of solute from the outermost layers removes 20% of the solute almost instantly. Since it was assumed that the cell wall complex also contained solute and had a finite diffusivity, even the arrangement containing intact external cells showed some extraction. However, if the cell wall complex had been assumed

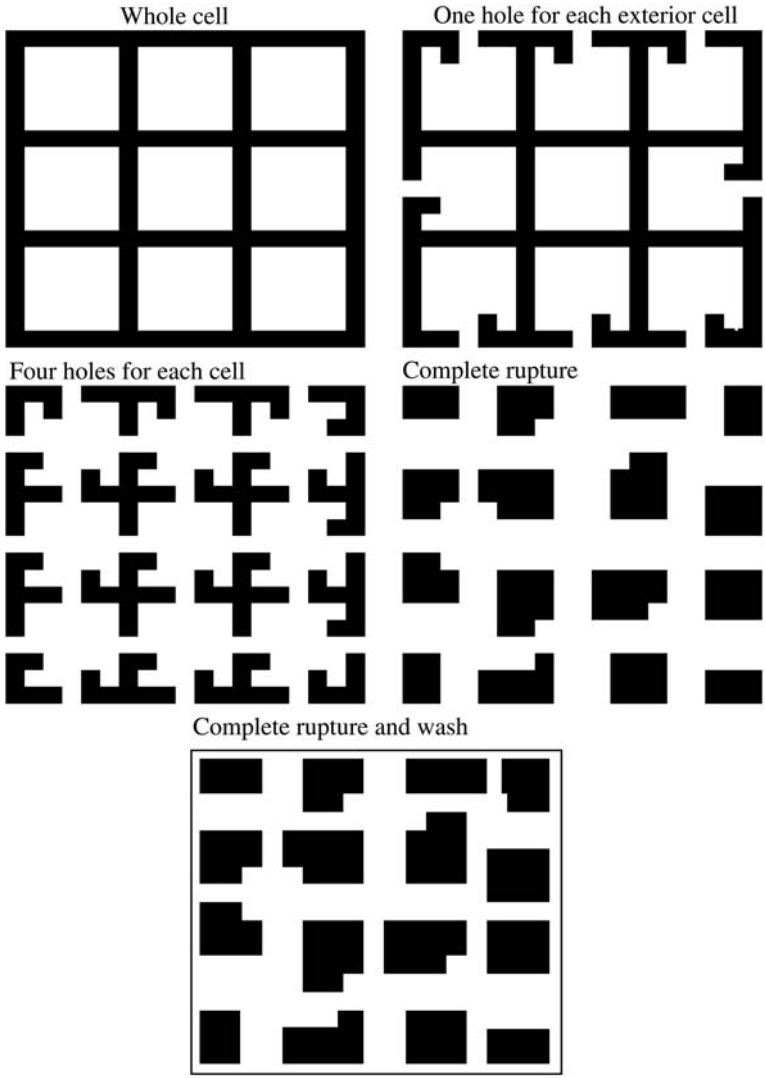

Figure 4 Architectural arrangement of cells of pickled cucumbers subject to different treatments (theoretical).

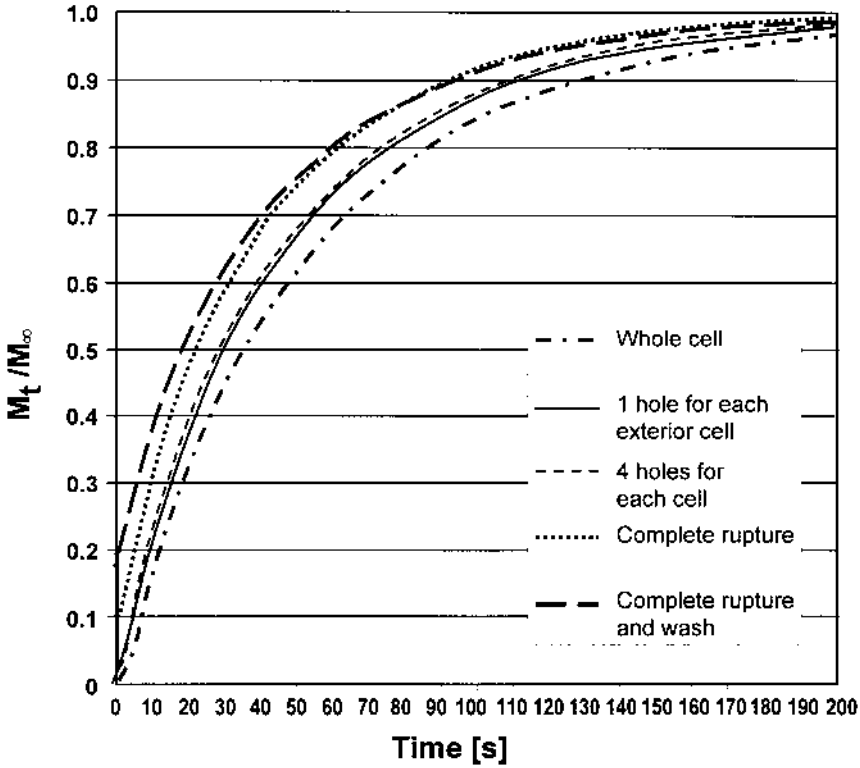

Figure 5 Resulting curves of the extent of extraction vs. time simulating salt diffusion in pickles with and without pretreatments to modify the microstructure.

impermeable, extraction would have been zero in this case for all times. Actual extraction of triglycerides from oilseeds having intact cells by organic solvents is extremely slow (1).

The fastest extraction is achieved in the situation of full rupture of the cell complex, and the slowest for intact cells. In the latter case, the curves start from zero concentration (no washing) and the time to achieve 90% removal of solute is 40% longer than in the previous case. Maintenance of intact cell membranes may be beneficial to selectively extract small solutes from the cytoplasm keeping large molecules and debris within the piece to facilitate downstream separation and purification (as in sucrose extraction from sugar beets).

The use of microscopy techniques to correlate the state of the microstructure and its effect on extraction is presented in Aguilera and García (19) for aqueous extraction of protein from lupins; Aguilera and Lusas (20) to assess the

extractability of oil from flakes, grits, and extrudates of high-oil corn using hexane; Fan et al. (21) for the extraction of peanut oil; and Rastogi and Niranjan (22) for osmotic dehydration of pineapple tissue, among others. With the advent of nonintrusive microscopy techniques and real-time video microscopy, structural features prior and during extraction may be observed and different architectural arrangements (presence of elements, phase ratios, geometrical parameters, etc.) characterized by image processing and analysis. Combination of microstructural information, better data on diffusivities of individual phases, and advanced computer techniques should lead to a more fundamental approach to the study of mass transfer phenomena in foods and other biological materials (23).

VI. USE OF MASS TRANSFER COEFFICIENTS

The problem with Eq. (1) is that the distance over which concentration changes occur (δ) must be known to determine the gradient. This is not easy task for processes that occur inside process equipment. Moreover, we are in the presence of interfacial mass transfer or transfer between two different phases (solid and liquid). Chemical engineers prefer to study interfacial mass transfer using mass transfer coefficients (individual or overall), which multiplied by a measurable driving force give the rate of mass transfer. Thus, the distance problem becomes hidden in the coefficient, which also contains implicitly the diffusivity. A practical expression for the rate of solute extraction takes the form:

$$\text{Rate} = \text{mass transfer coefficient} \times \text{driving force} \tag{16}$$

The driving force in extraction should be the difference between the chemical activity of the solute inside the solid and that in the bulk of the solution. For practical reasons, the rate is expressed as the product of the difference between an external solute concentration (c_{out}) and that in the interior of the solid (c_{in}), and a mass transfer coefficient based on concentration. For this difference to be meaningful it must be expressed in the same base; thus, c_{in} is usually taken as that concentration of solute in the liquid phase that would be in equilibrium with the concentration inside the solid c^*. Then the driving force for extraction becomes $(c^* - c_s)$, where c_s could be measured in the bulk of the solution and Eq. (16) takes the form:

$$N_1 = K_c(c^* - c_s) \tag{17}$$

This simple equation states that the rate of extraction N_1 depends on the difference in a thermodynamic variable (expressed as concentration) and a global mass transfer coefficient K_c that includes all physical and microstructural parameters of the process. If the interfacial area for transfer (a) is unknown, the coeffi-

cient becomes $K_c a$. If each phase is taken separately, individual mass transfer coefficients k_i can be defined for transport between the interface and the bulk of the respective phase [see Cussler (3) for details].

If a solid is modeled as series of structures (i.e., a plant cell with protoplasm, plasmalemma, cell walls, etc.), the observed global mass transfer coefficient may be related to individual mass transfer coefficients inside each of the structures as a sum of resistances in series:

$$\frac{1}{K_c} = \Sigma \frac{1}{k_{ci}} \tag{18}$$

and a rate-limiting step having the highest resistance (or the slowest flow) may be identified. This structure then controls the mass transfer process and efforts should be made to increase the rate within this phase. This approach can also be used when studying extraction as a series of sequential steps as shown in Fig. 1.

Theoretically, there is a relationship between D and K_c (e.g., K_c is proportional to D/δ, where δ is a thin film over which diffusion occurs) and, as previously concluded, study of the influence of microstructure on extraction rate is reduced to the analysis of its effects on the mass transfer coefficient. Mass transfer coefficients are often correlated to dimensionless numbers, allowing predictions to be made for other experimental conditions. Dimensionless numbers are ratios of transport parameters and have physical meaning. For example, the most relevant of these numbers for solid–liquid extraction is the Sherwood number (N_{Sh}), which is the ratio of mass transfer velocity (kL) to diffusion velocity (D). A large N_{Sh} in solvent extraction means that the controlling step is diffusion inside the solid, and reduction of particle size or restructuring into a porous material may prove effective in speeding extraction. N_{Sh} is in turn related to several other dimensionless numbers, e.g., to the Schmidt number representing flow effects (momentum transfer) by the expression:

$$N_{Sh} = \frac{k_c L}{D} = f\left(\frac{\nu}{D}\right)^{1/3} \tag{19}$$

where ν is the kinematic viscosity.

VII. CONCLUSIONS

Food engineers can make a significant contribution to the study of extraction or leaching by introducing the microstructural variable into the problem. A good architectural description of the solid being extracted together with fundamental data of diffusion coefficients in different structures or phases can be combined with modern computational methods to predict extraction rates from food solids.

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NOMENCLATURE

a	interfacial area of transfer (m^2/m^3)
A	area for diffusion (m^2)
B_n	parameter in eq. 4
c	molar concentration ($moles/m^3$)
C	concentration (g/L)
D	diffusion coefficient or diffusivity (m^2/s)
D_{eff} , D_{app}	effective or apparent diffusion coefficient (m^2/s)
E/R	extract-to-solid volume ratio
F_m	correction factor in eq. 6
J	mass flux (moles/s)
j	flux ($moles/s\ m^2$)
k	Boltzmann constant
k_c	liquid phase mass transfer coefficient
K_c	global mass transfer coefficient
L	characteristic length or slab thickness (m)
M	total amount of solute extracted (g)
N_0	Avogadro's number
N_{Sh}	Sherwood number
q	mass of solute in the solid (g)
q_n	parameter in eq. 4
R	gas constant
r	direction of flow or position inside the solid
t	time (s)
T	absolute temperature (K)
X	extent of extraction of solute (dimensionless)

Symbols

α	aspect ratio (length/width)
α	m.E/R
δ	film thickness
ε	porosity or void fraction
ϕ	volume fraction of platelets or spheres
η	viscosity
τ	tortuosity

λ	correction factor
ν	index (1 for infinite slabs, 2 for infinite cylinders, 3 for spheres)
υ	kinematic viscosity

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