Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Extraction of Organic Solutes from Vegetable Materials. Extraction of Pyrethrins from Chrysanthemum cinerariae folium

G. Casamatta[a]; C. Gourdon[a]; C. Haunold[a]; L. Boyadzhiev[b]
[a] ECOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS DE GÉNIE CHIMIQUE TOULOUSE, CEDEX, FRANCE [b] INSTITUTE OF CHEMICAL ENGINEERING BULGARIAN ACADEMY OF SCIENCES, SOFIA, BULGARIA

To cite this Article Casamatta, G. , Gourdon, C. , Haunold, C. and Boyadzhiev, L.(1995) 'Extraction of Organic Solutes from Vegetable Materials. Extraction of Pyrethrins from Chrysanthemum cinerariae folium', Separation Science and Technology, 30: 14, 2849 — 2864
To link to this Article: DOI: 10.1080/01496399508013718
URL: http://dx.doi.org/10.1080/01496399508013718

SEPARATION SCIENCE AND TECHNOLOGY, **30**(14), pp. 2849–2864, 1995

Extraction of Organic Solutes from Vegetable Materials. Extraction of Pyrethrins from *Chrysanthemum cinerariae folium*

G. CASAMATTA, C. GOURDON, and C. HAUNOLD
ECOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS DE GÉNIE CHIMIQUE
TOULOUSE, 31078 CEDEX, FRANCE

L. BOYADZHIEV
INSTITUTE OF CHEMICAL ENGINEERING
BULGARIAN ACADEMY OF SCIENCES
SOFIA 1113, BULGARIA

ABSTRACT

In order to elucidate the extraction kinetics of valuable organic substances from dried vegetable materials, extraction of pyrethrins from ground pyrethrum blossoms was taken as an example and studied at various conditions. It was shown that the apparent diffusivity is a nonmonotonous function of the solute content in the solid phase. Due to the superposition of several phenomena, its value passes through a maximum and may change a hundred or even more times. Simple laboratory batch experiments and numerical solution of the appropriate extraction models are necessary prerequisites for successful design of large-scale extraction processes of vegetable raw materials.

INTRODUCTION

Solid–liquid extraction is one of the most widespread unit operations in pharmaceutical, food, and other chemical and parachemical industries. A large spectrum of valuable substances are extracted from natural raw materials of vegetable origin. Among them, pyrethrins, extracted from pyrethrum blossoms (*Chrysanthemum cinerariae folium*), are of special interests due to their ecologically acceptable insecticide properties and almost total nontoxicity with respect to warm-blooded animals.

Dried and ground pyrethrum blossoms, containing between 0.7 and 3.00% pyrethrins, are usually extracted by hexane, petroleum ether, ethylene dichloride, carbon dioxide, or other solvents. The esters with insecticide properties are separated from the other extracted inactive species as waxes, fatty acids, resinoids, etc. by subsequent extraction with ethanol or methanol, followed by decolorization on active carbon. Finally, sinergists such as pyperonyl butoxide are added to inhibit the enzymatic detoxification of pyrethrins in insect bodies (1–4).

Since pyrethrins, like many other large natural molecules, are unstable in contact with air oxygen, some reagents, heat, and light (5, 6), the procedures applied and the extraction kinetics become very important for the process economics and product quality.

The purpose of this work is to elucidate the intraparticle diffusional transport in ground vegetable materials, as well as applying an adequate process modeling to derive reliable data for large-scale extraction of pyrethrins from dried pyrethrum blossoms.

EXTRACTION MECHANISM

Diffusion inside solid particles is described by Fick's second differential equation:

$$\frac{\partial X}{\partial t} = -D_x \nabla^2 X \tag{1}$$

This equation is also valid for solute diffusion in rigid porous bodies on the condition that their structure is considered quasihomogeneous and macroscopically isotropic (7, 8). In this case the coefficient of molecular diffusion of the solute D_x is replaced by the apparent diffusivity D_{xa}, which incorporates porosity ϕ and the so-called tortuosity factor τ, the subject of further discussion in this paper. For spherical particles (note that blossom stamens are the richest in oil particles), Eq. (1) can be written as

$$\frac{\partial X}{\partial t} = -D_x\left[\frac{\partial^2 X}{\partial r^2} + \frac{2}{r}\frac{\partial X}{\partial r}\right] \tag{2}$$

The initial condition is

$$X(r, t) = X_{in} = \text{constant} \tag{3}$$

One of the two standard boundary conditions,

$$\left|\frac{\partial X}{\partial r}\right|_{r=0} = 0 \tag{4}$$

stems from particle symmetry; the other, at the solid–liquid interface, depends on the type of process applied. When the ratio between the volumes of the outside solvent V_Y and that of the pores in the solid phase ϕV_X is very high or a fast chemical transformation of the solute takes place in the external medium, and therefore the continuous phase mass transfer resistance can be neglected, one can write

$$|X|_{r=R} = Y/\phi = \text{constant} \tag{5}$$

The meaning of this simple relation is that the liquid in the open pores at the interface has the same concentration of the solute as the continuous phase surrounding the particle, if some special secondary phenomena are not considered.

In practice, however, due to economic reasons, the volume ratio $V_Y/\phi V_X$ is not large enough to neglect the increase of solute concentration in the extract phase. Moreover, the local mass transfer coefficient in this phase, k_Y, cannot be considered to be infinite. In some processes, especially when the swarm of fine solid particles is not intensively agitated, its contribution may become rather important. In this case the boundary condition follows from the equality of mass fluxes at both sides of the particle interface; the first one—a solute supply to the interface—and the second one—its transportation into the solvent bulk—or:

$$D_X \left|\frac{\partial X}{\partial r}\right|_{r=R} S = -k_Y S(Y_s - Y) \tag{6}$$

Replacing Y_s, as mentioned above, with $\phi|X|_{r=R}$ and introducing the dimensionless radius $\eta = r/R$, Eq. (5) becomes

$$D_X \left|\frac{\partial X}{\partial \eta}\right|_{\eta=1} = -\text{Bi}(\phi X_s - Y) \tag{7}$$

where $\text{Bi} = k_Y R/D_X$ is the number of Biot.

The solute concentration in the bulk of the solvent Y is a time function, and for a closed mass transfer system it is given by the solute mass balance

$$Y = Y_0 + \beta(X_{in} - \bar{X}) \tag{8}$$

where $\beta = \phi V_X/V_Y$ and $\bar{X}$ = the mean solute concentration in the particle.

Therefore,

$$D_X \left(\frac{\partial X}{\partial \eta}\right)_{\eta=1} = -\text{Bi}[(\phi X_s - Y_{in}) - \beta(X_{in} - \bar{X})] \tag{9}$$

When $\beta \rightarrow 0$, Eq. (9) reduces to Eq. (7). Also, when $Bi \rightarrow \infty$, the boundary condition, Eq. (7) reduces to Eq. (5) since at $Bi = \infty$, $(\partial X/\partial \eta)_{\eta=1}$ cannot be infinite too.

Analytical solutions of Eq. (2) at various initial and boundary conditions are possible, assuming that solute diffusivity D_x is a constant. Since the classical work of Newman in 1931 (9), studying the process of particle drying, many solutions have been published, some of them related to solid–liquid extraction (10–13).

In the general case, applying boundary condition (9), the solution of Eq. (2) is (8):

$$\frac{X_{in} - \overline{X}}{X_{in} - Y^*} = \frac{1}{1 + \beta} - \sum_{1}^{\infty} \frac{6 \exp(-\alpha_n^2 D_x t/R^2)}{(3\beta - \alpha_n^2/Bi) + \alpha_n^2(1 - 1/Bi) + 9\alpha_n} \tag{10}$$

where α_n ($n = 1, 2, \ldots, \infty$) are the roots of the equation

$$\text{ctg}(\alpha) = \frac{1}{\alpha} + \frac{1}{(3\beta/\alpha - \alpha/Bi)} \tag{11}$$

When the external liquid is perfectly mixed ($Bi \rightarrow \infty$), Eqs. (10) and (11) reduce to

$$\frac{X_{in} - \overline{X}}{X_{in} - Y^*} = \frac{1}{1 + \beta} - \sum_{1}^{\infty} \frac{\exp(-\alpha_n^2 D_x t/R^2)}{3(1 + \beta)/2 + \alpha_n^2/6} \tag{12}$$

and

$$\text{ctg}(\alpha) = \frac{1}{\alpha} + \frac{\alpha}{3\beta} \tag{13}$$

respectively.

Further simplification of the model is possible if the solute concentration in the continuous phase is somehow kept constant (Y = constant) or an instantaneous chemical transformation of the extracted solute takes place in a perfectly mixed continuous phase ($Y = 0$). In this case the extraction efficiency E is given by the classical relationship (9)

$$\frac{X_{in} - \overline{X}}{X_{in} - Y^*} = 1 - \sum_{1}^{\infty} \frac{6}{\alpha_n^2} \exp(-\alpha_n^2 D_x t/R^2) \tag{14}$$

where $\alpha_n = \pi n$.

All above described solutions are valid for a single spherical particle with a uniform, isotropic porous structure or for a swarm of such particles and on the condition that the solute diffusivity inside the solids is a constant. In the extraction practice, however, these prerequisites are far from

the real cases. This explains why the experimentally obtained functions $Y(t)$ do not fit the theoretical curves.

Since particles of different sizes are exhausted with different rates in systems of finite volume, the solute concentration in the smallest fractions may pass through a minimum while the concentration in the larger ones will decrease monotonously.

The problem of particle polydispersity can be easily solved when the boundary condition of Eq. (5) is valid and the size distribution function $p(R)$ is known. Then the average efficiency with respect to the whole dispersion will be expressed as

$$\bar{E}(t) = (\bar{\bar{X}} - Y^*)/(X_{in} - Y^*) = \int_{(R)} E(R, t)p(R)dR \qquad (15)$$

where $\bar{\bar{X}}$ is the mean solute concentration for all particles.

When other boundary conditions apply, such an approach is impossible and the model Eq. (2) must be replaced by a series of equations, each corresponding to one particle size group. An approximate solution, when boundary condition (8) applies, can be found elsewhere (11).

It should be noted, however, that all the described solutions are derived for the conditions that (a) D_{xa} is a constant, although generally it is not true, and (b) these solutions are represented by an infinite series, not suitable for rapid calculation, even by computer.

Solute diffusion inside a porous particle is a complex phenomenon. The particle pores are usually considered to be open and completely filled with a solution after a short period of initial impregnation. Since the observed rates of diffusion are much slower than the free diffusion rates of the solute in the same liquid and at the same conditions, as mentioned above, apart of the porosity ϕ, a tortuosity factor τ is applied to account for all other phenomena which hinder solute diffusion. Figure 1 gives an idea about the macroscopic obstacles originating from the diversity in the form and the structure of the vegetable tissue pores, but does not consider the complex anisotropic morphology, cell structure, adsorption, and other phenomena.

Most studies on the extraction kinetics of such materials, including this one, have shown that extraction efficiency data calculated using a single constant value for the tortuously factor τ or for the apparent diffusivity D_{xa} do not match the experimental results.

There are various approaches to overcome the discrepancy between the theoretical and the experimental results. According to one of these approaches, the diffusivity is assumed to be a decreasing time function (11, 12, 14–16), whose average value for the whole extraction period represents the mean apparent diffusivity D_{xa}. If D_{xa} is variable, an analytical

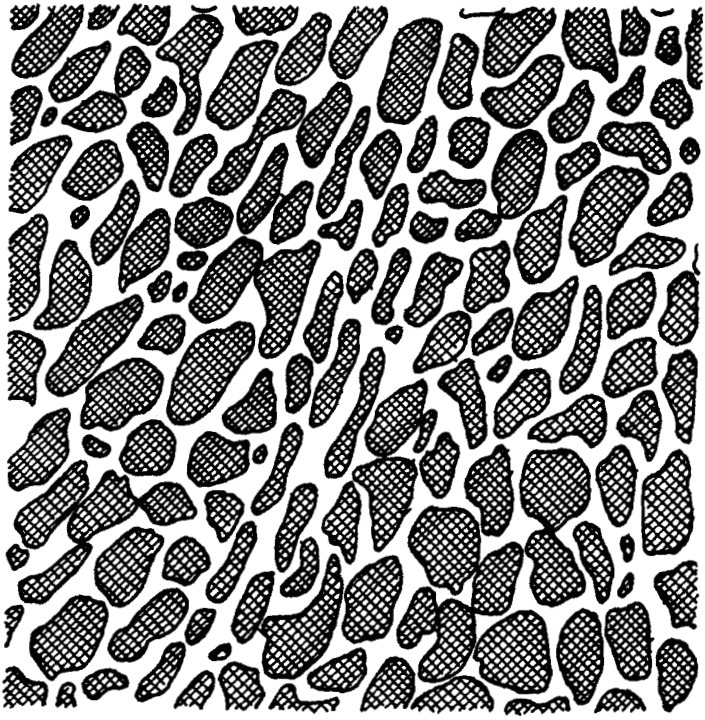

FIG. 1 Pore structure of vegetable tissues.

solution of Eq. (2) applying conditions (7) or (8) is impossible, except for some special functions for D_{xa} (11).

In another approach the real pores are replaced by a set of "ideal" pores with the same total volume ϕV_x, the same diameter, but with various lengths (8, 17). The diversity of pore lengths is represented by an experimental distribution function $\varphi(h)$ $(0 < h < \infty)$. Obviously, the length of some pores will exceed the size of the particle itself. This approach transforms the problem from the extraction of single particle or swarm of uniform particles into the extraction of a polydispersion particle population.

In this study we prefer to apply the first approach by expressing the apparent diffusivity of pyrethrins D_{xa} as a function of their local dimensionless concentration in the particles: $D_{xa} = \xi(\dot{X})$, where $\dot{X} = \overline{X}/X_{in}$, as proposed by Krasuk et al. (16). This seems quite reasonable because of the special structure of the vegetable tissues, where the capillary (pore) diameters vary from 10^{-9} m (the distance between the large linear cellu-

lose molecules) to 5×10^{-8} m (the mean distance between skeleton fibrils) or more. It should also be noted that in the case of large organic molecules, the capillary wall effect becomes very pronounced when the diameter ratio d_{mol}/d_{cap} is greater than 0.1 (18). Another important factor is solute distribution in the vegetable tissue. If it is predominantly concentrated inside the cells, the transfer across the cell membrane can be the rate-controlling step.

The variable and nonlinear character of the apparent diffusivity of the solute imposes the use of numerical techniques for solving the solid–liquid extraction problems, including evaluation of the model parameters. The latter, obtained through simple batch experiments and identification procedures, are indispensable in the design of large-scale extraction processes.

EXPERIMENTAL

Materials Used and Methods of Analysis

Dried blossoms of pyrethrum imported from Rwanda were used in the experiments. They were ground, homogenized, and several narrow fractions, in most cases 0.40–0.56 mm, were selected for the experiments. The initial content of the active insecticide components, namely the esters pyrethrin I and pyrethrin II, cinerin I and cinerin II, and jasmolin I and jasmolin II (the dry particles), obtained after 48 hours continuous extraction in a laboratory Soxhlet extractor, was found to be 1.25 wt%. The total extracted mass, however, also contained resins, waxes, and other substances soluble in the solvent.

Technical grade hexane (99% with $\rho = 670$ kg/m^3) was used as the solvent in all experiments.

A spectrophotometric method of analysis, proposed by Berkeley (19), was used to measure the concentration of pyrethrins. For this purpose, after solvent removal from the extract, the mass obtained was dissolved in absolute ethanol and the light absorbance of the latter solution was measured at 227 nm by means of a spectrophotometer. This UV analysis gives the total amount of the above-mentioned esters.

Preliminary tests proved that pyrethrin solutions in alcohol do not change their light absorbance value with time if they are kept in a cold and dark place.

Apparatus and Extraction Procedure

All experiments were carried out in a 1-L laboratory batch extractor made of glass, shown in Fig. 2. It is equipped with a magnetic stirring

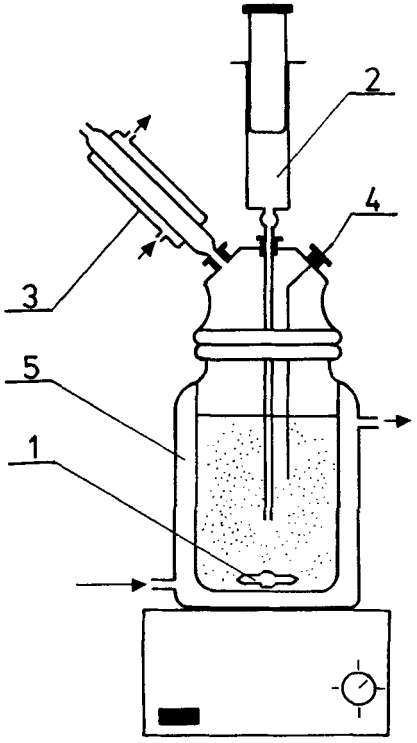

FIG. 2 Laboratory batch extractor. (1) Stirring magnetic bar. (2) Sampling probe. (3) Vapor condenser. (4) Temperature probe. (5) Water jacket.

bar (1), a sampling probe (2), a condenser for the solvent vapors (3), a thermometer (4), and a water jacket (5). In each run, 18 g dry particles of ground pyrethrum blossoms of a selected size were put into 450 mL hexane at the temperature of the experiment, and agitation was started. Periodically, filtered samples of the liquid were taken and the concentration of the pyrethrins was measured. At the end of each run, usually after 1 hour, the two phases were carefully separated and the weights and the volumes of the liquid and the solids were measured again. By taking into account the volume of the samples and comparing the phase volumes before and after the experiment, the new, expanded volume of the particles V_x was obtained.

Runs at various stirring speeds have shown that the mass transfer resistance of the external liquid film is completely negligible, and therefore

the process should be considered as a typical batch extraction with internal diffusion control.

To prove or to reject the hypotheses assumed above, the experiments were oriented toward the evaluation of the effect of two different, presumably independent process parameters: 1) the temperature, affecting mainly the rate of diffusion, and 2) the size of the particles, which does not modify the internal diffusional mechanism.

RESULTS AND DISCUSSION

Figures 3 and 4 show the experimental results obtained by varying the temperature and the particle size, respectively. In both figures the extraction efficiencies are expressed as time functions $E(t)$. The symbols represent the experimental data, while the continuous lines follow the numerical solutions.

Apart of the expected positive effect of the temperature and particle size reduction, note that 1 hour is not sufficient for complete removal of

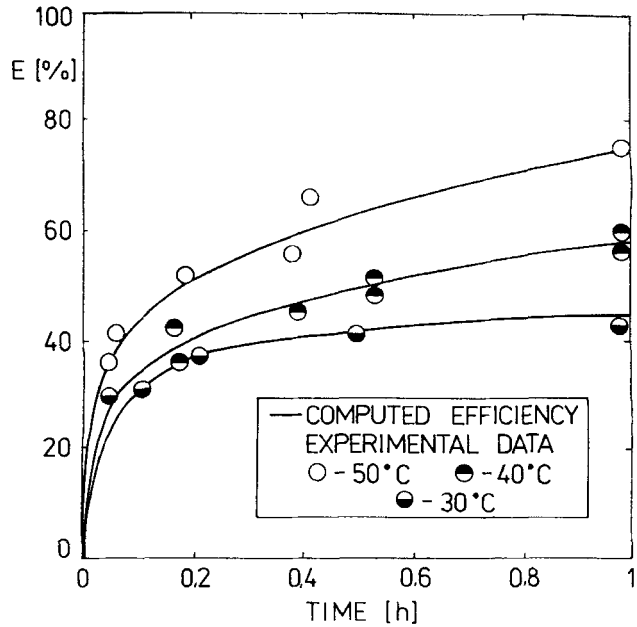

FIG. 3 Effect of temperature on extraction kinetics. Extraction efficiency (E) versus time at 30, 40, and 50°C for R = 0.025 cm.

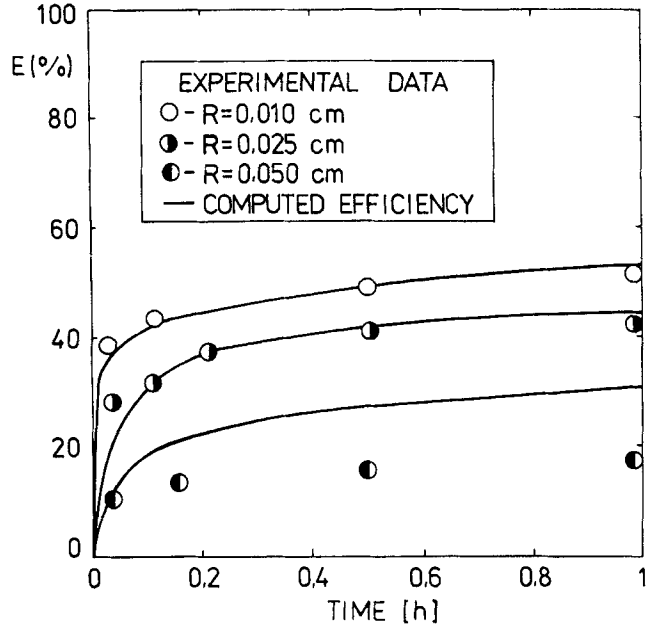

FIG. 4 Effect of particle size on extraction kinetics. Extraction efficiency (E) versus time for $R = 0.010$, $R = 0.025$, and $R = 0.050$ cm at 30°C.

pyrethrins, in spite of the very high extraction rate during the first period of the process. The reason is, as noted above, that the apparent coefficient of the molecular diffusion D_{xa} is not a constant but a function of the solute concentration in the particle, which decreases with exhaustion of the solid phase.

Moreover, long duration runs (Fig. 5) show that even a 30-hour continuous extraction is still not sufficient to reach the extraction equilibrium, e.g., to obtain equal solute concentrations in the pore solution and the external liquid.

The variable value of the apparent pyrethrin diffusivity, expressed as $D_{xa} = (X/X_{in})$, was evaluated for each case by a curve-fitting procedure by applying the batch extraction model, described by Eqs. (2), (3), (4), and (8). For this purpose, the Simplex optimization method of Nelder and Mead (20) incorporated in the dynamic process simulator TUTSIM (Meermann Automation) was used.

As stated above, the process of particle soaking with the surrounding liquid is usually very fast compared to the extraction process. This was

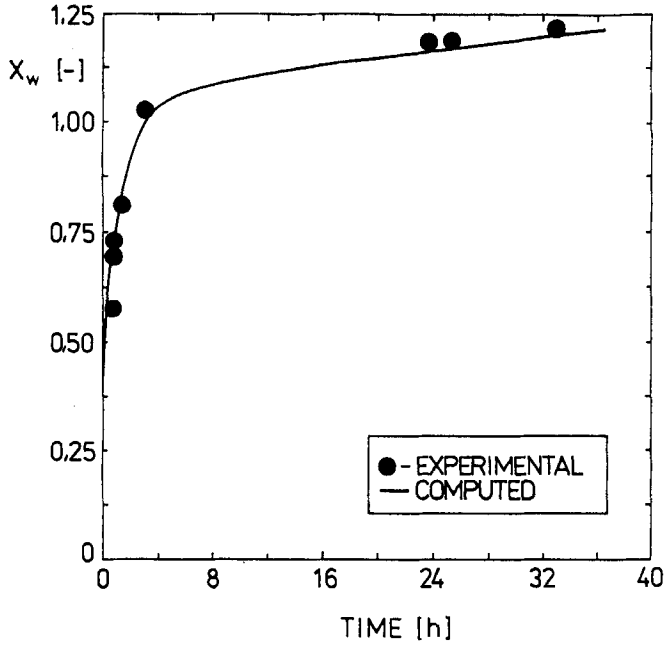

FIG. 5 Amount of extracted pyrethrins (X_w) versus time at 40°C, R = 0.025 cm.

found in all previous studies investigating this problem (8, 14, 21, 22). In the case studied, 5 to 10% of the initial solvent volume of 450 mL filled and expanded the particle pores in the first few minutes, dissolving all the soluble species (pyrethrins, fatty acids, waxes, etc.). During this period the initial volume, porosity, and diameter of the particles change drastically. These changes should be taken into account in the mass balance and extraction kinetics equations. Therefore, in the mathematical model, V_x, ϕ, and R denote values which correspond to a solid phase already impregnated. The relationships between the values of these characteristics for dry particles and for soaked particles are

$$V_x = V_{x,in} + \Delta V_x$$

$$R = R_{in}[V_x/(V_x + \Delta V_x)]^{1/3}$$

$$\Phi = \Phi_{in}(1 - \Delta V_x/V_x) + \Delta V_x/V_x$$

By applying the experimental procedure described above for dry particle samples of 18 mL swelled to more than twice the larger volume of the

solvent; the average experimental value for $V_x + \Delta V_Y$ was 53 mL. The dimensionless pore volume of the dry particle in their initial state was estimated to be 3.2%.

The results shown in Fig. 4 confirm the assumption that changes in particle size do not modify the mechanism of internal diffusion; there is a fairly good fit between the experimental results and the computed ones (changing only the value of R in the model) with exception of the curve corresponding to the largest, 1 mm fraction. This discrepancy can be explained by the fact that this fraction is not representative for the pyrethrin content in the plant; as mentioned before, the esters are concentrated in the blossom stamens, and hence fractions of 0.6 mm and lower are richer in solute and have a similar pyrethrin content.

The three curves in Fig. 6 demonstrate changes in the apparent diffusivity of the pyrethrins versus their average content in the particles, evaluated from the experimental data and obtained at 30, 40, and 50°C. During the initial period (the first 100-second period for two of them are shown in the figure), solute diffusion is hindered by the opposite flux of the solvent

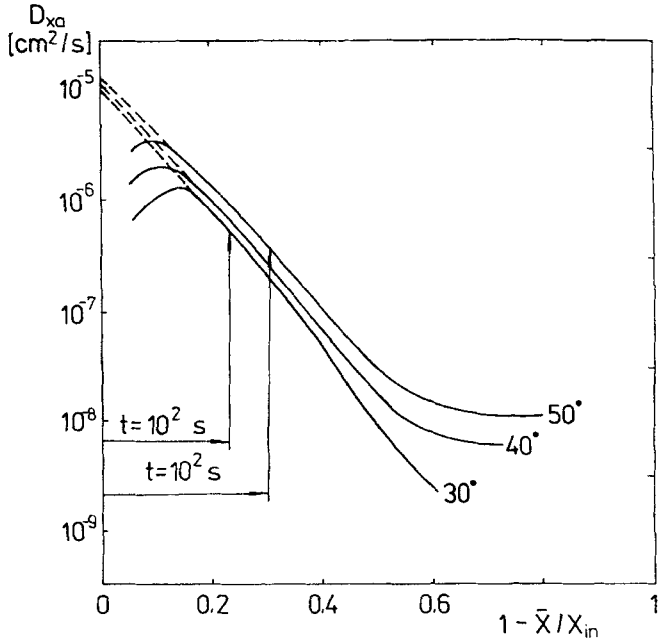

FIG. 6 Variation of D_{xa} versus solute content in the particles at 30, 40, and 50°C, R = 0.025 cm.

entering into the particle. In the second period the apparent diffusivity steadily drops more than hundred times and reaches the final, third period with its constant value, which can be attributed to transport across a semisolid barrier or to a desorption process since the observed temperature effect is very pronounced. Extrapolated values for D_{xa} at $t = 0$ presumably represent the "free" solute diffusivities D_x multiplied by the final porosities ϕ_{comp}. Free diffusivities found in this way are in the range of $D_x = 1.3 \times 10^{-5}$ to 1.6×10^{-5} cm^2/s. They are slightly higher than the $D_x = 1.06 \times 10^{-5}$ to 1.36×10^{-5} cm^2/s values calculated according the Wilke–Chang correlation with molar volumes as obtained by the Vetere group contribution method (23).

Some results obtained by other authors are similar in character. Variations of D_{xa} versus time for sunflower (24) and soybean (25) oil extraction with hexane are compared in Fig. 7 to our analogous results obtained at 30°C. The shift and the less pronounced form of the maxima are probably due to the interval-integration method used for D_{xa} evaluation in which

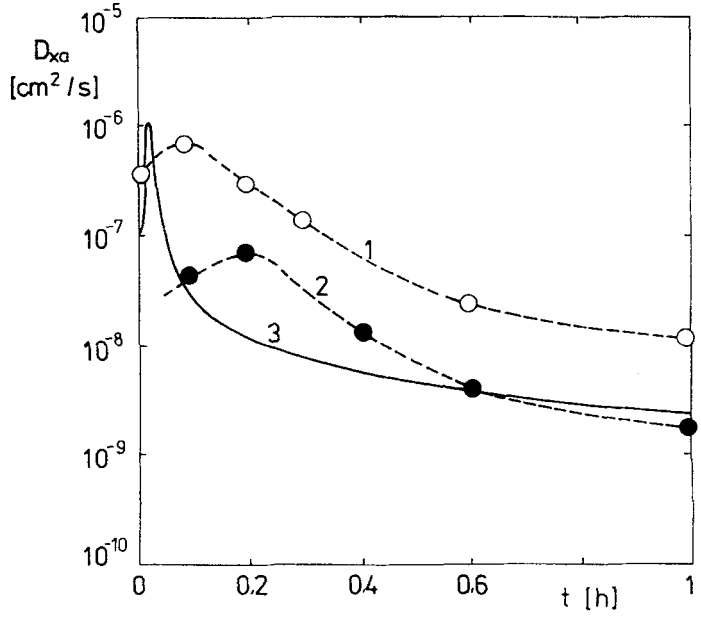

FIG. 7 Variation of D_{xa} versus time. (1) Extraction of sunflower seeds with hexane at 21°C, $R = 0.05$ cm (24). (2) Extraction of ground soybeans with hexane, $R = 0.017$ cm (25). (3) Extraction of dried, ground pyrethrum blossoms at 30°C, $R = 0.025$ cm, present data.

TABLE 1

In [mL]	30°C	40°C	50°C	Average
$\Delta V_{Y_{comp}}$	28.7	32.9	35.0	32.3
$\Delta V_{Y_{exper}}$	65	46	48	53
$V_{X_{comp}}$	46.7	50.9	53.0	50.4
ϕ_{comp} [—]	0.683	0.709	0.721	0.704

the experimental extraction curves are cut into several time segments and then calculating the mean D_{xa} values in each cut (11).

To prove the adequacy of the mathematical model used and the assumptions we made, the volume of the swelled solvent ΔV_Y was also considered to be an unknown model parameter. Its values, obtained through the above-mentioned identification procedure applied for our experiments, are given in Table 1, together with the experimental values found. It is evident that the computed values are more consistent and reliable than the experimental ones. The higher experimental values can be explained by solvent evaporation during sample manipulation and by liquid entrainment with the cakes of filtrated particles.

The relatively high values for expanded particle porosity ϕ render negligible any error made when estimating the initial, dry particle porosity.

CONCLUSION

Experiments carried out in an agitated batch extractor showed that the efficiency of pyrethrins extraction from ground, dry pyrethrum blossoms depends strongly on the size of the particles and the process temperature. The latter has an important influence on apparent solute diffusivity, which controls the overall process rate.

The apparent diffusivity is a nonmonotonous function of the solute content in the solid phase. In the initial period, due to the superposition of two opposite transport processes, solvent penetration in the particle, and solute extraction, D_{xa} passes through a maximum. For the case studied, this period is shorter than 10^2 seconds. During the following, main extraction period, D_{xa} decreases by more than 100 times, asymptotically reaching a constant value corresponding to molecular diffusivity in a semisolid medium or to a slow desorption process.

Comparison between the values for swelled solvent evaluated numerically and those found experimentally, as well as the good estimates for

the "free" solute diffusivity and the effect of particle size, proved the adequacy of the model used and the hypotheses made. Therefore, a large-scale batch extraction process can be designed by numerical solution of Eqs. (2), (3), (4), (5), and (8), provided laboratory information about the apparent diffusivity behavior is available.

SYMBOLS

Bi	Biot number, Bi = $k_Y R/D_x$ (—)
d	diameter (m)
D_{xa}	local apparent diffusivity (cm^2/s)
D_{xa}	mean apparent diffusivity (cm^2/s)
D_x	molecular diffusivity (cm^2/s)
E	extraction efficiency, $E = (X_{in} - X)/(X_{in} - \phi Y)$ (—)
h	pore length (cm)
k	local mass transfer coefficient (cm/s)
M	mass (g)
$p(R)$	size distribution function (—)
r	radial coordinate (cm)
R	particle radius (cm)
S	interfacial area (cm^2)
t	time (seconds)
V	phase volume (cm^3)
X	local solute concentration in the particle (g/cm^3)
$\overline{X}$	mean solute concentration in the particle (g/cm^3)
$\bar{\bar{X}}$	mean concentration for particle population (g/cm^3)
$\dot{X}$	dimensionless solute concentration, $X_w = X/X_{in}$ (—)
X_w	removed solute content, $X_w = (XV_x/M_{x,in})\cdot 100$ (%)
Y	solute concentration in continuous phase (g/cm^3)
Y^*	solute concentration in continuous phase in equilibrium with particle concentration X (g/cm^3)

Greek Letters

α_n	roots of Eq. (11) (—)
β	liquid volume ratio $\beta = \phi V_x/V_Y$ (—)
η	dimensionless coordinate (—)
ρ	density (g/cm^3)
τ	tortuosity (—)
ϕ	particle porosity (—)

Subscripts

in	refers to initial moment, $t = 0$
s	refers to solid/liquid interface
x	refers to the particle
Y	refers to the external, continuous phase

REFERENCES

1. R. L. Metcalf, "Insect Control Technology," in *Encyclopedia of Chemical Technology*, Vol. 13 (D. Othmer et al., Eds.), Wiley, New York, 1981, p. 424.
2. M. Sims, *Chem. Eng. (N.Y.)*, *89*, 50 (1982).
3. Gu Kequan, *Pyrethroids*, East China University Publishing House, Shanghai, 1984 (in Chinese).
4. G. Bunzenberger, E. Lack, and R. Marr, *Chem.-Ing.-Tech.*, *55*, 320 (1983).
5. C. F. Wilkinson (Ed.), *Insecticide Biochemistry and Physiology*, Plenum Press, New York, 1976.
6. C. M. Dickinson, *J. Assoc. Off. Anal. Chem.*, *65*, 921 (1982).
7. F. K. Lehrer, *Chem. Eng. Sci.*, *34*, 821 (1979).
8. P. G. Romankov and M. I. Kourochkina, *Extraction of Solid Materials*, Khimia, St. Petersburg, 1983.
9. A. B. Newman, *Trans. Am. Inst. Chem. Eng.*, *27*, 311 (1931).
10. J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1956.
11. G. A. Akselrud, *Teorya difusionnogo izvlecheniya veshtestv is poristich tel*, Lvov's Polytech. Ed., Lvov, 1959.
12. K. Tettamanti, J. Manczinger, J. Hunek, and R. Stomfai, *Acta Chim. Hung.*, *85*, 27 (1975).
13. J. O. Osburn and D. L. Katz, *Trans. Am. Inst. Chem. Eng.*, *40*, 511 (1944).
14. L. A. Syrota and V. M. Lysyansky, *Izv. Vuzov, Pisch. Tekhnol.*, *5*, 137 (1971).
15. I. A. Zayats, S. I. Blazhenko, and A. V. Lyssikov, *Zuckerind.*, *117*, 157 (1992).
16. J. H. Krasuk, J. L. Lombardi, and C. D. Ostrovsky, *Ind. Eng. Chem., Process Des. Dev.*, *6*, 187 (1967).
17. P. G. Romankov and C-Z. Bao, *Tr. Leningr. Tekhnol. Inst.*, *39*, 44 (1957).
18. B. V. Deryagin, V. V. Karassov, and N. N. Zazhavaeva, *Zh. Tekhn. Fiz.*, *27*, 1076 (1957).
19. V. A. Berkeley, *Pyrethrum Post (Kenya)*, *2*, 23 (1950).
20. A. Nelder and D. Mead, *Comput. J.*, *7*, 308 (1965).
21. M. A. Altshuler and B. V. Deryagin, *Dokl. Akad. Nauk SSSR*, *152*, 911 (1963).
22. G. A. Akselrud and V. M. Lysyansky, *Ekstragirovanie*, Khimia, Leningrad, 1974.
23. *Perry's Chemical Engineering Handbook*, 6th ed., McGraw-Hill, New York, 1991.
24. V. I. Serdyuk, *Izv. Vuzov, Pisch. Tekhnol.*, No. 5, p. 140 (1961).
25. A. G. Neshtadim, *Ibid.*, No. 4, p. 53 (1963).

Received by editor December 20, 1994