Solvent reduction in an industrial solid-liquid contactor
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Optimization of batch to continuous transposition: solid-liquid extraction from plant in an industrial contactor

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Abstract

Solid-liquid extraction is carried out from vegetable substrates in industrial continuous counter-current extractor. A batch study was conducted to obtain the extraction kinetic and the bulk phase saturation. An extraction model is proposed and compared with experimental data. This model is based on the general diffusion model including a shape factor of solid particle. A methodology for the batch to continuous transposition and the optimization of operating parameters is proposed.

Keywords: solid-liquid extraction, vegetable, solvent reduction

1. Introduction

Solid-liquid extraction represents an important part of many industrial processes. The transfer of solute from biological solids to an adjacent liquid is a traditional unit operation in the agro-industry or in pharmaceutical or para-pharmaceutical industries (Schwartzberg & Chao, 1982).

Vegetable substrates are complex by their non-homogeneity and their structure. Vegetable substrates have different geometric shapes, sizes, densities, so the hydrodynamic behavior changes from one plant to another (Aguilera, 2003). Moreover in one same lot, plant is non-homogeneous according to the storage, the harvesting time, etc… In industry, the difficulty lies in the variation of plant from one lot to another. The industrial extraction process must then take into account all these constraints (Prat et al., 2006).

In the present work, the solid-liquid extraction is performed in a Pierre Fabre Company's industrial unit using a counter-current continuous extractor. Advantages over the conventional batch extraction methods include a decrease in solvent consumption and shorter handling time. However, each material-solvent system shows a different behavior which can still change according to the contactor used. Influences and coupling of these three elements are of main importance. Then continuous extractor implementation at industrial level requires preliminary laboratory tests in order to optimize the operating conditions. The objectives are to

answer to three questions about industrial implementation in continuous extractor: which filling rate? which retention time? and what kind of policy of solvent management to be applied ?

2. Material, experimental device and modeling

For confidentiality reasons, names of the plant used and molecules extracted are not revealed. Values of concentration are multiplied by a factor between 0.8 and 1.2.

2.1. Plant

The solute, from secondary metabolites, is imbedded into the plant cells under free form. Its concentration depends on climatic growing, gathering, packaging and storage conditions. So, the plant quality changes from a production lot to an other. Average solute concentration is in the order of magnitude of gram per kilogram of raw material.

There are many general techniques to analyze solute such as high-performance thin-layer chromatography, gas chromatography, supercritical fluid chromatography, and high-performance liquid chromatography (HPLC). In this study, analyses are performed by HPLC with a system from Thermo Finnigan (Paris, France), Series AS1000XR, with a pump Series P1000XR and a Waters column (symmetry® C18, 3.9 mm x 150mm) with a UV detector (Thermo Finnigan, France), Series UV2000. The volume injection is 20 µL. The calibration curve is obtained using standard pure crystal coming from Pierre Fabre, Plantes & Industrie, France. The reproducibility of the analytical methods and the repeatability of the analysis were assessed by evaluating the peak area variation of pilot solution distributed regularly between the samples.

2.2. Continuous extractor: Vatron Mau

In previous work (Poirot et al., 2007), we described the Vatron Mau extractor shown in Fig. 1. Following paragraphs sum up the main information on this one.

The unit consists of a single-screw above a retention tank series. The screw (5) rotates continuously in one direction. The contact between solvent and raw material occurs by leaching. The direction of solvent flow (from 2 to 3) is opposed to the raw material one (from 1 to 4). The fresh solvent is in contact with the material depleted in solute, whereas the fresh plant is in contact with the extract which is enriched in solute.

Raw material is fed into the lower end of the barrel in section 1 and carried upwards by screw rotation. The time for the feed to travel to the discharge-end (4) from the feed-end is called the residence time. It is ranging from 0h40 to 6h20 function of the screw rotation speed. Solvent is fed into the top by tube (2), directly on the retention tank. The pump (10) ensures the solvent recirculation on the surface of material tanks to a dispersion nozzle (12). The bulk phase is separated to marc by means of a barrel, which behaves as a filter-media, and it is collected in retention tank (9). The solvent transfer from a tank to the next one is carried out by overflow. Temperature sensors and plate heat exchangers (11) are regularly distributed along the extractor.

The Vatron Mau unit is characterized by a plug flow. So, the residence time of plant in the Vatron Mau is equivalent to the unit length.
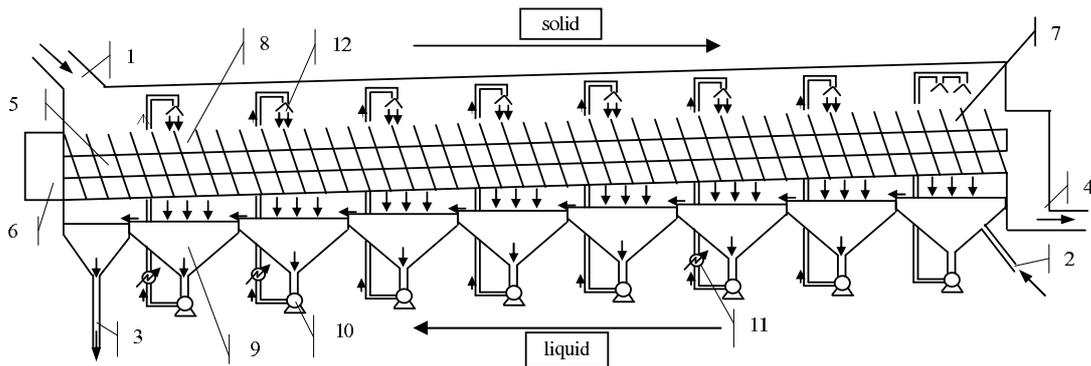
Figure 1: Scheme of Vatron Mau: (1) plant entrance; (2) solvent inlet; (3) solute exit; (4) marc exit; (5) screw; (6) motor; (7) drainage zone; (8) percolation section; (9) tank; (10) pump; (11) heat exchanger; (12) solvent distributor.

At the beginning, tanks are filled to capacity of solvent. The recirculation flow is about 12 m^3 h^{-1}. This adjustment corresponds to the maximum capacity of possible recirculation so that the juices fall down only in their origin tank without overflowing on the neighbour. Pump is starting when the plant enters on its stage. At nominal functioning point, raw material mass flow rate is 450 kg h^{-1}. The retention time is 2 h 30. Solvent flow rate is determined by the solid-liquid ratio applied.

2.3. Modeling

2.3.1. Model hypothesis

In order to describe the solute transfer, the following hypotheses were used:
- The solid particle can be represented by three shapes: plane, cylindrical or spherical shape. The solute diffusion takes place in the transverse direction and is monodirectional.
- Every particle is symmetrical and homogeneous.
- The particles size influence is negligible on the diffusion coefficient.
- The solvent in the batch is perfectly mixed. The transfer resistance in the interface liquid-solid phase is negligible.
- The solute concentration depends only on time and position.
- There is no reaction.

2.3.2. General equation

The general diffusion model of solid-liquid extraction (Simeonov, 1999; Seikova, 2004, Wongkittipong, 2004) is:

$$\frac{\partial C(t,x)}{\partial t} = D\frac{1}{x^{\varphi-1}}\frac{\partial}{\partial x}\left(x^{\varphi-1}\frac{\partial C(t,x)}{\partial x}\right) \tag{1}$$

where t is the time, x the radial characteristic distance in the direction of material transfer, D the diffusion coefficient, φ the geometric shape factor values ($\varphi = 1$ for plate, $\varphi = 2$ for cylinder and $\varphi = 3$ for sphere).

2.3.3. Initial and boundary conditions

The initial conditions (t=0) are:
  − for the continuous phase: $C_L = 0$
  − for the dispersed phase: $C = C_0 \; \forall x$.

The boundary conditions are:
  − at the center of a particle (x=0)

$$\left(x^{\varphi-1} \frac{\partial C(t,x)}{\partial x} \right)_{x=0} = 0 \quad \forall t \tag{2}$$

  − at the interface (x=e), equality of flux of solute (in mass):
    o the retiring flux of the solid is:

$$F = -DA \left(\frac{\partial C(t,x)}{\partial x} \right)_{x=e} \tag{3}$$

    o the incoming flux in the liquid is:

$$F = V_L \frac{dC_L(t)}{dt} \tag{4}$$

where V_L is the solvent volume and *A* the specific area.

2.3.4. Numerical treatment

The diffusive equation (1) was discretized in space with finite differences. The equations were treated with a Crank-Nicolson method (Wongkittipong, 2004). The diffusion coefficient was then modified to fit experimental points using a simple dichotomy method.

3. Experimental and modeling results

3.1. Kinetic experiments and modeling

The objective of batch experiments was to measure the global extraction kinetics of the solute.

A mass of 100 g not grinded raw material was inserted in a 2 L reactor, instrumented with a mechanical stirring. The experiment was carried out at ambient temperature. The solid-liquid ratio was stipulated by prior studies. Liquid samples were taken at different times and analyzed by HPLC. Since the global analytic sample volume was small compared to the introduced solvent volume, the measurement was assumed to have no influence on the process.

Fig. 2 shows the time course of the extracted percentage. Data are normalized by the plant potential of the plant lot used. The amount extracted tends towards the plant potential.
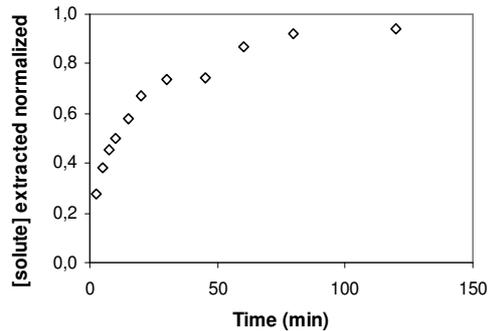
Figure 2: Batch kinetic

The diffusion coefficient was adjusted in order to fit experiment points of kinetic batch. Fig. 3 shows results of simulation with identified diffusion coefficient. The rising line is the time course of solute concentration in bulk phase. Downward lines correspond to the exhaustion at different levels inside the solid particles. The highest line is at the center of particle whereas the lowest is at the surface of particle. Data are normalized by the plant potential of the plant lot used. A good fitting was obtained between experimental and numerical values. The proposal model quite well described the extraction phenomena. The identified value for the coefficient diffusion D is 2.50 $10^{-13}\,\mathrm{m}^2\,\mathrm{s}^{-1}$.
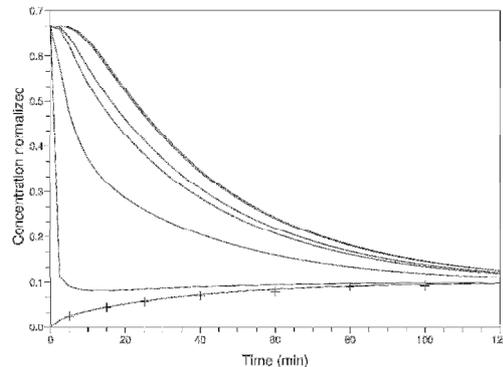

Figure 3: Diffusivity coefficient modeling

3.2. Saturation experiments and modeling

The objective of saturation experiments is to determine the influence of the solute concentration in the bulk phase on the extraction phenomena.

Experiments took place in a 2 L reactor, instrumented with a mechanical stirring. The experiment was carried out at ambient temperature during 1h. Various extractions with the same bulk phase were carried out successively. The solid mass was determined so as to have the same solid-liquid ratio each time. This ratio provided a good mixing. The solid-liquid separation was carried out by filtration. After each extraction, a liquid sample was taken and analyzed by HPLC.

Fig. 4 shows the bulk phase concentration according to the extraction number. Points are the experimental values. The line is the calculated values with hypothesis that the same amount of solute is extracted each time. Data are normalized by the

5

extracted amount in the first batch. Until the extraction number 5, experimental values are similar with calculated values. Then they tend to significantly differ.

Fig. 5 shows the extraction percentage according to the bulk phase concentration, normalized by the limit concentration. The limit concentration is obtained at equilibrium between solid and the only liquid necessary for solid impregnation. The extraction percentage is quite constant until point A, called rupture point, and then it decreases linearly until limit concentration. The extraction percentage falls between 40 % and 50 % of limit concentration. This extraction drop is linked with the saturation of the bulk phase and the decrease of the transfer flux.
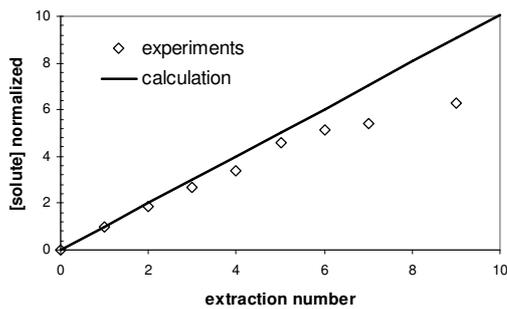

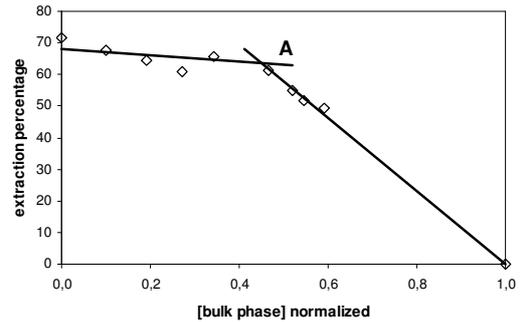Figure 4: Concentration time-course of solute

Figure 5: Extraction percentage according to bulk phase concentration

The saturation modeling is based on the model described previously. The bulk phase goes into the solid particles with the solute. But the solute in solid phase flows into the bulk phase only under the limit concentration. Fig. 6 shows experimental values and model for the extraction without pre-impregnation of raw material. The model predict well the extraction fall. On the Fig. 7, experiments were carried out with pre-impregnation before the extraction in order to limit solvent losses. The solute concentration increased according to the batch number. In this case, the model takes account with the fresh solvent contribution. In both cases, the model is appropriate in order to describe experiments.
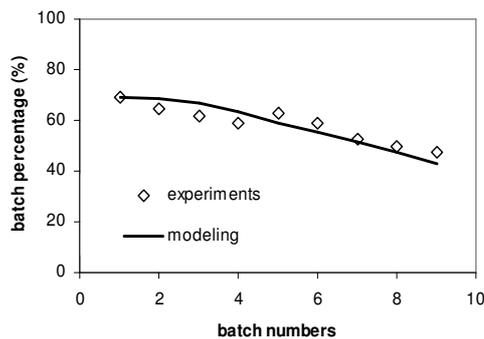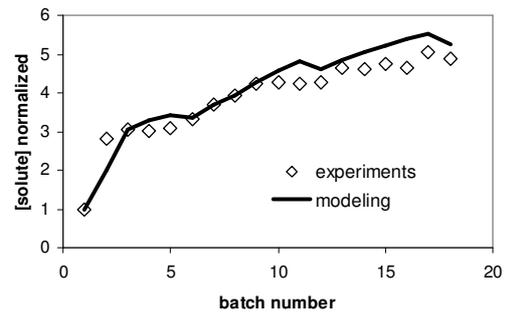

Figure 6: Extraction with pre-impregnation

Figure 7: Extraction without pre-impregnation

3.3. Continuous experiments

The objective of continuous experiments is to determine the similarities between batch and continuous extraction.

Continuous kinetic was carried out in the industrial Vatron Mau unit. Liquid and solid samples are taken at the same time along the length of Vatron Mau unit. The position of each sample corresponds to different extraction times. Liquid samples were analyzed by HPLC. Solid samples were re-extracted by three batches with fresh solvent. Fig. 8 shows the time course of extraction percentage in reactor batch and in continuous extractor. Data are normalized by the plant potential of plant lot used. Batch and continuous kinetics are similar.
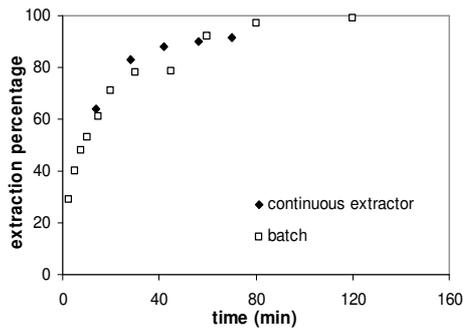

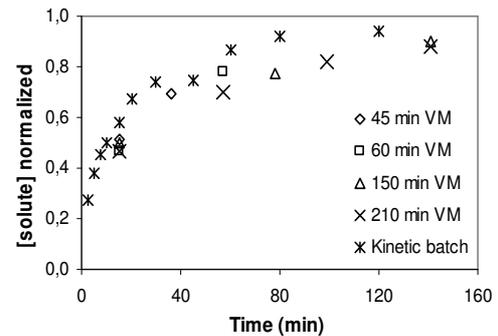Figure 8: Batch and continuous extraction kinetics

Figure 9: Vatron Mau kinetic at different extraction times

Experiment shown in Fig. 9 was carried out under non classical conditions which differ from the industrial usual ones, in a smaller Vatron Mau unit. The barrel length is 8 m and the tanks have an average capacity of 67 L. Fresh solvent was introduced only into the first stage to replace solvent absorbed by the plant. The recirculation flow was about 7 $m^3 h^{-1}$. Raw material mass flow was 15 kg h^{-1}. Experiment was carried out at ambient temperature. The screw speed is 0.23 rpm. The solid residence time was 2 h 30, while the solvent could be considered as stagnant (no counter-current). Then bulk phase concentration increased in tanks according to extraction time. However, continuous kinetics are little modified by the raising concentration of juice. So, the rupture point is not reached after 210 min an extraction. The higher concentration is equal to 20 % of limit concentration. The experiment could be continued without important loses of extraction during 200 min.

4. Discussion

Large coupling intervene between different phenomena in solid-liquid extraction. The fig. 10 shows this coupling and operations implying this coupling. Chemical characteristics of the solvent and the diverse structure and composition of the natural product ensure that each material-solvent system shows different behaviours, which cannot be easily predicted (Pinelo and al., 2004). The raw plants are various types (bark, root, sheet...) and various sizes (grinded no grinded). So the hydrodynamic behaviour in extractor changes from one matter to another. The solvent flow depends on the extractor and the contact type between solvent and raw material. The whole links make the study complex.
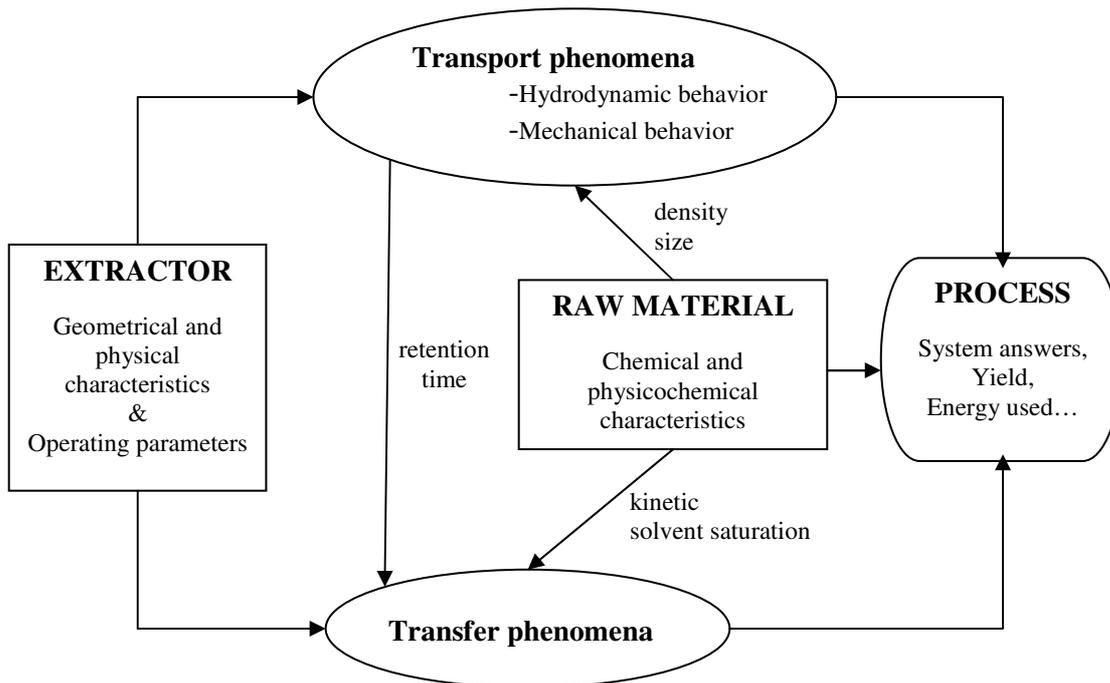
Figure 10: Links between different parts of system

The process depends on transport and transfer phenomena. Transport phenomena vary directly with the extractor characteristics and the raw material characteristics. For the raw material, the density and the size of solid particle are important. Transfer phenomena vary with extractor characteristics and raw material characteristics too and with transport phenomena through the retention time. The raw material influences the process by the kinetic extraction and the bulk phase saturation.

In order to optimize the process, many parameters are to be regulated. Solvent and operating temperature are chosen by previous studies according to selectivity, safety and economic criterion. The recirculation flow on each stage is regulated according to the leaching. The solid flow is determined from the filling rate and the retention time. Poirot and al. (2007) suggested that the filling rate must not go over the two third of the screen volume. Beyond that, plant accumulations on the level of solvent distributors were observed. The retention time is determined from desired yield and batch kinetic, because in Vatron Mau unit it is the same. The policy of solvent management represents the choice of solid-liquid ratio according to time. The extraction is not altered under the rupture point. Initially, the solvent flow can just balance the plant impregnation. In the second time, when the bulk phase concentration in the first tank is equal to the rupture point, the flow is adjusted in order to keep the concentration at this value.

The transfer batch to continuous extraction can be set up with few batch experiments. The developed model is well appropriate in order to simulate experiments. In the programming, plant potential, impregnation volume and limit concentration are necessary. The plant potential can be obtained by batch extraction or soxhlet extraction. Limit concentration is calculated from the two other values. In conclusion, four batches are necessary, three for the plant potential and one for the kinetic. From these experiments, all parameters are determined.

5. Conclusion

In solid-liquid extraction, continuous extractors are commonly used. Each system (raw material, solvent and extractor) is complex and differ from one to the other. Preliminary laboratory tests are necessary to implement and to optimize the process.

In this work, a specific system has been studied of course. Data on the kinetic and saturation are necessary to maximize the efficiency of the process. This data can be obtained by batch experiments. The proposed model quite well described the extraction phenomena. The use of the simulation allows minimizing the numbers of experiments to be performed. Indeed, the needed information to completely choose the operating parameters of the industrial process is reduced to (i) evaluation of the coefficient of diffusion which drives the kinetic in each stage; (ii) evaluation of a rupture concentration characterizing the limit over which the extraction flux is limited.

On the basis of the minimal information, an optimization of the process operating parameters can be done. In this study case, the solid-liquid ratio has been decreased by a third compared to usual conditions. This change of ratio decreases the solvent amount used and its recovery. Moreover in following treatment operations, solvent come more concentrated. So the concentration phases will be less important, and then less energy will be necessary.

Nomenclature

A	specific area of the solid particle, m^2
C	concentration in solid, kg/kg
C_0	initial concentration in solid, kg/kg
C_L	concentration of solute in solvent, kg/l
D	diffusion coefficient, m^2/s
F	flux, kg/s
t	time, s
V_L	volume of solvent, m^3
x	radial distance, m
φ	geometric shape factor, dimensionless

References

Aguilera, J.M., (2003) Food Sciences and Technology, 128, 35-55.

Pinelo, M., Rubilar, M., Sineiro, J., Núñez, J., (2004) *Food Chemistry*, 85, 267-273.

Prat, L., Wongkittipong, R., Angelov, G., Gourdon, C., (2006) *Chemical Engineering & Technology*, 29 (3), 401-407

Poirot, R., Prat, L., Gourdon, C., Diard, C., Autret, J. M., (2007) *Chemical Engineering & Technology*, 30 (1), 46-51.

Seikova, I., Simeonov, E., Ivanova, E., (2004) *Journal of Food Engineering,* 61, 165-171.

Simeonov, E., Tsibranska, I., Minchev, A., (1999) *Chemical Engineering Journal,* 73, 255-259.

Schwartzberg, H. G., Chao, R. Y., (1982) *The Canadian Journal of Chemical Engineering*, 64, 80-86.

Wongkittipong, R., Prat, L., Damronglerd, S., Gourdon, C., (2004) *Separation and Purification Technology*, 40, 147-154.