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Fast Batch to Continuous Transposition

Application to the Extraction of Andrographolide from Plants

By L. Prat*, R. Wongkittipong, G. Angelov, C. Gourdon, and S. Damronglerd

A fast development method for batch to continuous process transposition is proposed. This method is based on transient regime experiment analyses and is applied to a solid-liquid extraction. The application under consideration is the extraction of an active principle from a plant in a non-sinusoidal pulsed column. Typically, the proposed signal is composed of two different periods: firstly, a classical sinusoidal pulsation step is used to mix the liquid and solid phases in the active part of the column and allow an optimal mass transfer and, secondly, an impulsion phase, used generally for the transport of solids. The extraction is carried out in a disc and doughnut column of 54 mm diameter and 3.5 m height. Liquid and solid are flowing co-currently and downwardly. This technological improvement has been implemented to solve the difficulties due to the significant heterogeneity of the matter: one part tends to float and other to sink, which always leads to a definitive flooding in classical operations. The effects of the solid flow rate and the solvent characteristics on the hydrodynamic behavior of the column are studied. The mean residence time and the total solid holdup are calculated by using a transient regime mass balance on the experimental results. These experiments allow the identification and quantification of opposite effects of the operating parameters. Mass transfer experiments have been performed and the results fit calculated values obtained by coupling the hydrodynamic and batch extraction results. Despite the simplifications made, this validates the fast development method proposed to help batch to continuous transposition.

1 Introduction

Natural bio-products obtained from vegetal raw materials have found increasing application in pharmacy, cosmetics, perfumery, and related domains [1, 2]. Usually a solvent extraction technology is applied for the production of such substances [3].

In order to increase production capacity and to decrease operational costs, more advanced extraction schemes have been developed including continuous operating devices. An external energy source is often used to provide better phase mixing, which intensifies the interphase mass transfer [3]. Pulsed flow offers an interesting alternative means for agitation in continuous contact processes and is broadly applied in column type apparatuses [4–7] (used as liquid-liquid or solid-liquid contactors).

The particles of disintegrated vegetables often show different hydrodynamic behavior due to their difference in shape, structure, and size. Generally, this inhomogeneity does not create problems in batch operations or in extraction equipment with mechanical transportation of the solid matter (for example, screw extractors) [8]. However, in continuous grav-

itational contactors, short residence times and early flooding problems are often met. In our opinion, they can be better controlled by application of the pulsation flow concept.

This article presents results of andrographolide extraction from *Andrographis paniculata* in a discs and doughnuts pulsed column, using a water-ethanol mixture as a solvent. *Andrographis paniculata* is an erect annual herb varying in height from 30–100 cm, and 2–6 mm in diameter. It has been used as a traditional medicinal plant in Southeast Asia, China, and India, and to treat common colds and sore throats in Europe and in South America [12]. The active substance of *Andrographis paniculata* is andrographolide, a very bitter compound found in the plant's aerial parts (leaves and stems). It is an unsaturated trihydroxy lactone ($C_{20}H_{30}O_5$) [13, 14]. From a process point of view, the main characteristics of the plant have been described in [15], including diffusion phenomena.

The considered case of recovery of active components from plants cannot be easily handled by a conventional continuous solvent extraction column. The trouble lies in the different hydrodynamic behavior of the particles. Some of them are lighter than the solvent, the others are heavier. Furthermore, the shape influences the behavior when coupling with the liquid, e.g., through the Stokes number. In our case, the stems tend to float, while the leaves sink. The floating fraction is accumulated at the column top and provokes flooding. Consequently, it seems difficult to organize a continuous mode extraction process. It looks favorable to apply a batch extraction process or to develop a complex multiple step processing including a stage of preliminary particle classification and separation.

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Nevertheless, a simple technical solution has been developed and described in a previous paper [9]. The leading design idea is to create a continuously operating device which is able to integrate several actions in a single apparatus:

- Separation of solids into fractions lighter and heavier than the solvent,
- Elimination of the light particle fraction,
- Intensive mixing in order to provide good phase contact.

In the considered case, the heavy solid fraction is moving down the apparatus by gravity. The light fraction accumulates at the top on the liquid surface and should be withdrawn from the apparatus in order to avoid flooding. As has been noted, the light fraction contains mainly stems, which represent a minor part of the plant and are poor in solute. Consequently, the elimination of the floating fraction will permit the realization of continuous operation without significantly affecting the solute yield. The phase mixing can be provided by a pulsed flow.

So, a pulsed extraction concept has been selected as an appropriate basis. Pulsed columns with internals of discs and doughnuts have demonstrated their advantages as phase contact apparatuses [10,11]. Such a column has been adapted for the studied case, introducing several important constructive and operational modifications.

This article presents the methodology used to develop the continuous process based on transient regimes analysis. From the experimental results, the hydrodynamic behavior of the column is described and the mass transfer operation is quantified and compared with previous batch process results.

2 Column Description

2.1 The Column

The disk and doughnuts column used is composed of a vertical cylindrical body, 54 mm in diameter, divided into compartments by alternating internals of discs and doughnuts. They are maintained by braces of constant length (25 mm). The disc diameter is 25 mm and the doughnut aperture is 14 mm, resulting in a free area nearly equal to classical value of 23%. The column active part is 3.5 m long. Fig. 1 shows a schematic view of this column.

In addition to the classical design, an exit tube has been added to the column top. It serves for purging of the floating light solid fraction.

A pneumatic system has been used for the creation of a pulsed flow. A special regulation cycle was developed in order to create a non-sinusoidal pulsation pattern, which was used for periodical elimination of the floating solid, thus making possible a continuous mode operation.

Also, batch extraction experiments have shown that there is no solubility limit to the mass transfer [15], and practically there is no need to perform a multi-stage counter-current operation. A co-current mode is also appropriate for the

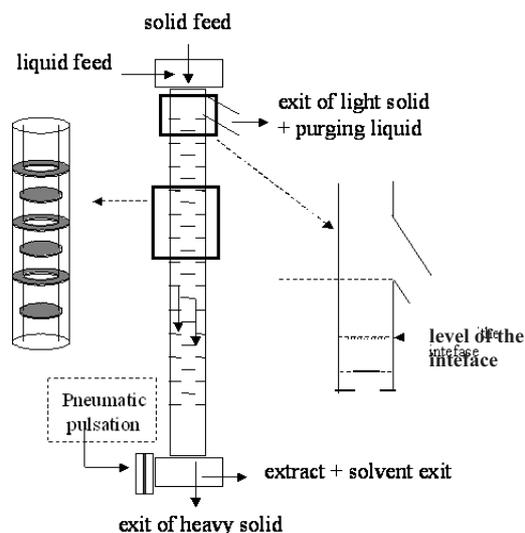


Figure 1. The discs and doughnuts pulsed column in co-current flow with pneumatic pulsation.

considered case because of the low phase density difference, which is not sufficient to allow an easy counter-current operation. So, *Andrographis paniculata* is fed continuously at the column top along with the solvent (ethanol solution), which is continuously removed from the column bottom through a pressure compensation leg. The solid phase downward flow is collected in the column bottom tank.

2.2 Pulsation System

The pulsation system is composed of a three-way valve linked to a storage tank, which insures a constant 2 bars pressure, and linked also to room pressure (1 bar). The delivery pressure is then connected to the pulsed leg of the column, providing an active range of 1–2 bars. The pressure is supervised and controlled by a computer.

The liquid movement is separated into two steps:

- Pulsation step: classical sinusoidal pulsations are used to agitate the solid-liquid system in the column body, providing intensive phase mixing. They also reduce the dispersed phase sedimentation velocity, thus increasing its residence time. This pulsation pattern is characterized by its frequency¹⁾ f_m and amplitude A_m .
- Impulsion step: this is a periodical rise of pressure, which produces a brief rise in the interface level inside the column in order to transport the accumulated floating solid to the top outlet tube, from where it is purged. This impulsion is characterized by its frequency and amplitude, f_i and A_i .

Fig. 2 shows a record of a typical overall pulsation pattern in the experimental device.

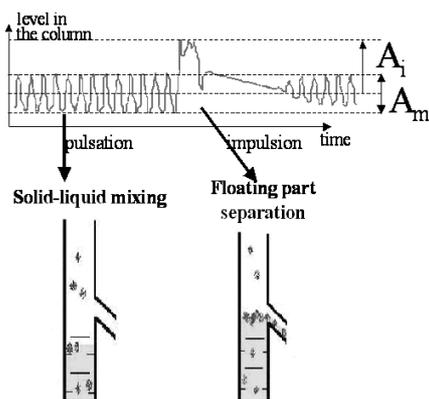


Figure 2. Experimental pressure profile and pulsation periods (from [9]).

The results of a preliminary study have confirmed the feasibility of this pulsation mode, which has made the column operational with the tested solid-liquid system [9].

3 Steady-State Results and Feasibility

The hydrodynamic behavior of the solid-liquid system in a steady-state regime has been studied and described in [9]. The main objectives were the following:

- Obtaining a good separation of floating and sinking particles;
- Minimizing the solvent loss at the top solid outlet;
- Maximizing the solid fraction going through the column;
- Avoiding flooding.

The operating parameters are:

- The level of the interface inside the column;
- The frequency and amplitude of the pulsation step;
- The concentration of ethanol in the solvent;
- The frequency and amplitude of the impulsion step.

The liquid level has to be properly chosen in order to minimize the solvent loss while purging the solid. Furthermore, when the interface level is in the vicinity of the disc, the solid phase is better impregnated with solvent due to its natural accumulation over the disk. In contrast, when the interface level is close to the upper purge exit, agglomerations with dry solid kernel have been formed. Consequently, it is recommended to operate in the vicinity of the first disc.

Searching to minimize the energy and air consumption, it has been found expedient to operate at the natural frequency of the column [16,17], which in our case takes the value $f_m = 1.67 \text{ s}^{-1}$.

Also, it has been found that the heavy/light particle separation is more efficient at smaller solid feedings.

Finally, the concentration of ethanol has a significant influence on the solid phase behavior. With higher ethanol concentrations, the solvent absorption kinetics is faster and the floatability of the particles is reduced, thus the solid mass down outlet increases with the percentage of ethanol. The separation of solids into light/heavy fractions is also facilitated.

A higher ethanol concentration promotes both the solid downward flow and sinking/floating particle separation.

If the liquid level (around the first disc) and pulsation amplitude are chosen appropriately, there is no solvent loss at the top exit during the mixing period. The impulsion amplitude has to be experimentally adjusted: it has to be chosen so as to be slightly higher than the pulsation amplitude and high enough to allow the accumulated light solid to exit through the purge top outlet, though on the other hand this amplitude must be as small as possible in order to minimize solvent losses during the purging.

The impulsion frequency depends on the solid feeding flow rate. A higher flow rate means faster accumulation of floating particles, which requires more frequent impulsion in order to purge this floating mass and to avoid column flooding.

Applying the developed asymmetric pulsation mode, the column has been run at various solid feedings and solvent concentrations in order to estimate the domain of non-flooding operation. The operating points are reported in Fig. 3, along with the limit line of the flooding area. It is clearly seen that by using higher ethanol concentrations, the operational zone can be significantly enhanced towards higher apparatus capacity.

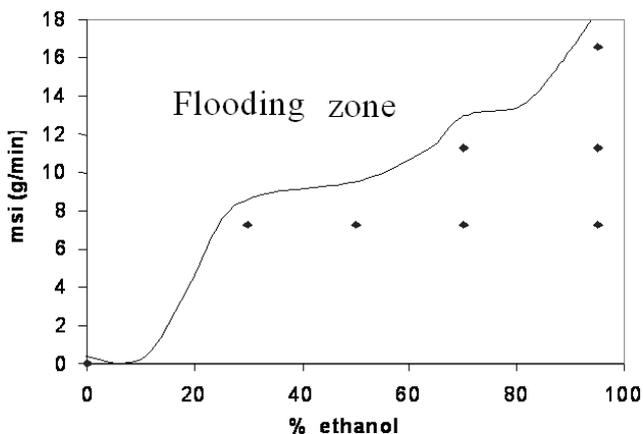


Figure 3. Experimental functioning zones (from [9]).

It should be stressed once again that, due to floating particles, no operation is possible when performing this extraction in a classical column with a simple sinusoidal pulsation.

4 Transient Regime Operation

Operation in the transient regime has served to obtain useful information for the characterization of solid phase flow inside the column.

During these experiments the column was initially started as described in the permanent regime operation. The difference consists in the manner of solid feeding, which is stopped at a certain moment, then started again, thus main-

taining a transient operational regime. The cumulative bottom outlet solid flow has been measured with the course of time.

4.1 Typical Experimental Results

Fig. 4 illustrates a typical time evolution of the cumulative solid mass at the column bottom when operated in the described dynamic mode. Several zones are to be distinguished:

- Transient zone 1. This runs from the moment of solid feed start (zero time) till the moment at which the solid outlet flow rate is considered as being constant.
- Steady-state operation zones 1 and 2. These are periods of constant solid output flow rate, characterized as straight lines.
- After establishing the steady-state 1 regime, the solid feed is stopped and is started again when no more solid is leaving the column bottom. Transient zone 2 reflects the evacuation of solid from the apparatus body.
- Transient zone 3 (analogue to Transient zone 1) reflects a new filling-up of the column with solid until the steady-state 2 regime is attained. Transient zone 1 is longer than the transient zone 3 period because initially the column does not contain any solid, while after the solid evacuation during transient period 2 some solid stays on the column internals. So, a smaller quantity of solid, (and respectively, a shorter time) is necessary to restore the permanent solid flow.

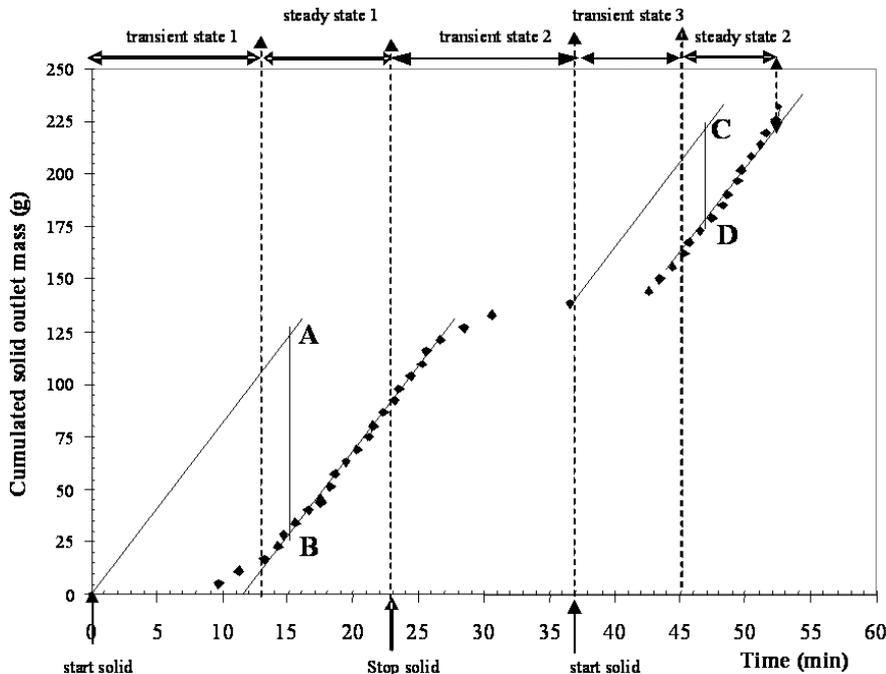


Figure 4. A typical experimental curve showing the cumulated mass solid outlet at the bottom of the column as a function of time.

- The steady-state 2 regime is attained in a certain time after the solid feed is started again. The corresponding straight line has nearly the same incline (slope) as for the steady-state 1 regime, which is evidence for the reproducibility of column operation (reconstitution of the same steady-state regime).

From this graph it is possible to get information on solid mass outlet flow rates, on transient state characteristic times, on total solid holdup, and on mean residence times of the solid.

4.2 Experimental Error and Reproducibility

All the presented dynamic experiments have been performed twice. Due to this, and to the fact that at least ten experimental values from the curves are used, the error in the calculated terms (solid holdup, dead mass, mean solid residence time) is very low. Furthermore, in order to have a good reproducibility all the solid plant samples came from the same lot.

4.3 Transient State Characteristic Time

Transient state duration time was measured as a function of the mass solid flow rate for 95 % ethanol (see Fig. 5) and as a function of the percentage of ethanol in the solvent for a 11.33 g min^{-1} solid flow rate (see Fig. 6). The two curves decrease, showing that the final solid holdup in the column is reached more quickly at high solid flow rates and at a high percentage of ethanol. The first effect is linked to a classical dynamic mass balance, while the second is due to the absorption of solvent into the plant, which is more important at high ethanol percentages [9].

4.4 Total Solid Holdup

Total solid retention (m_{holdup}) is defined as the solid mass residing in the column during an experiment. It has two contributions: a “dead mass” (m_{dead}), accumulated over the internals and staying there throughout the experiment, and a “moving mass” (m_{moving}) which flows down through the column.

The moving mass can be measured by stopping the solid feed and collecting the solid output until there is no more solid flow. The total solid holdup can be calculated when in the

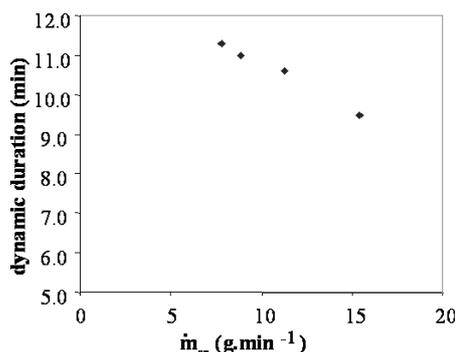


Figure 5. Dynamic duration time as a function of the solid outlet mass flow rate (95 % ethanol).

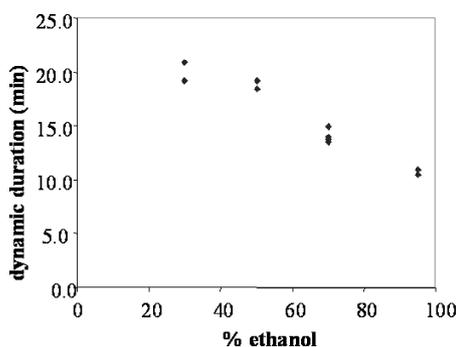


Figure 6. Dynamic duration time as a function of the ethanol concentration ($\dot{m}_{ST} = 11.33$ g min⁻¹).

steady state by measuring the difference between the cumulated solid outlet mass and the cumulated total inlet mass (i.e., the difference between points A and B in Fig. 4). The moving mass was calculated in the steady state, after a stop, by measuring the difference between the cumulated solid outlet mass and the cumulated total inlet mass (i.e., the difference between points C and D in Fig. 4). Of course, these three values are linked by the following relation:

$$m_{holdup} = m_{moving} + m_{dead}$$

The experimental evolution of the moving mass and dead mass is presented as a function of the solid mass flow rate in Fig. 7 and as a function of the percentage of ethanol in Fig. 8.

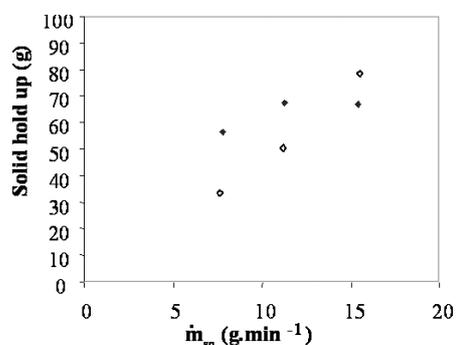


Figure 7. Moving mass (\diamond) and dead mass (\blacklozenge) as a function of the solid mass flow rate (95 % ethanol).

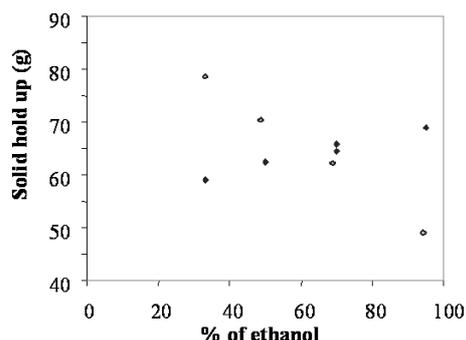


Figure 8. Moving mass (\diamond) and dead mass (\blacklozenge) as a function of the percentage of ethanol ($\dot{m}_{ST} = 11.33$ g min⁻¹).

An increase of the solid flow rate in the column increases the moving mass and the dead mass until a limit is reached. The effect on the dead mass must be linked to the turbulence created by a high concentration of solid particles in the fluids.

The influence of the ethanol concentration on the total solid holdup seems to have two opposite effects. As has been shown earlier, for more concentrated solvents the separation of floating and sinking fractions is better, and the amount of sinking solid is higher. This might lead to higher holdup. On the other hand, the solid residence time becomes smaller at higher ethanol concentrations because of better and faster solvent absorption resulting in a higher velocity of downward solid flow. A superposition of these opposite tendencies probably produces the maximal retention at intermediate solvent concentration (70 %).

4.5 Mean Solid Residence Time

The solid mean residence time is obtained by dividing the moving mass by the total solid outlet flow rate at the bottom of the column. The solid mean residence time increases with increasing solid flow rate (see Fig. 9), showing that high solid holdup helps to slow down the solid. Of course, this effect is limited by the flooding of the column. The percentage of extraction has two opposite effects on the solid mean residence

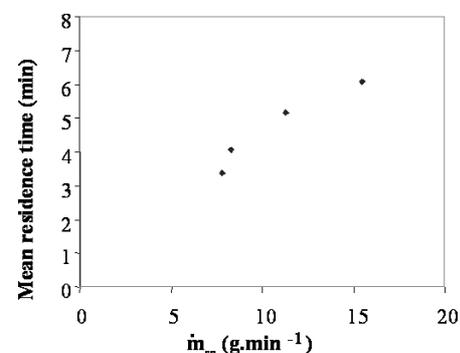


Figure 9. Mean residence time as a function of the solid outlet mass flow rate (95 % ethanol).

time. On one hand, it helps to increase the capacity of the column as a plant sink [9]. On the other hand, the amount of absorbed solvent is higher, increasing the particles terminal velocity. This can be seen in Fig. 10, the mean solid residence time as a function of the percentage of ethanol has a maximum value at about 40 %.

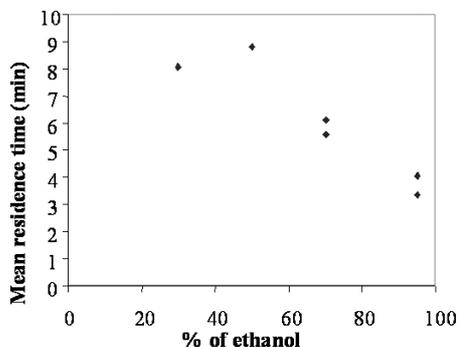


Figure 10. Mean residence time as a function of the percentage of ethanol ($\dot{m}_{SI} = 11.33 \text{ g min}^{-1}$).

5 Mass Transfer Experiments

In order to illustrate the general column performance as a contact apparatus, some mass transfer results in the transient regime are given below.

Batch kinetic experiments have shown that andrographolide is better extracted with more concentrated ethanol [15]. In continuous column operation it is expected that a higher contact time will result in a better extraction yield. However, as it has been found, the solid residence time is shorter with more concentrated solvent. Nevertheless, 95 % ethanol has been chosen because of faster extraction kinetics and better hydrodynamic behavior of the system (in that condition, no flooding is expected).

The operational conditions of the illustrative extraction experiments are as follows: solvent input flow rate $\dot{m}_{LI} = 420 \text{ g min}^{-1}$, solid input flow rate $\dot{m}_{SI} = 11.33 \text{ g min}^{-1}$.

Samples of liquid extract have been taken from the column middle and bottom at various times and the andrographolide concentration analyzed (the analytical method is described in [15]).

Fig. 11 represents the time evolution of solute concentration at the middle and bottom sampling points. Obviously, the general trend of both lines is the same, the bottom samples being more concentrated, as expected, and with a time shift of about 3 min. The initial rise of concentration corresponds to the initial filling-up with solid. The maximum is due to the complete extraction of the solute contained in the dead mass. The plateau corresponds to the steady state operation when only downward flowing solid is extracted.

The extraction yield E can be calculated by referring to the results of batch experiments [15], which supply the total content of solute (andrographolide) in the solid:

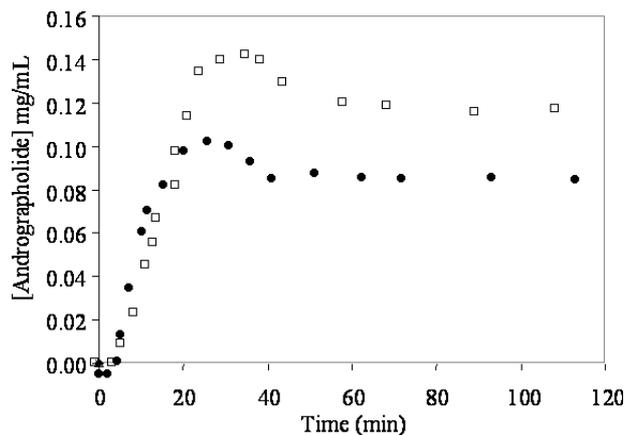


Figure 11. Andrographolide concentration as a function of the time at the middle (■) and the bottom (□) of the column.

$$E = \frac{\text{quantity extracted by the solvent}}{\text{total quantity in the solid}}$$

A mean experimental extraction rate of about 12 % has been obtained. For the particular operational regime, the solid residence time in the column is 4 min. Compared to the batch extraction yield for the same time (13 %) [15], the result is very similar. It means that the extraction process in the column is as efficient as in batch operation, where very good phase mixing is provided. Thus, the column creates good conditions for solid-liquid contact (the limiting step remains the diffusion inside of the plant). The similarity of the middle and bottom profiles is evidence that a fairly good plug flow is realized. Moreover, if the extraction rate at the mid-column is compared with the same extraction yield on the batch extraction kinetic curve, the apparent solid residence time at mid-column can be derived. It corresponds to half of the bottom (total) residence time, which additionally confirms the existence of plug flow.

6 Conclusions

A continuous process of solvent extraction of natural substances from vegetal bio-resources has been studied for the case of the extraction of andrographolide from the plant *Andrographis paniculata*. The main difficulty comes from the raw material inhomogeneity (floating and sinking particles). The existence of a floating fraction provokes flooding within a short time and makes continuous operation impossible.

A pulsed extraction column has been adapted to resolve the case. An air pulsing technique has been applied to create a specific pulsation mode that makes it possible to unify in one apparatus the processes of separation of solid fractions and the extraction itself. The pulsation cycle integrates two pulse patterns, one of them being a regular sinusoidal pulsation used for phase mixing, while the other is a low frequency impulsion used for periodical evacuation of the light vegetal fraction.

A column with internals of discs and doughnuts is used to perform the process. A transient operating method is described for obtaining parameters and characterizing the solid phase flow. The apparatus appears to display a plug flow pattern and has an efficiency comparable to that of a well mixed batch reactor. Within a few experiments, the information acquired is sufficient to be able to predict the extraction yields and then to design and optimize a continuous solid-liquid column.

This particular example illustrates the possibility for managing difficult cases of heterogeneous solid materials by using pulsation techniques. The developed method, coupling technological improvement and experimental design, led to fast and efficient transposition from batch to continuous processes.

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Symbols used

A_i	[cm]	amplitude of impulsion
A_m	[cm]	amplitude of mixing pulsation

E	[-]	extraction yield
f_i	[s ⁻¹]	frequency of impulsion
f_m	[s ⁻¹]	frequency of mixing pulsation
m_{Li}	[g min ⁻¹]	inlet liquid flow rate
m_{Si}	[g min ⁻¹]	inlet solid flow rate
m_{So}	[g min ⁻¹]	outlet solid flow rate at the bottom exit

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