Coupling DIC and Ultrasound in Solvent Extraction Processes

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1 Introduction

Intensification of the main industrial unit operations is designed to reduce treatment time, decrease energy consumption, and preserve or even improve the multidimensional quality of the end products. The philosophy behind intensification involves identifying different processes and determining their possible interaction. In order to do so, it is first essential to shed light on the limiting phenomena in order to intensify them, thereby improving the kinetics of the entire operation.

2 Fundamental Aspects

2.1 Solvent Extraction

Solvent extraction involves a solid/liquid interaction that removes the soluble components from solids. This operation, from a technological point of view, is a phenomenon that involves the diffusion of a carrier fluid (liquid) through a porous solid. The carrier fluid transports a solvent capable of "dissolving" one or more specific molecules from a solid (plant) or a liquid. The solute-in-solvent is also transferred within the porous solid through a diffusion process.

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The gradient of solute concentration between the solution at the surface in the solid phase (more concentrated) and the liquid phase results in a transfer by diffusion of these dissolved active molecules to the surroundings. At the end of the operation, the system tends toward equilibrium and the diffusion transfer becomes nil.

In contrast, if the liquid phase is continuously renewed, the diffusion continues until the complete exhaustion of the solid phase. At the end of the operation, the solid (residue), inert or insoluble, contains very little or no solute at all (Allaf et al. 2011).

Part III—Chap. 3—presents solvent extraction transfer in detail so we will only highlight the general elements of this process in this chapter.

A first stage of solute dissolution in the solvent is carried out at the surface of the product (illustrated by the starting accessibility). It is followed by diffusion phenomena of the solvent towards the core of the solid matrix and of the solute within the filled-with-solvent pores. This specific transport occurs as a Fick-type diffusion process.

The type of solvent used and its polarity depend on the solute that is to be extracted, and the temperature is limited by the boiling temperature and the thermal sensitivity of the compounds. Thus, it can be assumed that the interaction between the solvent and the product results in the solute directly reaching equilibrium.

Agitation of the solvent in the external environment allows the solute that is accessible at the exchange surface to be easily and quickly extracted and transported far from the exchange surface. This first intensification of the solvent extraction process significantly replaces natural convection. Internal solvent diffusion, followed by solute-in-solvent diffusion within the matrix, becomes the limiting processes.

In this chapter, we will therefore be focusing on the intensification of this specific limiting process.

2.2 Extraction Intensification

Subsequently, solvent extraction can be intensified in several ways:

A *grinding process* that increases the exchange surface, thus augmenting starting accessibility while maintaining effective diffusivity constant	*DIC* texturing to expand the granules and increase the material's porosity. Thus, the effective diffusivity of both solvent and solute-in-solvent within the plant medium also increases. Indeed, the natural structure of vegetables and more specifically the cytoplasmic membrane and the cellular wall cannot support the liquid transfer processes. The resistance of the structure often seems to be the principal restricting factor for the kinetics of the operation

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Solvent agitation to allow more effective transport of solute from the product surface towards the external medium by convection instead of diffusion	*Ultrasound* (US) to establish an internal micro-convection within the pores instead of the very prejudicial diffusion process
Renewing the solvent at low solute concentration by a counter-current exchange system, etc.	

3 Ultrasound: Fundamental Aspects

3.1 Principle

Ultrasounds are mechanical waves that require an elastic medium to spread. Ultrasound frequencies are above the upper limit of human hearing (from 16 Hz to 16–20 kHz) and below the frequency of microwaves (20 kHz to 10 MHz). Ultrasounds can be divided into two groups with regard to their frequencies:

- Diagnostic ultrasounds: these ultrasounds are also called low-power or high-frequency ultrasounds. They range from 5 to 10 MHz and are used in several fields such as medical imaging (med scan) or even for defect detection (bond inspection for plastics). Diagnostic ultrasounds are used to make measurements without altering the medium, unlike power ultrasounds.
- Power ultrasounds or low-frequency ultrasounds are used to produce physical or chemical effects in the medium. They are used in sonochemistry (to facilitate or accelerate chemical reactions), agriculture (water dispersion), and in industry (cutting, plastic welding).

In order to visualize an ultrasonic effect, its action can be described as a piston on the surface of the medium (Pingret et al. 2013) (Fig. 1). This results in a succession of compression and rarefaction phases in the medium. When the piston is in the open position it induces a compression in the medium and when the piston is in the contracted (pull) position it creates a rarefaction phase.

On a molecular scale, as the sound wave passes through the medium, the molecules are temporarily dislodged from their original position and can enter into collision with the surrounding molecules (Vinatoru 2001) (Fig. 1). Then, during the rarefaction phase the first group of molecules will be pulled back towards their original position and the kinetic energy involved will pull them further back from this position. This will create regions of rarefaction in the medium but due to their elastic properties all the molecules will go back to their original location when the sound wave has fully passed through the medium.

With regard to solvent extraction, oscillatory particle motion produced by high-intensity ultrasonic waves can also induce secondary flows, known as acoustic streaming. This kind of agitation produces an internal convection motion of the

solute within the solvent which is inside the holes of the porous material. Moreover, cavitation produces micro-jets at the surface of the food material that may increase the exchange surface, the effect of which has to be revealed through a high starting accessibility. Both effects can increase mass transfer of solute within the solvent which is present within the solid (Mason 2000; Toma et al. 2001).

In other words, ultrasonic treatment involves an internal motion/agitation of the liquid within the pores, resulting in a solute transfer by convection instead of or coupled with diffusion (Toma et al. 2001).

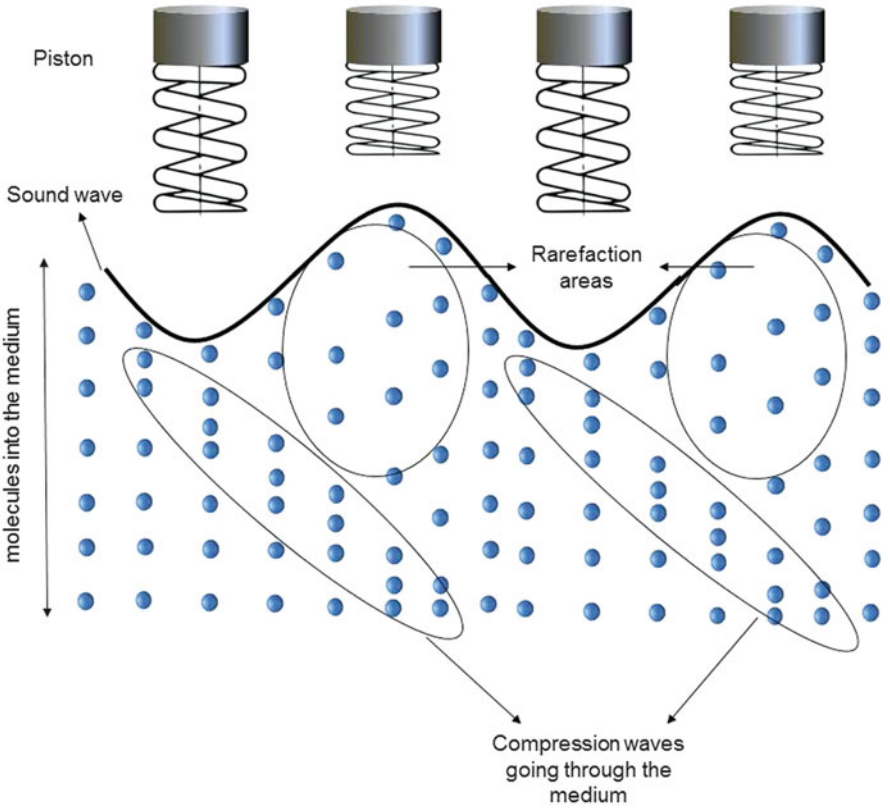

Fig. 1 Adiabatic compression and rarefaction cycles induced by a sound wave

3.2 Mass Transfer

3.2.1 External Transport

Transport of a solute in an external solvent from the surface of a solid is possible by *diffusion* from the zone of high concentration of solute (close contact with the solid exchange surface) toward the low concentration zone, with the gradient of solute concentration as the driving force.

$$\frac{\rho_{\text{solute}}}{\rho_{\text{solvent}}}\left(\vec{v}_{\text{solute}} - \vec{v}_{\text{solvent}}\right) = -D_{\text{solute-solvent}}\vec{\nabla}\left(\frac{\rho_{\text{solute}}}{\rho_{\text{solvent}}}\right) \quad (1)$$

Different methods are generally used to intensify these external transfer phenomena, such as:

- Choosing the best solvent in terms of:
  - Obtaining the highest solute dissolution
  - Obtaining the lowest viscosity to achieve the best diffusivity (D) of solute within the solvent
- Establishing external mechanical agitation to achieve external mass transport by *convection* rather than *diffusion*
- Renewing external solvent to reduce solute concentration:
  - Improving the difference between the exchange surface and the total solvent concentration
  - Maintaining the concentration of solute in the solvent as far as possible from the saturation level

3.2.2 Internal Transfers

Once the external transport is adequately intensified, internal transfers become the limiting processes.

Two main types of internal transfer phenomena have to be analyzed: the solvent to be transferred from the exchange surface to the internal solid matrix and the solute to be transferred within the solvent situated inside the holes of the porous material. The choice of an appropriate intensification method depends on two phenomena:

1. The first point to be noted in an intensification process is that in the transfer of solvent from the exchange surface to the internal solid matrix, the various processes of diffusion, capillarity, and osmosis from a high solvent concentration toward a low solvent concentration occur with the gradient of solvent concentration as the driving force and with D_{eff} as effective diffusivity.

$$\frac{\rho_{\text{solvent}}}{\rho_{\text{solid}}}\left(\vec{v}_{\text{solvent}} - \vec{v}_{\text{solid}}\right) = -D_{\text{eff}}\vec{\nabla}\left(\frac{\rho_{\text{solvent}}}{\rho_{\text{solid}}}\right) \quad (2)$$

   The intensification must then be achieved by:

   (a) Expanding the matrix structure by détente instantanée contrôlée (DIC, which is French for "instant controlled pressure drop") to increase effective diffusivity D_{eff} and the effective exchange surface.

(b) Selecting the lowest viscosity solvent to increase solvent diffusivity within the solid.
(c) Reducing cell wall resistance through cavitation (ultrasound) with a possible destruction of cell walls, mainly by using a more intense DIC or US treatment.

2. The transfer of solute within the solvent situated inside the holes of porous materials is usually achieved by diffusion from high solute concentration zones toward low solute concentration zones with the gradient of solute concentration in the solvent as the driving force and D as the standard solute–solvent diffusivity.

$$\frac{\rho_{\text{solute}}}{\rho_{\text{solvent}}}\left(\vec{v}_{\text{solute}} - \vec{v}_{\text{solvent}}\right) = -D_{\text{solute-solvent}}\,\vec{\nabla}\left(\frac{\rho_{\text{solute}}}{\rho_{\text{solvent}}}\right) \tag{3}$$

The different intensification methods which can be envisaged:

(a) To expand the matrix structure: since the solute–solvent process closely depends on the amount of solvent inside the holes of the porous material, the solvent has to be present in higher concentrations inside the solid and this is achieved by increasing porosity using DIC.
(b) To ensure a solute-in-solvent *micro-convection* inside the holes instead of *natural diffusion*: US results in micro-convection in the internal solvent and the operation can be postulated to be a similar type of diffusion within the porous solid, with an effective diffusivity D_{US} that is generally much higher than standard solute–solvent diffusivity D:

$$\frac{\rho_{\text{solute}}}{\rho_{\text{solid}}}\left(\vec{v}_{\text{solute}} - \vec{v}_{\text{solid}}\right) = -D_{\text{US}}\,\vec{\nabla}\left(\frac{\rho_{\text{solute}}}{\rho_{\text{solid}}}\right) \tag{4}$$

Thus the advantages of ultrasonic extraction are: a reduction in both extraction temperature and time; a decrease in the quantity of solvent; and an improvement in solute extraction yield. Oscillatory particle motion produced by high-intensity/variable frequency ultrasonic waves also induces a secondary flow that is known as acoustic streaming.

3.3 Conclusion: Subsequent Combination of DIC and US

To summarize, the expanded structure of DIC products significantly intensifies the extraction kinetics by improving effective diffusivity in a solid, whatever the solvent; solute diffusion in the solvent inside the pore is generally considered to be the limiting process within the expanded structure.

Coupled to ultrasound, internal transfer of solute present within the pore can likewise be intensified by inducing convection transfer rather than diffusion (Amor et al. 2008; Ben Amor and Allaf 2009).

4 Experiments

The following shows experimental results obtained for the extraction of antioxidants using ultrasound with DIC-treated orange peel (Allaf et al. 2012).

Orange peel is an interesting product for several reasons:

1. Orange peel is a by-product and today there is a considerable emphasis on therecovery, recycling, and upgrading of waste products (Garau et al. 2007). This is particularly valid for food and the food processing industry in which waste, effluents, residues, and by-products can be recovered and often upgraded to produce higher value and useful products (Reddy and Yang 2005).
2. Orange peel is a product that contains essential oils and antioxidants. Usually essential oil extraction is achieved after a grinding step. With DIC we can recover essential oil (without grinding) and enhance solvent extraction/ultrasound-assisted extraction (UAE) (Allaf et al. 2013).

To summarize, essential oil extraction was achieved using DIC technology. The DIC-textured solid residue (Fig. 2) was then recovered to extract antioxidants using both solvent extraction and UAE.

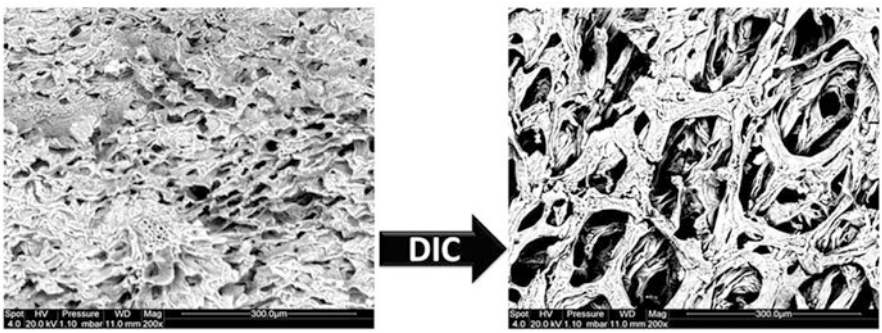

Fig. 2 Scanning electron microscopy of untreated (*left*) and DIC-treated (*right*) orange peel

4.1 Comparative Extraction Yields and Kinetics

Yields and kinetics of naringin and hesperidin extracted from untreated and DIC-treated orange peel followed by 1 h of SE or UAE were compared using HPLC analyses.

The flavanone kinetics results are grouped in Fig. 3. The extraction kinetics of naringin and hesperidin were mostly similar, making it possible to perceive and deduce the action of each process used. It is, however, interesting to note that regarding hesperidin extraction, DIC-SE and RM-UAE showed similar trends, yet combining them gave a complementary effect. Indeed, they act on two different aspects to enhance the extraction. DIC opened the cells, enabling an easy diffusion; ultrasound, through the agitation it provokes, generated an internal convection motion of the solute within the solvent.

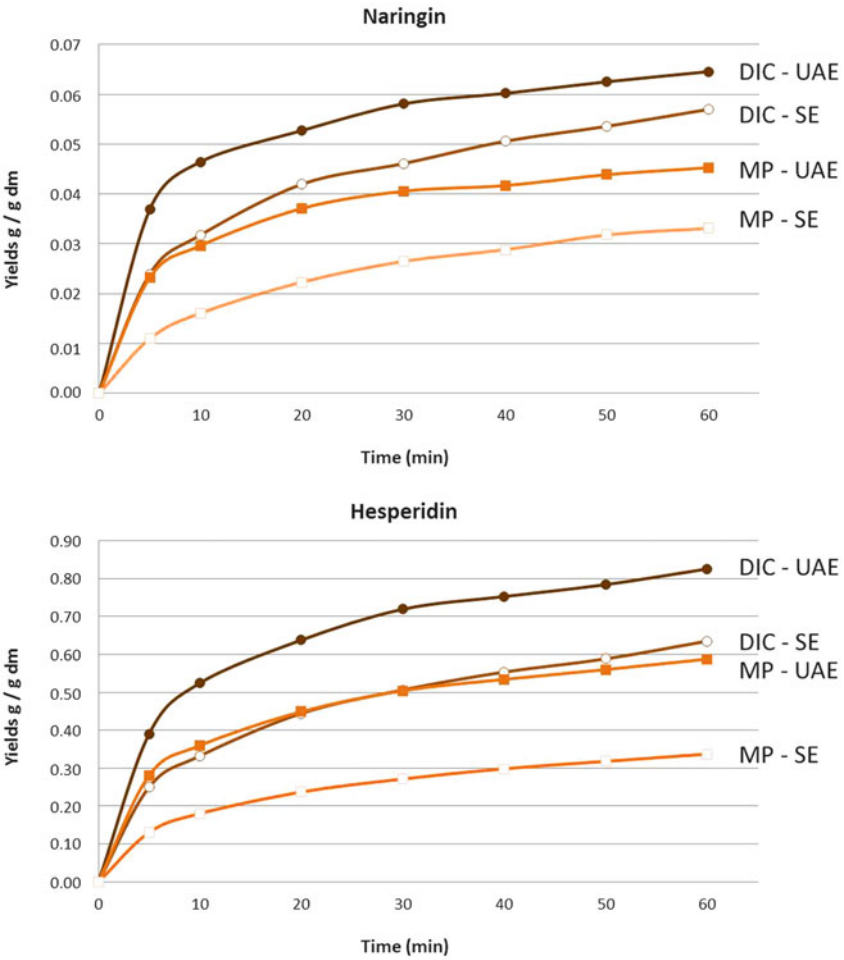

Fig. 3 Naringin and hesperidin extraction kinetics using HPLC analysis

After 60 min of extraction, it was possible to observe large differences in terms of yield and extraction rate.

Consequently, combining DIC with UAE greatly improved the antioxidant extraction yields with markedly improved kinetics compared to standard processes.

To obtain a thorough kinetics analyses, diffusivity and starting accessibility were calculated. The results of a modeling analysis of the extraction kinetics based on the exchange surface and internal diffusion revealed by starting accessibility and effective diffusivity, respectively, are shown in Table 1.

Table 1 Diffusivity and starting accessibility of solvent within different matrices—time for getting 95 % of final extraction

Orange peel	Effective diffusivity (D_{eff}) (10^{-11} m^2/s)	Improvement (%)	Starting accessibility δX_S (g/100 g dry matter)	Starting accessibility ratio (%)	Time (min) for getting 95 % of final extraction ($t_{95\%}$)
Naringin					
RM-SE	4.23	100	1.04	16	310
RM-UAE	5.71	135	2.10	32	211
DIC-SE	13.11	310	2.66	40	100
DIC-UAE	25.22	597	4.31	66	47
Hesperidin					
RM-SE	2.74	100	12.17	14	479
RM-UAE	6.31	231	26.99	32	193
DIC-SE	8.91	326	26.64	32	150
DIC-UAE	26.10	954	50.60	60	49

RM-SE raw material extracted by solvent extraction, *RM-UAE* raw material extracted by ultrasound assisted extraction, *DIC-SE* DIC treated material extracted with solvent, *DIC-UAE* DIC treated material extracted by ultrasound assisted extraction

The raw material extracted with standard SE (RM-SE) was taken as a basis for comparison. Regarding naringin extraction, the effective diffusivity and starting accessibility of DIC-UAE were six and four times higher, respectively, than that of RM-SE. With regard to hesperidin extraction, the effective diffusivity and starting accessibility of DIC-UE were 9.5 and 4 times higher, respectively, than that of RM-SE.

The time taken to achieve 95 % of the final extraction of naringin (assuming that the availability was the same for all the samples) resulted in significant differences between the different materials. Indeed, $t_{95\%}$ was around 5 h for RM-SE, 3 h 30 min for RM-UAE, while it was 1 h 30 min for DIC-SE and less than 1 h for DIC combined with UAE.

4.2 Antioxidant Activity

Phenol antioxidants can reduce reactive oxygen species, including free radicals, at variable rates. Antioxidant activities indicated that the extracts had an anti-radical activity that corresponded to the higher antioxidant concentration. The antioxidant activity of each sample was expressed in terms of IC_{50} (micromolar concentration required to inhibit DPPH radical formation by 50 %) (Mimica-Dukic et al. 2004).

Table 2 IC_{50} (%) as indicator of antioxidant activity of matrices (lower is better)

	DIC + UAE	DIC + SE	RM + UAE	RM + SE
IC_{50} (%)	0.54 ± 0.01	0.62 ± 0.02	1.06 ± 0.03	1.20 ± 0.07

As shown in Table 2, ultrasounds enabled increasing the antioxidant activity of the extract by approximately 13 % (IC_{50} was 1.20 ± 0.07 % for the raw material with SE and 1.06 ± 0.03 % with UAE). Moreover, DIC pretreatment triggered a rise of antioxidant activity twice as high as untreated material regarding both SE and UAE; indeed IC_{50} was 0.62 ± 0.02 % with SE and 0.52 ± 0.01 % with UAE.

5 Conclusion

Fundamental studies on solvent extraction allowed us to define the limiting processes, and thus to propose an expansion by instant controlled pressure drop (DIC), subsequently combined with UAE, as a means of intensification. The operations were coupled to increase the kinetics through the parameters of effective diffusivity D_{eff} and starting accessibility δX_s.

Studies on both the fundamental and experimental aspects regarding various other innovative technologies, DIC/US, DIC/SCF (supercritical fluids), and DIC-MW (microwaves), improved the extraction process in terms of energy consumption, yields, δX_s, D_{eff}, etc. and the end product quality in terms of antioxidant activity.

Pretreatment by DIC and UAE can both improve antioxidant extraction yields and kinetics. The highest yield of hesperidin with the best kinetics was obtained by coupling the treatments. We also note that UAE treatment generated a higher antioxidant activity than standard SE and this was even higher when UAE was performed on a DIC-treated matrix. The impact of DIC on the microstructure provided a reliable explanation for our results. The swelling of the cells enabled a better kinetic extraction in terms of diffusivity and starting accessibility. Accordingly, previous experimental results were highlighted here and the fundamental aspects incorporated into the model.

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