Filtration-compression step as downstream process for flavonoids extraction from citrus peels: performances and flavonoids dispersion state in the filtrate

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Keywords: downstream process; filtration-compression; enzymatic treatment; grapefruit peels; flavonoids

Highlights:

- Filtration-compression for downstream processing of flavonoid extraction from peel
- Identification of the maximum extractable liquid of peel by filtration-compression
- Cell-wall degrading enzymes favour naringin and narirutin extraction from peel
- Identification of the dispersion state of flavonoids for a relevant post-extraction

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Abstract

Initiative of waste treatment has to be based on user-friendly technologies, using robust, cost-effective and low-energy consuming processes. The global objective of this study was to reduce technical steps for the extraction of flavonoids (naringin and narirutin) from citrus peel (grapefruit peel). After a first fresh peel grinding, the relevance of a simple filtration-compression, as a first downstream process, of the obtained slurry was studied. An optimization of this solid-liquid separation was proposed and the impact of a pectinolytic enzymatic treatment, resulting potentially in a larger release of flavonoids, was investigated. The results demonstrated that a preliminary step of filtration-compression, directly realized on fresh grinded peels as downstream processing for flavonoids extraction could be pertinent and that the enzymatic treatment improved the slurry filterability. An optimal separation was obtained with a transmembrane pressure of 5 bar, leading to highest extractable liquid phase volume and to an extraction around 80% of naringin and narirutin. A modelling of the filtration step, essential for the scaling of a filtration-compression process on site, was proposed. An originality of this work was to identify the dispersion state of the flavonoids within the liquid phase, capital identification for a relevant choice of the subsequent extraction step of these compounds.

Abbreviations and nomenclature

d_{50}	Mean diameter (µm)
J	Filtration rate ($m.s^{-1}$)
J_0	Initial filtration rate ($m.s^{-1}$)
K_b	Blocking constant for complete blocking law (m^{-3})
K_c	Blocking constant for cake filtration law (m^{-3})
K_i	Blocking constant for intermediate blocking law (m^{-3})
K_s	Blocking constant for standard blocking law (m^{-3})
M	Filtrate mass (g)
$M_{add.}$	Mass of water added for the enzymatic treatment (g)
M_{DM}	Mass of dry matter in slurry (g)
$M_{ext.liq.}$	Mass of extracted intrinsic liquid
M_F	Maximum filtrate mass (g)
$M_{liq.}$	Total liquid mass of the grinded peel (g)
t	Filtration time (s)
TMP	Transmembrane pressure (bar)
V	Filtrate volume (m^3)
w	Enzymatic solution/slurry mass ratio (g/g)

Greek letters

η	Theoretical filtration efficiency (%)
η*	Experimental filtration efficiency (%)
Ω	Filtration surface (m^2)

Index

DM	Dry matter
ET	Enzyme treated slurry
H	Heating (50°C, 2 hours)
NT	Non-treated slurry
W	Water addition in a ratio 1/1
W+H	Water addition in a ratio 1/1 + Heating (50°C, 2 hours)

1. Introduction

Citrus genus (orange, mandarin/tangerine, grapefruit and lemon/lime) is among the largest cultivated fruit crops in tropical and subtropical regions worldwide, with a global production of 92.088 million metric tons in 2017/18, and is expected to increase further in the future [1]. About a quarter of the harvested fruit is transformed into various commercial products such as juice, jam, marmalades and flavouring agents, using only about 50% of the total fruit. Hence, these transformations generate yearly 11 million metric tons of wastes and by-products, which are considered harmful to soil and water bodies due to their low pH (3-4), high water (around 80-90%) and organic matter (95% of total solids) contents [2–4]. Yet today waste management is at the heart of the concerns with the sustainable food systems development aiming at a « 0 waste » production but also with the biorefinery tendency of the food industry [3,5,6]. For Southern citrus industries (ensuring 70-80% of the total citrus production [1,7]), due to their insufficient infrastructure, little or no valorisation are ensured. Thus, peels, pulp and seeds are generally discarded on adjacent land leading to the generation of putrefying waste. Sometimes, theses by-products are valorised as cattle feedstock but with a low economic interest as this valorisation requires a previous drying which is a high-energy consuming operation.

These practices are particularly unfortunate, as *Citrus* by-products can be considered as a cheap source of high-added value components such as vitamins, minerals, essential oils, fibres and bioactive compounds mainly carotenoids, and polyphenols [2–4,8,9]. Flavonoids are polyphenolic compounds with a wide spectrum of beneficial effects; this includes anticancer, antiatherosclerotic, cardiovascular, anti-inflammatory, neuroprotective, hypolipidemic, antidiabetic, hepatoprotective activities and applications in the treatment of bone disorders [10–13].

In the literature, one of the most studied valorisation ways for Citrus by-products is the recovery of flavonoids from peels. This recovery purpose requires not only efficient extraction technology

106 but also various preliminary treatments of the peel, facilitating first its storage before extraction
107 and secondly the solid/liquid separation step. Generally, a safe storage is ensured by drying (hot
108 air, freeze-drying….). Then, with an objective to facilitate the mass transfer during extraction,
109 grinding eventually followed by sifting is carried out to reduce and homogenize the particle size
110 [14]. Extraction of the target compounds is generally combined with treatments or technologies
111 facilitating the flavonoids transfer from the solid to the liquid phase. This step has attracted
112 considerable scientific interest and thus several traditional or emerging extraction technologies
113 are proposed in the literature: solvent extraction [15], hot-water extraction [16], ultrasound-
114 assisted [15,17,18], microwave-assisted [19–21], enzyme-assisted [22], pulsed electric fields
115 [23,24], high voltage electrical discharge [25] subcritical water [26–28], and supercritical CO_2
116 [29–32].

117 However, in Southern countries, the sustainability of waste treatment is threatened by the lack of
118 financial resources and technical support. Moreover, most of the aforementioned processes,
119 mostly studied at laboratory scale, require a high investment or high-energy consumption making
120 these technologies non-suitable for those countries. As the success of valorisation initiative is
121 based on the user's acceptance toward easy and user-friendly technologies, it seems pertinent to
122 think about a high-added-value compounds recovery chain using optimized green, simple, robust,
123 cost-effective and low-energy consuming processes. Our study fell within this context, with the
124 aim to avoid a maximum of preliminary stages, especially the highly energy consuming drying
125 step, before the extraction of flavonoids from Grapefruit (*C. paradisi*), rich source of naringin
126 and narirutin [33].

127 Thus, the objective of this work was to study the relevance of a simple filtration-compression
128 step directly done on the fresh grinded peels as a first downstream process for flavonoids
129 extraction. The optimization of the solid-liquid separation was based on the estimation of the
130 mass of the mechanically extractable liquid phase from the slurry under different transmembrane

pressures, combined with the quantification of the flavonoids (narirutin and naringin) content in the filtrate. Before the filtration in a pressurized filtration-compression cell, fresh peels were grinded to form a slurry with an objective to favour mass transfer by an increase of the exchange surface and a disruption of plant tissues, flavonoids being considered to be largely stocked within the cell vacuoles [24]. The potential impact on the solid-liquid separation of a pectinolytic enzymatic treatment, causing a cell wall degradation resulting potentially in a larger release of flavonoids, was investigated. An originality of this work was also to identify the dispersion state of the flavonoids within the mechanically extractable aqueous phase obtained after this preliminary solid-liquid separation. This last investigation was supposed to be capital for a relevant choice of the following extraction of these compounds.

2. Materials and Methods

2.1. Grapefruit peel supply and storage

Grapefruits (*Citrus paradisi*, Star ruby from Turkey, provided by Terreazur, Saint-Jean-de-Védas, France) were first bleached. Flavedo, which can be valorised through the extraction of essential oils [4], was then manually removed from the peel, the target flavonoids being mostly contained in the albedo [34–38]. Then, juice was extracted using an electric juice extractor (ZX7000, Krups). Albedo and pulp rests (core, juice sacs and segment rests), representing in our experiments about 35% of the weight of the total fruit, were then manually cut into small pieces (around 10 x 10 mm) and stored at -25°C.

2. 2. Experimental methodology

2.2.1 Grinding

After defrosting at room temperature (45 min to 1 hour), peels were subjected to grinding. Grinding was ensured using a hand blender (Moulinex DD873D10 Infiny Force ultimate, France) for

156 1.5 minutes at 1 kW (corresponding to a 9.10^5 J·kg^{-1} of fresh peel). After grinding, a thick
157 suspension, i.e. a slurry, was obtained.
158
159 *2.2.2. Enzymatic treatment*
160 The enzymatic treatment was based on the use of Peclyve® PR (Soufflet biotechnologies®), a
161 commercial pectinolytic enzyme preparation with two main pectinase activities, Pectin-methyl-
162 esterase (EC3.1.1.11; 150 U/g) and Pectin-lyase (EC4.2.2.10; 1100 U/g). An enzymatic solution
163 was prepared with the objective to provide 0.3 g of enzyme per kg of slurry, with a mass ratio
164 solution/slurry (*w*) of approximatively 1/1. The enzymatic treatment consisted in the mixing of
165 the slurry and the enzymatic solution during 2 h at 50°C. These operating conditions were
166 recommended by Soufflet biotechnologies® for an optimal enzyme activity.
167
168 *2.2.3. Filtration-compression*
169 The liquid phase of the raw (NT) or enzyme treated (ET) slurry was extracted by filtration-
170 compression.
171 Filtration-compression experiments were carried out with a pressurized cylindrical cell of 70 mm
172 internal diameter and 0.60 L volume (Figure 1). A perforated disk was located at the bottom of
173 the cylinder to support a plane cotton cellulose membrane of 6 µm in pore size (Whatman,
174 Maidstone, UK); the pore size of 6 µm was supposed to retain the great majority of the suspended
175 solids, while allowing acceptable filtration rate. Transmembrane pressure (TMP) was applied by
176 a pneumatically driven-piston dragged by nitrogen gas.
177 With an objective to compare and discuss flavonoids extraction efficiencies, filtrations were
178 operated from same mass of dry matter (around 3.5 g), whatever the type of slurry (ET or NT);
179 thus the initial slurry mass (or volume) to be filtered was different for NT and ET slurry (20 g
180 and 40 g respectively, according to their different water content).

Filtration-compression experiments were carried out at different transmembrane pressures (1, 3, 5, 7 and 10 bar).

The filtrate mass (M) was monitored during time until its stabilization; M_F, maximum filtrate mass, was considered as the maximum mass of the liquid phase that could be extracted from slurry by filtration-compression at the defined operating condition (i.e. TMP).

At the end of the filtration, filter cake and filtrate were recovered and characterized.

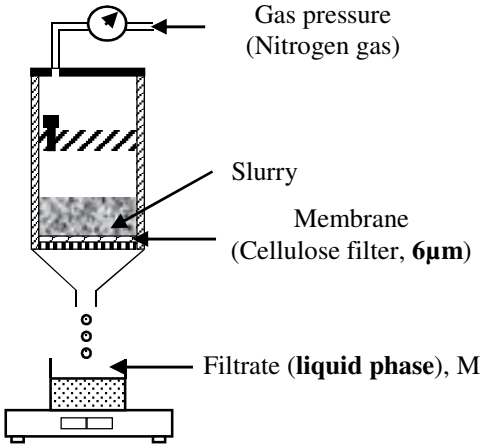


Figure 1. Filtration-compression cell

The filtration efficiency, in terms of extracted liquid volume, was estimated for the two slurries, i.e. the raw (NT) one and the enzyme treated (ET) one.

The NT slurry filtration efficiency η_{NT} (given by Eq.(1)) was defined by the ratio between the extracted liquid mass, $M_{ext.liq.NT}$, and the total liquid mass of the grinded fresh peel $M_{liq.}$.

$$\eta_{NT} = \frac{M_{ext.liq.NT}}{M_{liq.}} \quad (1)$$

Regarding ET slurry filtration, the total liquid mass corresponding to the liquid mass present in the grinded fresh peel $M_{liq.}$ plus the added water ($M_{add.}$ due to addition of the enzymatic solution), η_{ET} was given by Eq.(2):

$$\eta_{ET} = \frac{M_{ext.liq.ET}}{M_{liq.} + M_{add.}} \quad (2)$$

With the suppositions that (i) the enzymatic treatment did not modify the part of the mechanically removable liquid of the slurry and (ii) all the water added ($M_{add.}$) for the enzymatic treatment is easily removed by filtration, then, the theoretical ET slurry filtration efficiency η_{ET} can be given by Eq.(3):

$$\eta_{ET} = \frac{M_{ext.liq.NT} + M_{add.}}{M_{liq.} + M_{add.}} \quad (3)$$

Considering the enzymatic treatment protocol (with $M_{add.} = w(M_{DM} + M_{liq.})$, where M_{DM} is the mass of dry matter in slurry), η_{ET} can be deducted from η_{NT} by Eq.(4):

$$\eta_{ET} = \frac{\eta_{NT} + w\,(1 + \frac{M_{DM}}{M_{liq.}})}{1 + w\,(1 + \frac{M_{DM}}{M_{liq.}})} \quad (4)$$

2.3. Physicochemical and biochemical characterization

2.3.1. Physicochemical characterization

Dry matter content determination: Slurry, filter cake and filtrate dry matter content was determined according to the AOAC method with some modifications [39]. Samples were homogenously distributed on aluminium dishes and kept in a vacuum oven (Heraeus RVT 360, Hanau, Germany) at 70°C for 48h. Water content was determined from the weight difference before and after drying. Each measure was done in triplicate.

Particle size distribution: Particle size distribution (in percentage of volume density) and mean diameter (d_{50}) of NT and ET slurries were determined by Laser diffraction using a Malvern Mastersizer (Mastersizer 3000, Malvern Instruments Limited, Worcestershire, UK) equipped

214 with a HydroMV® cell. Refractive indices of 1.73 and 1.33 were used for cloud particles and
215 dispersion phase and 0.1 was used as the absorption index of cloud particles [40]. Samples were
216 introduced into the volume presentation unit, which already contained deionized water; in this
217 unit, the diluted sample was gently stirred and pumped through the optical cell.
218 *Flavonoids dispersion state:* Filtrate was considered as an aqueous solution in which colloidal
219 and supra-colloidal particles were suspended. These insoluble particles were supposed to be
220 remaining vegetable tissue and cellular rests and therefore to be susceptible of containing
221 flavonoids. In order to identify the dispersion state of naringin and narirutin within the filtrate,
222 centrifugation of the filtrate for 4 hours at 20 000 g was proposed; this centrifugation operating
223 condition was chosen with the objective of separating the soluble fraction from the rest of the
224 suspension. According to Stokes law, a cut-off size of approximately 100 nm was supposed to
225 be reached with this chosen centrifugation time and acceleration; the separation selectivity has
226 been subsequently confirmed by means of particles-size measurements (Dynamic Light
227 Scattering). Flavonoids (naringin and narirutin) present in the centrifugation pellet, supposed on
228 crystallized form or bound to some larger solids, were considered as *insoluble* flavonoids.
229 Flavonoids present in the supernatant, supposed solubilized or potentially bound with some
230 colloids or macromolecules, were considered as *soluble* ones.
231
232 *2.3.2. Flavonoids biochemical characterization*
233 Naringin and narirutin content of the slurry and filtrates was estimated by High Performance
234 Liquid Chromatography (HPLC) analyses. A solvent extraction was performed using a modified
235 method based on [41] to estimate the total content of flavonoids in the samples.
236 A mass of slurry (corresponding to 250 mg of dry matter) or a volume of 500 µl of filtrate was
237 withdrawn and diluted with 5 ml of dimethylformamide (DMF) and 5 ml of ammonium oxalate
238 (0.05 M). Afterwards, samples were placed in a hot oil bath (90°C) for 10 minutes, cooled and

adjusted to 18 ml for filtrates and 25 ml for slurries. Solutions were then filtered through 0.45 µm Whatman cellulose acetate syringe filters (Sigma-Aldrich, St Louis, MO) before injection.

Naringin and narirutin content was quantified using an Agilent 1200 series HPLC system equipped with a degasser, a quaternary pump, an auto-sampler, a thermostated column compartment, and a diode array detector DAD. Separation of flavanones was performed using a C18 column (Uptisphere HDO 5 µm, 250 mm × 4.6 mm, Interchim, Montluçon, France). The mobile phase consisted of an isocratic solvent system combining solvent A (water/acetic acid, 99/1, v/v), solvent B (acetonitrile), and solvent C (tetrahydrofuran) - A/B/C 80/16/4, v/v/v. The flow was set at 1 mL/min and the column was heated at 25°C. UV detector was set at 280 nm, an aliquot of 20 µL was injected.

3. Results and Discussion

3.1. Slurry characterization

The physicochemical and biochemical properties of fresh peel and slurries with (ET) and without an enzymatic treatment (NT) are shown in Table 1.

The fresh peel and the NT slurry presented similar characteristics in terms of dry matter (DM) and water content, around 17 and 83 g per 100 g of wet matter (i.e. fresh peel or slurries) respectively; these values were coherent with the ones available in the literature [42,43]. The enzymatic treatment, requiring a water addition, increased the water content of the ET slurry until 91 g per 100 g of wet matter, coherent value considering the addition of an enzymatic aqueous solution close to a 1/1 ratio.

Table 1
Physicochemical properties of fresh peel and slurries

	Fresh Peel	NT slurry	ET slurry
Dry matter			
g/100 g wet matter	17.3 ± 0.9	17.3 ± 0.5	8.6 ± 0.2
Water content			
g/100 g wet matter	82.6 ± 0.9	82.7 ± 0.5	91.4 ± 0.2
d_{50}			
µm	-	716 ± 19	575 ± 17
Naringin			
g/100 g dry matter		5.1 ± 0.4	
g/100 g wet matter		0.9 ± 0.1	
Narirutin			
g/100 g dry matter		0.57 ± 0.02	
g/100 g wet matter		0.1 ± 0.01	

The particle size distributions of NT and ET slurries are given in Figure 2. The NT slurry was composed of particles ranging from approximately 25 to 3500 µm, with a relatively important volume percentage of particles around 1000 µm; the d_{50} was about 716 µm. If the enzymatic treatment did not significantly modify the size distribution shape, it was however noted that the amount of particles with size from 300 to 2000 µm was reduced while the percentage of particles with size from 10 to 300 µm increased. These results suggested that a part of the larger particles were broken under the effect of the enzymatic treatment. Pectin-methyl esterase and pectin-lyase had almost certainly catalysed the demethylation and the depolymerisation of pectin in the albedo [44], leading to the weakening of cell structures and a consequent particle size reduction [45]. As a consequence of this size distribution modification, a decrease of the d_{50} was observed after the enzymatic treatment.

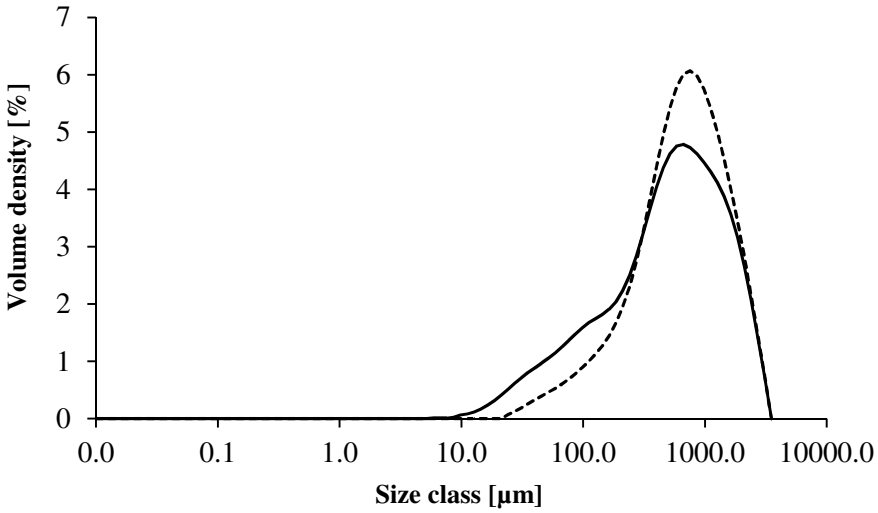


Figure 2. Particle Size distribution of: – ET slurry and --- NT slurry

The total concentration of naringin and narirutin in NT slurry, estimated per 100 g of dry matter and wet matter, are given in Table 1. The concentration of naringin was about 10 times higher than the narirutin one. Grapefruit naringin and narirutin concentrations found in the literature for the different parts of the fruit are reported in Table 2. This bibliographic review indicated that the measured concentrations were in the same range of those found in literature for albedo and confirmed the large presence of naringin and narirutin in peel, and specifically in albedo. The significant variability observed in the values reported in Table 2 could be easily explained by various factors (e.g. fruit origin, fruit variety, manufacturing procedures, storage conditions…) but also variation in the degree of maturity of the fruit [35,36,46–48].

Table 2
Naringin and Narirutin content in grapefruit (*C. paradisi*)
[a] *g/100g juice*
[b] *g/100g wet matter*

	Juice	Flavedo	Albedo
Naringin	0.006 – 0.087[a,[36-38]]	0.35 – 0.99[b,[34,35]]	0.62 – 2.7[b,[34,35]]
Narirutin	0.009 – 0.012[a,[4]]	0.11[b,[2]]	0.23[b,[2]]

3.2. Filtration-compression of the slurry

Figure 3 presents the evolution of the filtrate mass (*M*) versus time, for NT and ET slurries during filtration at different transmembrane pressures.

As it can be observed, the applied transmembrane pressure influenced the quantity of collected liquid at the end of each filtration, i.e. M_F. Recovered filtrate mass was higher for ET slurry than for NT one, which was coherent with the filtration protocol (filtration of the same mass of dry matter, whatever the slurries), leading to the filtration of a higher mass of ET slurry than of the NT slurry (considering the addition of the enzymatic solution and consequently of water to the slurry).

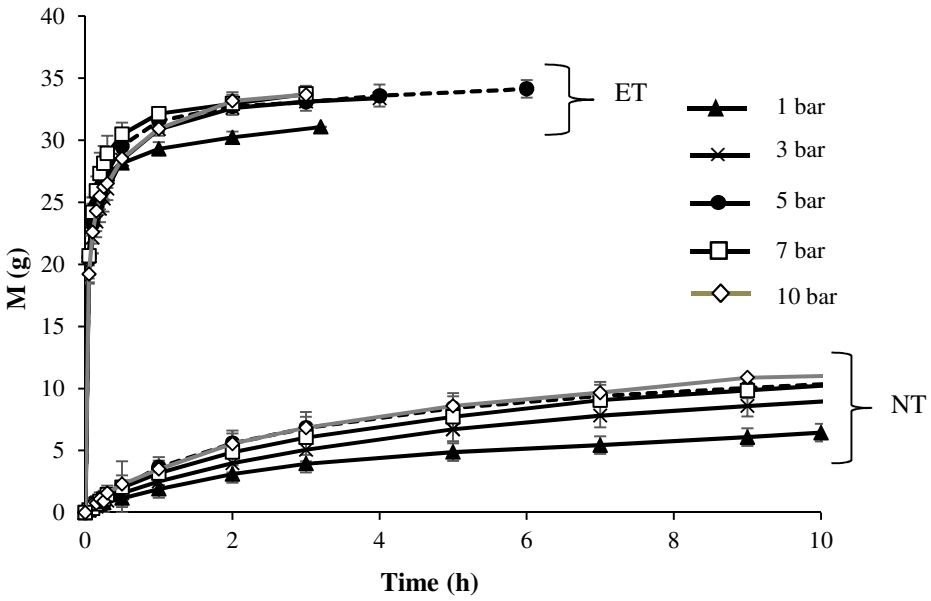


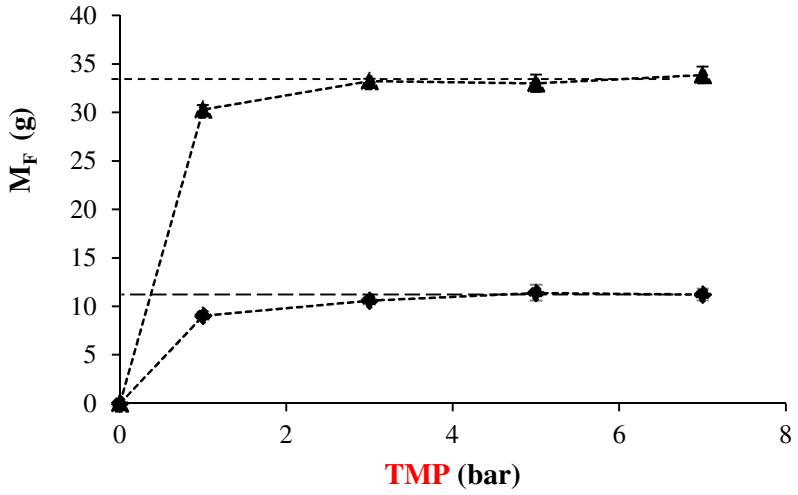
Figure 3. M_F versus filtration time at different transmembrane pressures, for NT and ET slurries

The influence of pressure and of the enzymatic treatment on the solid/liquid separation efficiency of filtrations is discussed below. The description of the evolution of the filtrate mass, through the study of the fouling mechanisms, is also proposed with an objective to provide some indication about the fouling propensity of NT and ET slurries.

321 *3.2.1. Solid/liquid separation efficiency*

322 Figure 4 represents the maximum recovered filtrate mass (M_F), corresponding to the steady
323 filtrate mass, versus each applied transmembrane pressure.

324 An increase of the transmembrane pressure TMP, from 1 to 5 bar, induced an increase of M_F.
325 For NT and ET slurries, all the curves tend towards an asymptote corresponding to a M_F value
326 closed to 12 and 34 g respectively.



327

328 **Figure 4.** M_F value versus TMP (NT ♦, ET ▲)

329

330 Figure 4 shows that, in the presence or absence of an enzymatic treatment, a transmembrane
331 pressure of 5 bar appeared to be sufficient to reach the asymptote and thus to extract all the
332 mechanically extractable liquid part of the slurry. The nature of the interactions between the
333 liquid (aqueous solution) and solid (e.g. pieces of vegetable tissues as cell wall fragments,
334 proteins, pectin and fibres …) phases of the slurry could explain this result. In a complex medium,
335 as slurry, the solid/liquid interactions can be low or high, in relation with the liquid binding forces
336 [49–52]; at least two types of water can be defined: free and bounded water, respectively
337 concerned by low and high interactions with solids. The experimental distinction between these
338 two types of water can be based on water activity [53], freezable and non-freezable ability [54]

or extractability by mechanical means [55]. This last definition, according to our experimental strategy and the obtained results, led us to admit that mechanical action imposed by pressure in a filtration-compression cell promoted the release of the slurry free liquid. Thus, results revealed that, for grinded grapefruit peels, with or without enzymatic treatment, a pressure of 5 bar appeared to be sufficient to extract all the easily removable liquid, i.e. free water. For ET slurry, the extracted liquid phase corresponded not only to the free liquid of the fresh grinded peel, but also included the water added for the enzymatic treatment, water considered as free water and therefore very easily extractable by filtration-compression.

However, with an objective to verify if enzyme presence and action were susceptible to modify the interactions between solids and liquid, i.e. if enzymes were susceptible to modify the quantity of the mechanically removable liquid part of the slurry, the estimation of the theoretical filtration efficiency η_{ET} (estimated from η_{NT}, through Eq. 4) was compared to the experimental one, η^*_{ET}, estimated through the quantification of dry matter and water content of the filtrate and filter cake. Table 3 presents the characteristics of the slurry, filter cake and filtrate in terms of dry matter and water content and extraction efficiencies, from 5 bars-trials (i.e. for pressure conditions allowing to extract the maximum of the liquid phase). Mass balance was approximately verified, considering the losses of matter (between approximately 10 and 20%, i.e. stagnant water in filtrate tube, arduous separation of filter cake from filtration membrane, deposit on the walls of the filtration-compression cell…).

Table 3
Slurry, filter cake and filtrate characterization

	Slurry (g)				Filter cake (g)			Filtrate (g)			η
	Total mass	Added water mass	DM mass	Water mass	Total mass	DM mass	Water mass	Total mass	DM mass	Water mass	
NT	20.1 ± 0.0	0.0	3.5 ± 0.1	16.6 ± 0.1	5.21 ± 0.3	1.97 ± 0.17	3.05 ± 0.20	11.6 ± 0.3	1.2 ± 0.0	10.4 ± 0.3	**63 ± 2%**
ET	39.9 ± 0.3	20.0 ± 0.1	3.5 ± 0.1	36.5 ± 0.2	3.14 ± 1.3	0.94 ± 0.09	2.20 ±1.06	33.5 ± 1.3	2.2 ± 0.1	31.3 ± 1.2	**86 ± 2%**

360 The enzymatic action was first observed through the difference between ET and NT filtrate dry
361 matter content, as well as ET and NT filter cake one (Table 3). The evolution of the slurry particle
362 size distribution after enzymatic treatment (Figure 2) had induced a reduction of solids retained
363 by the membrane (pore size around 6 µm) and inversely an increase of solids in the filtrate
364 (greater presence of finer fragments).

365 Concerning the comparison between the experimental and theoretical (i.e. calculated) filtration
366 efficiency, an experimental efficiency of 86% was obtained while the theoretical one, that was
367 based on the fact that the enzymatic treatment did not modify the mechanically removable part
368 of liquid, was equal to 83% (according to η_{NT} and Eq. 4). This comparison demonstrated that, in
369 modifying the cell structures and solids physicochemical characteristics, the enzymatic treatment
370 could slightly increase the mechanically removable part of liquid of the grinding fresh peel
371 (ANOVA, $p < 0.01$).

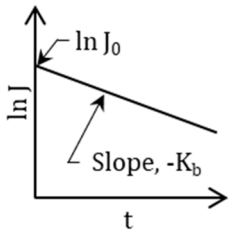
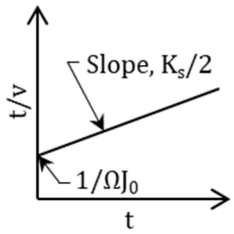
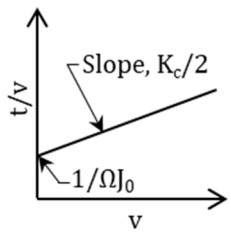
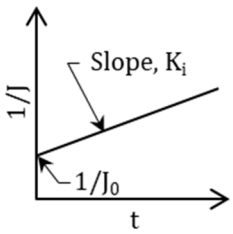
372

373 *3.2.2. Filtration modelling and fouling propensity of the slurry*

374 We proposed to describe the filtrate mass (M) evolution during filtration time through classical
375 filtration modelling at constant pressure, i.e. Hermia models. The Hermia models consist of four
376 different filtration mechanisms: complete blocking, standard blocking, intermediate blocking,
377 and cake formation. The cake formation model, initially established by [56,57], considers that
378 during filtration, fouling is due to a cake formation on the surface of the filter medium,
379 corresponding to the deposit of particles of larger size than the membrane pore size. Both
380 complete and intermediate blocking laws describe the pore plugging due to foulants reaching the
381 top surfaces of pores. In contrast, the standard blocking law deals with the pore constriction
382 caused by the deposition of foulants onto the pore wall. Table 4 presents mathematical equations
383 giving the relation between the filtrate volume V and the filtration time t, for each filtration law

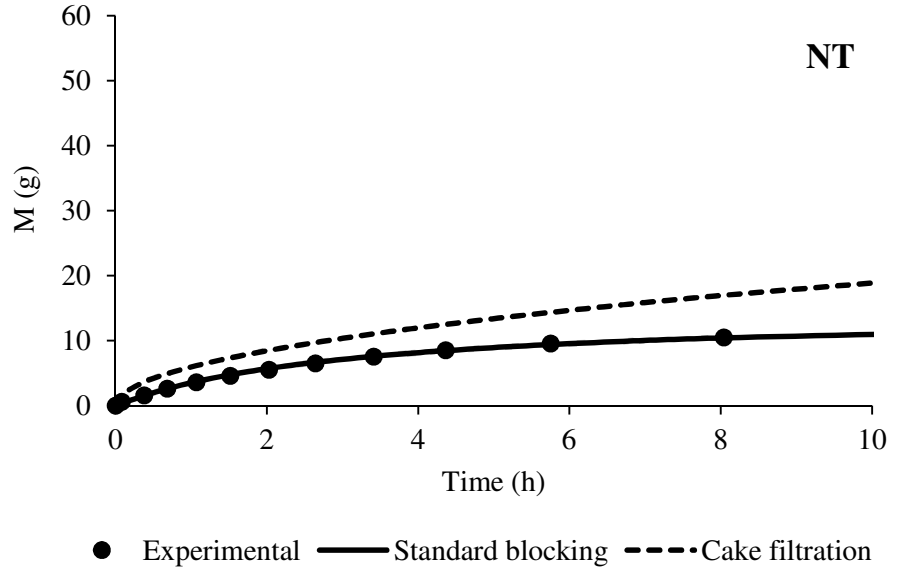
384 at constant pressure condition [58]. As proposed by [58], the predominant blocking filtration
385 laws describing fouling pattern were determined from plots based on linear expressions of the
386 law (Table 4), allowing a rapid identification of the relevant fouling mechanisms. If standard
387 blocking and cake filtration models could describe experimental pattern for NT slurry, standard
388 blocking and intermediate blocking were more suitable to describe the fouling evolution of ET
389 slurry.

390 **Table 4**
391 Blocking filtration equations for constant pressure filtration [55]

Function	**Complete blocking**	**Standard blocking**	**Intermediate blocking**	**Cake filtration**
$v = f(t)$	$v = \frac{J_0}{K_b}\{1 - exp(-K_b t)\}$	$\frac{t}{v} = \frac{K_s}{2}t + \frac{1}{J_0\Omega}$	$K_i v = ln(1 + K_i J_0 t)$	$\frac{t}{v} = \frac{K_c}{2}v + \frac{1}{J_0\Omega}$
$J = f(t)$	$J = J_0\, exp(-K_b t)$	$J = \frac{J_0}{\left(\frac{K_s J_0}{2}t + 1\right)^2}$	$K_i t = \frac{1}{J} - \frac{1}{J_0}$	$J = \frac{J_0}{\left(1 + 2K_c {J_0}^2\right)^{1/2}}$
Linear graphical representation				

392
393

394 Figure 5 presents the theoretical evolution associated to the models providing the better
395 description of the experimental one for 5 bar experiments; similar results were obtained for the
396 other filtration pressures.



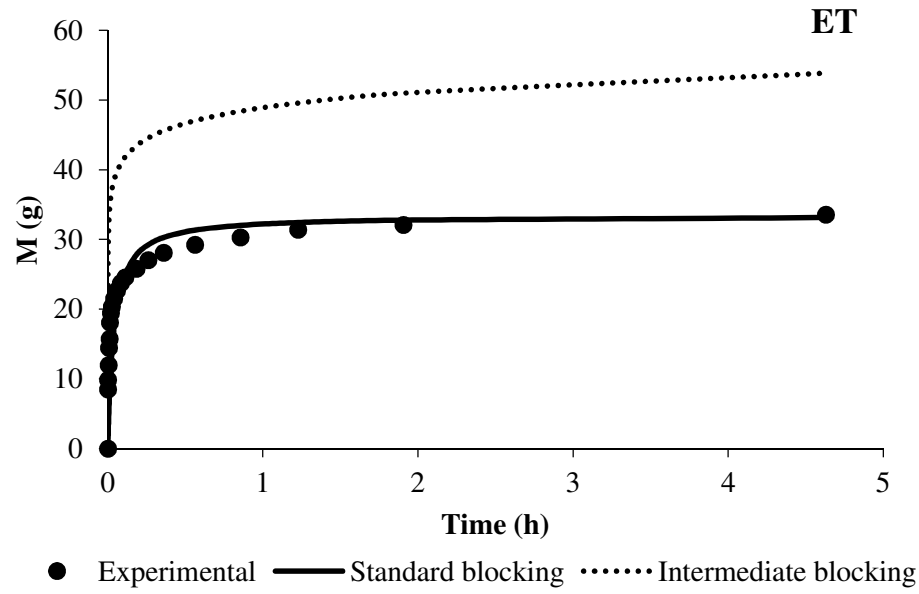


Figure 5. Theoretical and experimental evolution of M versus time (5 bar, filtrate density of 1040 kg.m^{-3})

As it can be observed in Figure 5, the standard blocking law is the only law describing properly the evolution of M versus time, demonstrating a possible membrane pore constriction caused by the deposition of foulants into the pore wall, and this, independently of the slurry modification induced by the enzymatic treatment. Thus, filtration models demonstrated that if the filtration kinetic of NT and ET slurries was different, the filtration behaviour of these two suspensions were comparable in terms of fouling mechanisms whatever the applied pressure.

Table 5 presents the value of K_s, blocking constant for standard blocking law, in m^{-3}, for the two types of slurry at 5 bar. Considering that lower is K_s, higher is the filtrate volume V for a filtration time t, the enzymatic treatment was supposed to be favourable to a weak fouling and consequently a rapid filtration. This result was consistent with the use of pectin-methyl esterase and pectin-lyase to enhance juice filterability notably through a reduction of the juice viscosity [59]. This modelling and the estimation of the K_S constant could be very useful for the implementation of a filtration-compression process, with an objective of providing and achieving a sustainable productivity.

Table 5
Standard blocking constant (5 bar, filtrate density of 1000 $kg.m^{-3}$)

Standard blocking model	$\frac{t}{v} = \frac{K_s}{2}t + \frac{1}{J_0\Omega}$	
	NT	**ET**
Ω (m^2) x 10^4	38	38
J_0 ($m.s^{-1}$) x 10^7	3 ± 0.2	1 210 ± 800
K_s (m^{-3})	**139 000 ± 1400**	**70 000 ± 10 000**

3.3. Flavonoids extraction efficiency

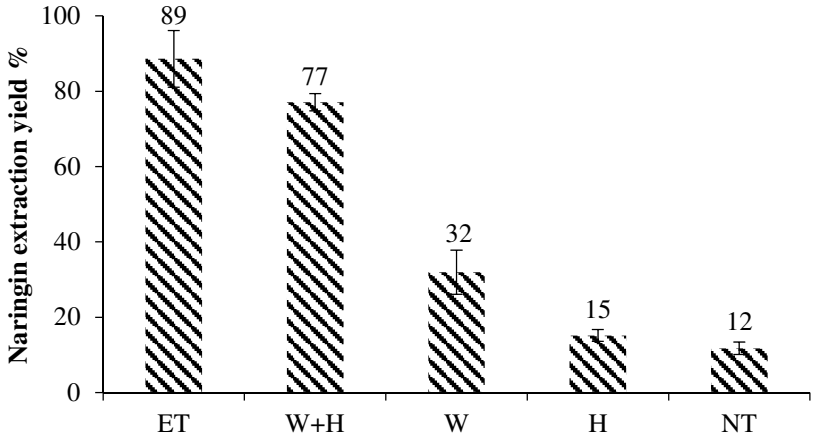
3.3.1. Identification of the role of the operating conditions

Figure 6 and Figure 7 show the extraction yields of naringin and narirutin for filtration at 5 bar (i.e. the lower transmembrane pressure inducing the maximum liquid extraction).

For ET slurry, approximately 89% (4.5 g per 100 g of peel dry matter) of the naringin and 92% (0.5 g per 100 g of peel dry matter) of narirutin were recovered in the filtrate; lower yields were obtained without enzymatic treatment, i.e. 12% and 61% respectively. Similar data were reported by [60] and [15] with recovery of 4.1 g (hot methanol extraction) and 3.6 g (ultrasound-assisted extraction) of naringin per 100 g of peel dry matter respectively.

429 The high recovery of naringin and narirutin obtained for the ET slurry could be explained by the
430 hydrolytic effect of the enzyme on pectin, inducing cell wall disruption and consequently
431 enhancing the release of these flavonoids into the extracellular liquid phase recovered by
432 filtration.

433 However, with the objective to discriminate the effect of the added enzymes from that of the
434 operating conditions associated with the enzymatic treatment (heating and water addition),
435 complementary experiments were carried out: (i) heating of the NT slurry in the same conditions
436 as for the enzymatic treatment (50°C for 2 hours) (H), (ii) addition of water to the NT slurry in
437 the same ratio (w) as for the enzymatic treatment (W) and (iii) heating and water addition in the
438 same conditions as for enzymatic treatment (50°C for 2 hours, same w) (W+H). This
439 complementary study could also be pertinent, with an objective to propose other pre-treatments
440 than an enzymatic one to enhance flavonoids extraction by filtration-compression.



441
442 **Figure 6.** Naringin extraction yield at 5 bar
443 *Enzymatically treated **ET**, raw **NT**, water addition with heating **W+H**, water addition **W**, heating **H***
444

445 As it is observed on Figure 6, heating the slurry (H) did not lead to a significant increase of
446 naringin recovery in comparison with raw slurry. Even if high temperatures are susceptible of
447 increasing the diffusion rates of flavonoids, the low water content limit the transfert phenomena
448 of the flavonoids towards the mechanically extractable liquid. By adding water to the slurry (W),

449 a marked increase on the recovered naringin was noticed; an extraction twice as efficient as the
450 one obtained with heating was observed. The addition of water, which diluted the medium,
451 facilitated the mobility of flavonoids from the solid matrix towards the free extracellular liquid,
452 through an increase of the concentration gradient at the solid/liquid interface and a possible
453 increase of the diffusion coefficient by a decrease of the viscosity of the medium.
454 The twinning effect of heating and water addition (W+H) led to an important increase of the
455 naringin extraction resulting in an efficiency close to 78%. The addition of pectinases, which
456 hydrolysised pectins of the cell walls, increased the naringin extraction efficiency from 78 to
457 89%.
458 These results demonstrated that, if the enzymatic treatment enhanced the naringin extraction,
459 water addition and heating, due to their synergistic effect, could be simple and low-cost slurry
460 pre-treatments to enhance naringin extraction. Thus, the benefit of an enzymatic treatment on the
461 naringin recovery has to be considered, given the enzyme cost.

462 Regarding narirutin recovery (Figure 7), the lower concentration in peel residues combined with
463 its higher solubility allowed a higher release of this flavonoid (between 61% and 92 % depending
464 on the treatment) into the aqueous phase. In this case, the most impacting factor is the water
465 quantity available for rapid narirutin diffusion and dissolution; thus, a single water addition could
466 recover the same quantity of narirutin than an enzymatic treatment.

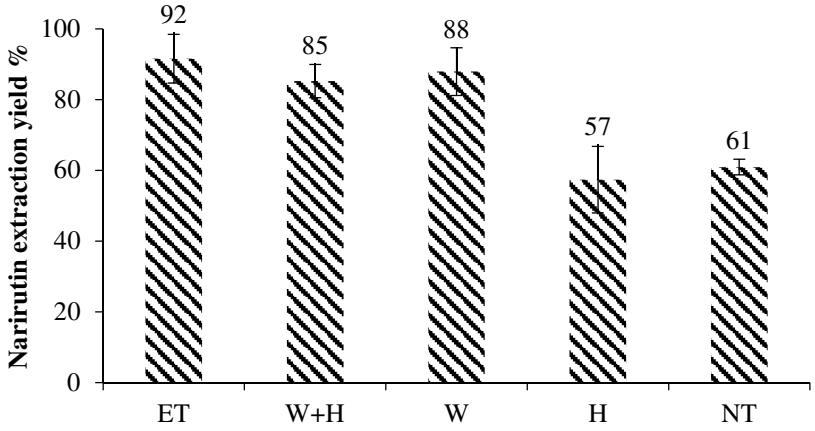


Figure 7. Narirutin extraction yield at 5 bar
*Enzymatically treated **ET**, raw **NT**, water addition with heating **W+H**, water addition **W**, heating **H***

3.3.2. Identification of the dispersion state of extracted naringin and narirutin

With an objective to identify the dispersion state of the extracted naringin and narirutin according to the different pre-treatments, centrifugations of the different filtrates were realized to separate the *soluble* and *insoluble* part of naringin and narirutin (see methodologies in 2.3.1).

Figure 8 presents the total naringin content compared to the *soluble* one. While naringin was only on a *soluble* state in H and NT filtrates, *insoluble* naringin appeared in the filtrates obtained with other pre-treatments.

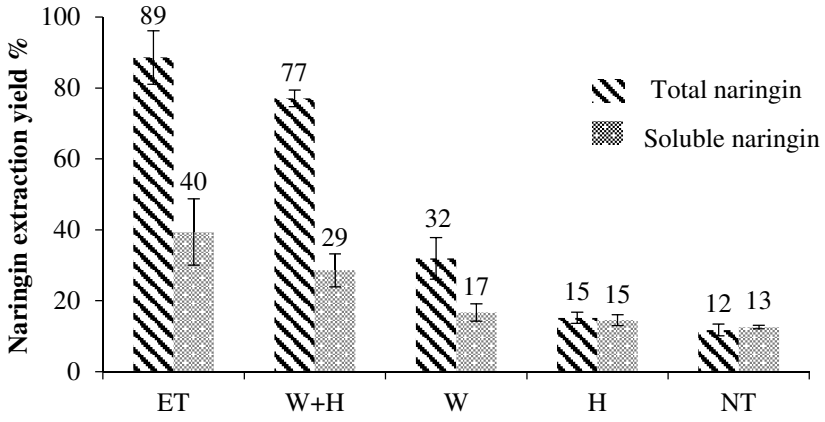


Figure 8. Naringin total and soluble extraction yields at 5 bar for different slurries
*Enzymatically treated **ET**, raw **NT**, water addition with heating **W+H**, water addition **W**, heating **H***

The presence of *insoluble* naringin was directly linked to the enhancement of the total naringin extraction. Water addition, alone or combined with heat treatment, had favoured the diffusional transfer and consequently the extraction of a higher part of naringin within the filtrate; the enzymatic treatment had led to a weakening of vegetable cell wall due to pectinases, facilitating naringin diffusion and thus extraction [22]. The results seemed to establish that these released flavonoids, initially mainly on *soluble* state in the filtrate, could rapidly form large aggregates, explaining the increase of an *insoluble* fraction. Thus, about half of the total naringin was on insoluble state after these different pre-treatments. It was supposed that naringin could form colloidal structures with macromolecules (e.g. proteins, phospholipids…) that could be present in large quantity and with a great diversity in the supernatant after such pre-treatment (because of the facility of the diffusional transfer of other compounds or of the enzymatic action on the vegetable tissue). Additional specific tests need to be performed to complete these hypotheses, and notably to quantify the naringin solubility in such complex medium.

Concerning narirutin, the supernatant analysis of the filtrates showed that this flavonoid was entirely present under its *soluble* form probably due to its higher solubility and lower concentration within the peel residues (Data not shown).

4. Conclusion

In order to promote circular and sustainable food systems, various strategies are proposed to valorise wastes. In the case of Citrus transformation industry, grapefruits flavonoids (naringin and narirutin), presenting interesting pharmaceutical properties, could be extracted from peels, constituting a source of income for Southern countries. Most of the extraction processes require high investment or high-energy consumption making these technologies non-suitable for the Southern countries. Thus, it seems pertinent to think about a high-added-value compounds

506 recovery chain using optimized robust, cost-effective and low-energy consuming processes. The
507 objective of this work was to study the relevance of a simple filtration-compression step directly
508 done on the fresh grinded peels as a first downstream process for flavonoids extraction. The
509 potential impact on the solid-liquid separation of a pectinolytic enzymatic treatment was
510 investigated.

511 The results demonstrated that a preliminary step of filtration-compression, directly realized on
512 fresh grinded peels, as downstream processing for flavonoids extraction could be pertinent. The
513 optimization of solid/liquid separation was obtained with a transmembrane pressure of 5 bar,
514 providing the removal of the maximum of the extractable liquid phase from peel. Filtration
515 modelling demonstrated that the standard blocking law properly described the evolution of the
516 filtrate mass versus time, whatever the operating conditions (pressure, enzymatic treatment or
517 none…). If the fouling mechanisms were similar for enzymatic treated slurry and no-treated one,
518 the enzymatic treatment improved significantly the filterability of the slurry. The blocking
519 constant of the standard blocking law, indispensable for the scaling of a filtration-compression
520 process on site, was, under 5 bar, two times higher for non-treated than enzymatic treated peel.
521 The quantification of naringin and narirutin content in this removable liquid phase (i.e. filtrate)
522 demonstrated that the enzymatic treatment or a hot-water addition were suitable to enhance the
523 naringin and narirutin extraction yield, which could reach 80 and 90% respectively. The
524 dispersion state of the flavonoids within the mechanically extractable aqueous phase obtained
525 after this preliminary solid-liquid separation was identified; the part of the *insoluble* (crystallized
526 or bound to some larger solids) naringin could represent half of the total extracted naringin.
527 These last results require further investigations, with an objective to provide pertinent elements
528 to guide the choice of the subsequent extraction step.

529

Acknowledgements

This research was partially supported by the National Council on Science and Technology (CONACYT, Mexico). We are thankful to our colleagues, Bénédicte Marion and Céline Roques, who provided expertise in analytical measurements. We are also immensely grateful to Soufflet Biotechnologies ® for providing enzymes and operating conditions choice guidance.

Declaration of interest

The authors report no declarations of interest.

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Grapefruit peel (without flavedo) and pulp rests

Grinding

Pectinolytic treatment

NT Slurry

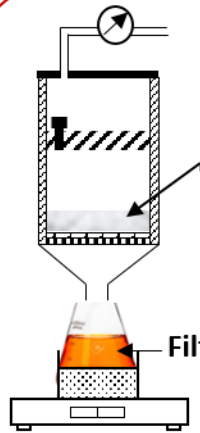
ET Slurry

Slurries characterization

Particle size measurement

Dry matter content

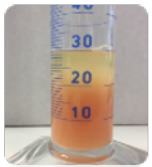
Naringin and Narirutin content



Estimation of filtration efficiency

Estimation of the maximum of the extractable liquid phase (filtrate volume)

Identification of the size-location of flavonoids in filtrate



Filtrate

Dry matter content

Naringin and Narirutin content

Centrifugation

***Quantification of the soluble* flavonoids (supernatant)**

Naringin and Narirutin content