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Debittering of Citrus Juices: Pilot Experience Carried out Using Adsorbent Resins

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Introduction

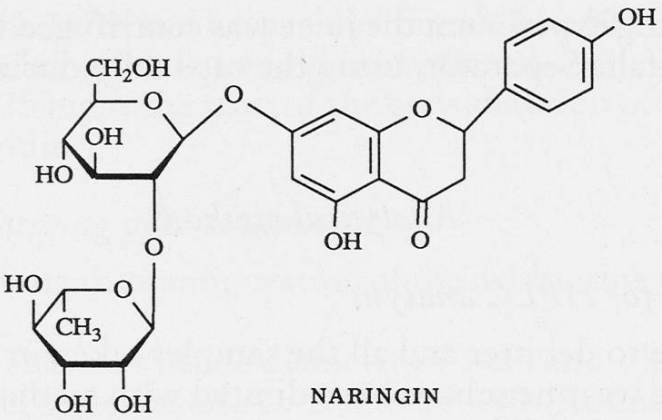
The presence of flavanone neohesperidosides is, notoriously, the cause of the «bitter» taste of citrus juices (1–5) just obtained by pressing. The gradual and retarded development of the same «bitter» tone, instead, is caused by limonin (6).

Several papers have been published in the past on the problem of the bitter taste associated to limonin (7) and flavanone neohesperidosides: furthermore, several processes have been proposed for the elimination of bitterness from citrus juices (8). An interesting study was also published by *Kimball* on the industrial solution of citrus juice bitterness (9). There are production areas for the application of debittering processes which are even more justifiable: you only need to think of products derived from the peel of citrus fruits for the food industry or of peel derivatives to be added to juices (for example: to confer turbidity, to enrich some nutritional principles and other uses).

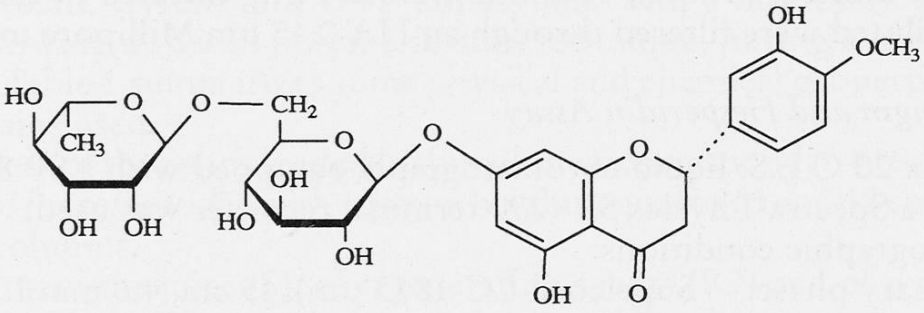
It is possible to find citrus fruits derivatives, which may benefit from debittering processes, in commercial products such as soft drinks, fruit syrups, fruit squashes, juice drinks, comminutes.

Currently, different laws regulate the production of citrus juices and derivatives in the various countries and therefore this paper shall not discuss legislations or restrictions as far as the debittering process is concerned. Among the processes which may have a practical interest from the industrial point of view, there is the one based on the use of selective adsorbents: this paper shall present the results of a pilot experience using styrolic and acrylic adsorbent resins.

The content of two flavanones, naringin and hesperidin, was used as markers to monitor the process.



NARINGIN



HESPERIDIN

The main citrus flavanones (naringenin, isosakuranetin, eriodictyol and hesperetin) are known to be present in juices not as aglycones but combined through the C-7 hydroxyl group either with betaneohesperidose or with rutinose (10).

Flavanone neohesperidosides are characterized by organoleptic properties different from those of flavanone rutinosides: neohesperidosides have a bitter taste while rutinosides are practically tasteless. Naringin (betaneohesperidoside) is the most bitter flavanone glycoside, while hesperidin (the most ubiquitous of citrus flavonoids) is substantially tasteless.

This work considers two different flavanone glycosides (naringin and hesperidin) also in order to check possible different behaviours, as far as the adsorption process on two different types of resins is concerned, brought about by different «glycosidic structures» (neohesperidosides and rutinosides).

Experimental

Materials

The experiment was carried out using a citrus juice, produced by pressing oranges, bergamots and a mixture of citrus peel, in an industrial plant.

For the debittering experiment the juice was centrifuged twice at 12 000 rev/min in a LWA 205 Westfalia Separator, using the caps only during the second centrifugation.

Analytical methods

Sample preparation for HPLC analysis

The juice sample to debitter and all the samples taken in correspondence of the various stages of the treatment have been diluted with methanol in a 1:1 ratio. After mixing and filtering using Whatman paper No. 4, the filtrate was diluted with the mobile phase used for the HPLC analysis in a 1:5 ratio and, consequently, the juice samples were diluted, in total, 10 times. Before being injected in the HPLC, the juices thus diluted were filtered through an HA 0.45 µm Millipore membrane.

HPLC Naringin and Hesperidin Assay

A Phoenix 20 C.E.S. liquid chromatograph, equipped with a SP 87 C.E.S. UV detector and a Spectra-Physics SP 4290 terminal recorder was used.

Chromatographic conditions:

Stationary phase:	Supelcosil LC-18 (3 µm), 15 cm, 4.6 mm I.D.
Mobile phase:	(A) H_2O/H_3PO_4 (pH 2,8), (B) CH_3CN, A:B = 75:25
Flow:	1 ml/min
Wavelenght:	275 nm
Injection volume:	50 µl

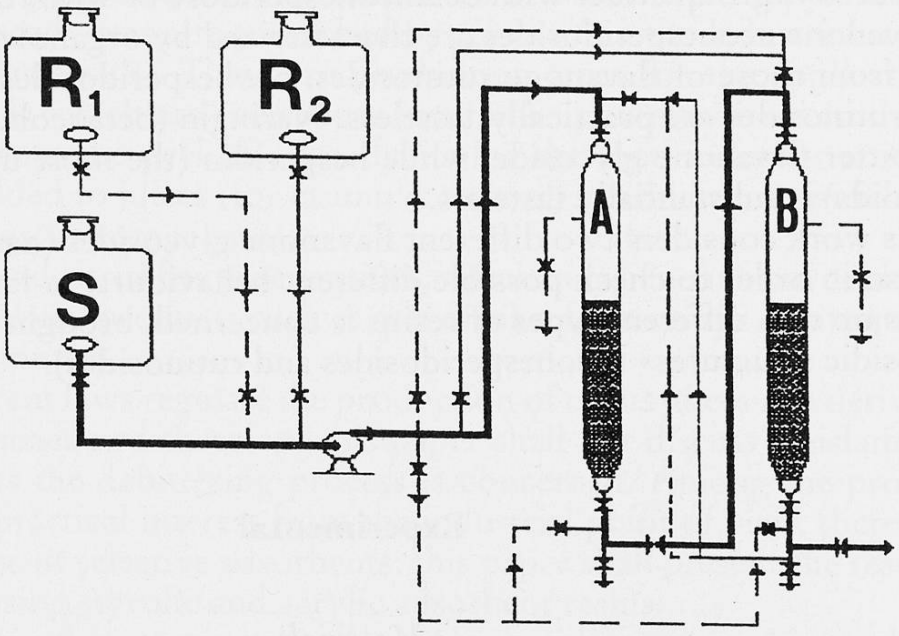


Fig. 1. Layout of the pilot system for juice debittering (see text):
R_1 = service water
R_2 = regenerating agents
S = juice
A = column containing acrylic resin
B = column containing styrolic resin

Naringin (Sigma, No. 1376) and hesperidin (Sigma, No. 5254) standard solutions were prepared by dissolving the flavonoid in methanol.

The choice of $\lambda = 275$ nm is the fruit of the consideration of the two UV spectra of naringin and hesperidin.

Description of the debittering pilot equipment

The diagram describing the configuration of the debittering equipment is reported in figure 1.

Columns A) and B) have an inside diameter of 3 cm and a length of 150 cm; the resins they contain are, for column A): Relite SP 490 (Resindion) a new type of synthetic adsorbent with a methacrylic high porous matrix having a medium hydrophobicity value and, for column B): Relite SP 460 (Resindion) a highly porous adsorbent, styrene and DVB copolymer, with a macroreticular structure obtained following a special polymerization technique, having a high hydrophobicity value. Table 1 summarizes some physical and chemical properties of the two adsorbent resins used.

The volumes of the resins loaded in the columns correspond *to 450 ml for column A) and 300 ml for column B),* with stratum heights equal to 65 and 45 cm respectively for the two columns.

The feeding of the juice (S), of regenerating agents (R2) and of water (R1) may be carried out, in the pilot equipment being considered, using a peristaltic pump with variable and controlled speed and flow rates.

Table 1. Physical and chemical properties relative to Acrylic resin (A) and Styrolic resin (B)

	A	B
Physical form	Spherical beads	Spherical beads
Moisture content at delivery	60–65%	55–60%
Pore volume (approx.)	1.15 mg/g	1.18 ml/g
Pore radius peak (approx.)	150–300 Å	200–300 Å
Surface area (approx.)	470 m^2/g	510 m^2/g
Solubility(*) index (approx.)	8.4	9.7
Particle size range	0.3–0.8 mm	0.3–0.8 mm
Swelling tendency – water – methanol – acetone	 1.0 1.01 approx. 1.06 approx.	 1.0 1.26 approx. 1.32 approx.
Specific density (approx.)	1.09 g/ml	1.01 g/ml

(*) Solubility index is a measure of the hydrophobicity and, accordingly, adsorbents with a larger solubility parameter have higher adsorption strenght. When the adsorption strenght is higher, the adsorption proceeds more effectively although the elution becomes more difficult.

Description of the debittering process

The adsorbent resins, before being used, are treated for one night with a 1:1 water/acetone solution and after being loaded in the column they are washed at lenght until the solvent is totally eliminated.

The debittering treatment cycle implies the passing of orange juice at 10 Bx*), according to the plant flowsheet, from the acrylic to the styrolic resin, in series.

It is therefore possible to differentiate the a) «adsorption cycle» and b) «regeneration cycle»:

a) Adsorption cycle

At the beginning of the process, the juice was separated until the percentage of dry substance reached 1.5 Bx, working with a flow speed of approximately 450 ml/h.

After the indicated value of dry substance was reached, we then proceeded with the sampling of the juice flowing out of both column A) and B): the sampling frequency was of 4 batch-volumes (BV) calculated on the volume of acrylic resin (practically once every 1800 ml of treated juice).

The working cycle was considered as concluded after the collection of samples corresponding to the 16th BV (7200 ml of treated juice as a whole).

At this point, after juice feeding was concluded, demineralized water was introduced until the effluent showed a content of dry substance of approximately 1.5 Bx.

b) Regeneration cycle

The regeneration phase is preceded by a counter-flow washing with water, working singly for the two columns. The regeneration is carried out by introducing a 4% KOH solution (1400 ml), with flow speed of 2.5–3.0 BV/h (contact time approx. 40 min) in series from column B) to column A).

These are then fed with demineralized water in the same direction for the removal of the regenerating agent (approx. 750 ml of water). This operation is terminated by feeding with water only column A) with a consumption of approx. 3 BV (1350 ml).

The two columns are then newly fed in series, from column A) to B) with demineralized water with a flow rate of 3.5–4.0 l/h.

Results and Discussion

Analytical evaluations

The juice samples produced by the two columns have been collected, for process monitoring purposes, after the passage of juice quantities equal to 4, 8, 12 and 16

*) Bx = Brix, measured by refractometry

BV for every column. As a whole, 4 samples taken from column A) and 4 samples taken from column B) were analyzed after passing over the A) and B) series system. The samples flowing out of column A) were labeled 1A, 2A, 3A and 4A, while those flowing out of the A) and B) series system were labeled 1B, 2B, 3B and 4B.

Figures 2 and 3 report the HPLC chromatograms carried out for naringin (N) assay and hesperidin (H) assay after the four phases of the process. The peaks, corresponding to naringin and hesperidin contained in the effluent juice are visually compared in order to highlight the adsorption effect of the two columns: the comparison is made, visually, with the peaks corresponding to the starting juice (S). Naringin and hesperidin were identified in each sample by fortification.

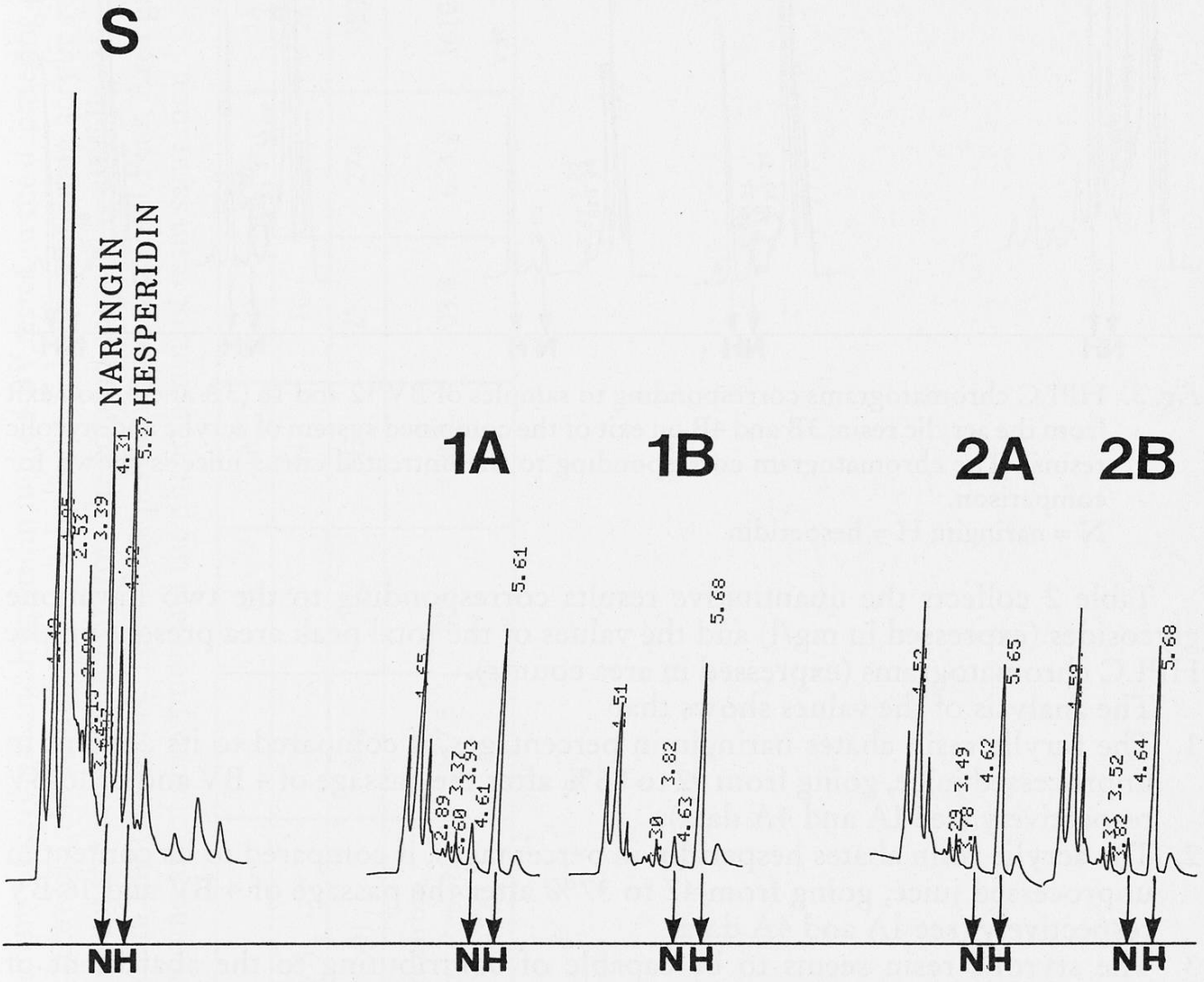


Fig. 2. HPLC chromatograms corresponding to samples of BV 4 and 8 (1A and 2A on exit from the acrylic resin; 1B and 2B on exit of the combined system of acrylic and styrolic resins). The chromatogram corresponding to the untreated citrus juice is shown for comparison.
N = naringin; H = hesperidin

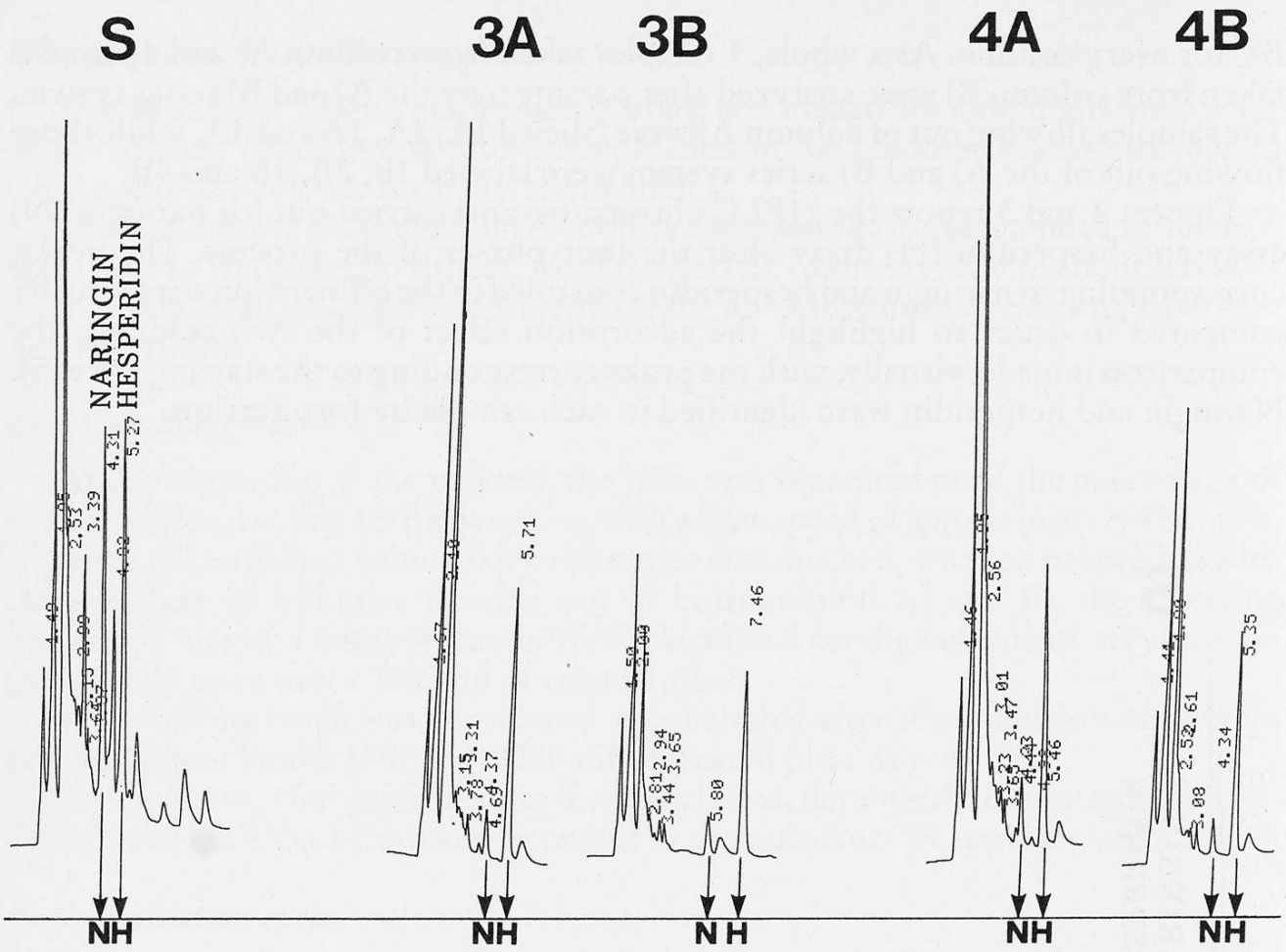


Fig. 3. HPLC chromatograms corresponding to samples of BV 12 and 16 (3A and 4A on exit from the acrylic resin; 3B and 4B on exit of the combined system of acrylic and styrolic resins). The chromatogram corresponding to the untreated citrus juice is shown for comparison.
N = naringin; H = hesperidin

Table 2 collects the quantitative results corresponding to the two flavanone glycosides (expressed in mg/l) and the values of the total peak area present on the HPLC chromatograms (expressed in area counts).

The analysis of the values shows that

1. The acrylic resin abates naringin in percentages, if compared to its content in unprocessed juice, going from 92 to 86% after the passage of 4 BV and of 16 BV respectively (see 1A and 4A data).
2. The acrylic resin abates hesperidin in percentages, if compared to its content in unprocessed juice, going from 47 to 37% after the passage of 4 BV and 16 BV respectively (see 1A and 4A data).
3. The styrolic resin seems to be capable of contributing to the abatement of naringin even if not too drastically (see, for example, the comparison between 1A and 1B, between 4A and 4B).
4. The styrolic resin seems to contribute to the abatement in the content of hesperidin (see, for example, the comparison between 1A and 1B and between 4A and 4B).

Table 2. Contents of naringin and hesperidin in the 4 BV tested in the debittering process. The values 1A, 2A, 3A and 4A represent the contents on exit from the column containing acrylic resin. The values 1B, 2B, 3B and 4B represent the contents on exit from the column containing styrolic resin and so are the result of the passage through the two resins. The values pertaining to the Total Peak Area give information regarding the total phenomenon of absorption and the phenomenon of resin saturation

Note	S	1A	1B	2A	2B	3A	3B	4A	4B
Naringin (mg/l)	246	20	14	16	17	26	24	35	17
Hesperidin (mg/l)	564	300	245	257	274	350	290	358	269
Total Peak Area from Chromatogram Report (Area Counts x 10^3)	3437.5	806.3	458.9	705.8	603.8	1610.9	940.1	2083.5	1070.0

5. The «watchdog» effect of the styrolic resin seems to be rather evident, and therefore particularly useful, especially in the phases which precede resin saturation (from the 12th BV onwards).
6. From the analysis of the «total area» values, the «watchdog» effect played by the styrolic resin for what concerns the entire series of compounds detectable in HPLC in analysis conditions seems to be rather evident.

Organoleptic evaluations

The results of the assessment of the «bitter» and «orange» tones for the samples which underwent the HPLC analysis are expressed in table 3.

The «bitter» tone seems to sensibly decrease in function of the passage of the juice over the acrylic resin; the styrolic resin seems to contribute to this reduction. In this sense, there seems to be not reduction of resin efficiency even after the passage of 16 BV of orange juice.

Similarly, the reduction of the characteristic «orange» aroma, in particular due to the effect of the styrolic resin, seems rather significant.

Table 3. Evaluation of the «bitter» and «orange» tastes of citrus juice flowing from the columns of absorbing resins in correspondence of the 4 BV (see Table 2). The numbers refer to the intensity of notes «bitter» and «orange»: i. e. for untreated juice the intensity is considered as 10

Note	S	1A	1B	2A	2B	3A	3B	4A	4B
Bitter	10	3	2	3	2	3	2	3	1
Orange	10	10	6	10	6	8	5	6	3

Conclusions

The experience carried out allow us to state that the adsorbent activity of the acrylic resin seems to be more significant of naringin rather than of hesperidin. At least in the operative conditions adopted in this experiment, it is not possible to highlight a definite selectivity of behaviour for the styrolic resin, may be because it was used downstream of the acrylic one, and therefore with «watchdog» functions.

Generally speaking, the series coupling adopted seems to show significant efficiency from the application point of view. It is in fact possible to recover citrus juice named «orange» rich in bitter flavanone glycosides for various uses in the food industry.

The debittering process, adequately carried out, is an interesting tool for the recovery of by-products (e. g. juices extracted from peel pressing) with high content of bitter flavanone glycosides.

Furthermore, the consideration of greater adsorption efficiency shown by the acrylic resins for naringin, a bitter flavanone glycoside, rather than for hesperidin, is extremely interesting.

Acknowledgements

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Summary

This paper reports the results of the experience acquired using a flavanone glycosides adsorbing system consisting in the coupling of an acrylic resin with a styrolic one.

In a pilot equipment, the debittering process was carried out on industrial orange juice very turbid, obtained using lots of peel from different citrus fruits (bergamot, grapefruit, etc.). The efficiency was assessed by means of the HPLC analysis of naringin and hesperidin.

The system's selectivity for naringin adsorption allows to draw interesting conclusions on the process' feasibility and usefulness.

Debittering efficiency is confirmed by the results of organoleptic controls.

Zusammenfassung

Die vorliegende Arbeit beschreibt die Erfahrungen mit einem Entbitterungsverfahren von Fruchtsäften basierend auf einem aus Acryl- und Styrolharz gebildeten Adsorptionssystem zur Entfernung der Flavanon-Glykoside.

In einer Pilotanlage wurde die Entbitterungsbehandlung eines sehr trüben industriellen Fruchtsafts, der durch Verwendung grosser Mengen von Schalen verschiedener Zitrusfrüchte (Citrus bergamia, Grapefruit usw.) hergestellt wird, durchgeführt. Die Effizienz wurde über die HPLC-Analyse von Naringin und Hesperidin bewertet.

Die Selektivität des Systems zur Adsorption von Naringin ermöglicht interessante Schlussfolgerungen über die Machbarkeit des Prozesses und die Nützlichkeit desselben.

Die Ergebnisse der Entbitterungseffizienz wurden durch organoleptische Prüfungen bestätigt.

Résumé

Cette étude présente les résultats d'expériences concernant un système d'adsorption pour flavanon-glycosides. L'adsorption se fait à l'aide d'une résine acrylique accouplée à une résine styrolique.

Un traitement visant à éliminer l'amertume d'un jus industriel d'orange très trouble, obtenu avec de grandes quantités d'écorces à partir de différents types de fruits citriques (bergamote, pamplemousse, etc.), a été effectué dans une installation pilote.

L'efficacité de ce procédé d'adsorption a été évaluée à travers l'analyse HPLC de naringine et d'espéridine.

Le caractère sélectif du système pour l'adsorption de naringine permet de tirer des conclusions intéressantes relatives à la faisabilité et à l'utilité du procédé.

Les résultats quant à l'efficacité du traitemant visant à éliminer l'amertume sont confirmés par des contrôles organoleptiques.

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