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Effluent content from albedo degradation and kinetics at different temperatures in the enzymatic peeling of grapefruits

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A B S T R A C T

This work studies the variation in the effluent content from the reactor in enzymatic peeling of grapefruits, to determine the loss of soluble solids, reducing sugars and galacturonic acid, the main component from the albedo of the skin to model the solid–liquid transfer in this process. Experiments to study the efficiency of the enzymatic reaction include the effect of the temperature on the kinetics of albedo degradation to find an equation relating both variables and also the activation energy of this process, its value being 36.9 kJ/mol.

Keywords: Grapefruit; Enzymes; Peeling; Effluents; Kinetics; Temperature

1. Introduction

One of the stages in the preparation of the minimally processed fruits is peeling and traditional industrial processes for peeling citrus fruits consist of manual or mechanical skin removal and the further chemical degradation of both the albedo remains and segment membranes. These methods imply a high cost in labour force, require large amounts of water for the washing stages and cause serious damage to the environment due to the use of caustic agents in the peeling process. These problems specially the ones caused by the chemical peeling of citrus which produces strange tastes (Ben-Shalom et al., 1986) led several investigators to study enzymatic peeling as an alternative to traditional chemical peeling. This consists of treating the fruit with a high-activity enzymatic solution containing polysaccharide hydrolytic enzymes, especially pectinases, cellulases, and hemicellulases since pectin, cellulose and hemicellulose are the polysaccharides most responsible for the adherence of the peel to the fruit. These enzymatic preparations were obtained by fermentation of genetically modified fungal micro-organisms in fermentation plants by biotechnological industries. Bruemmer and Griffin (1978) developed a pectinase solution for digesting grapefruit peel albedo by applying vacuum infusion. Adams and Kirk (1991) obtained a patent for enzymatic peeling of citrus fruit by vacuum pressure. This method was found to be more efficient. Rouhana and Mannheim (1994) assayed the optimisation of enzymatic peeling of grapefruit. The results showed that pectinases and cellulases were the enzymes that led to a more efficient peeling process. Pretel et al. (1998) optimised enzymatic peel removal of mandarins and with the data obtained, a mathematical model was developed which predicted the infusion of enzyme as a function of pressure and vacuum time. The best peeling results were achieved in those combinations of pressure and vacuum time that allowed a saturation of approximate 90% to be reached in less than 10 min.

Toker and Bayindirli (2003) applied different combinations of Peelzym (I, II, III and IV) at different temperatures, concentrations and times to optimise the enzymatic peeling of apricots, nectarines and peaches. Pretel et al. (2005) also assayed the enzymatic activity of four commercial enzymatic preparations (Peelzym I, II, III and IV) on citrus pectin and the effectiveness in the enzymatic degradation of the albedo and the segment membrane from Cimboa fruits was assessed. The highest activity on citrus pectin was shown by Peelzym II. The same authors (Pretel et al., 2007a) developed a study to determine the optimum conditions for enzymatic peeling

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of two morphologically different varieties of oranges (Thomson and Mollar). The potential enzymatic saturation of albedo (PESA) was determined by submerging the orange fruit with perforated flavedo in an enzymatic solution with Chinese ink and applying several vacuum pressures for different times. The PESA was evaluated as well as the incubation time using Peelzym II. The means of visual assessment for five characteristics were chosen and scaled for peeling and final product quality. Results showed that vacuum application in pulses was more effective than that in continuum. Pagán et al. (2006) optimised the peeling process of oranges with respect to process parameters such as temperature, enzyme concentration and incubation time. They conclude that the best results were obtained at 28 min, 40.4 °C and 0.17 mL of the enzymatic preparation at each gram peel per litre solution. Pretel et al. (2007b) performed an enzymatic peeling process for obtaining fruit segments from Sangrina orange by infusion under vacuum conditions using the Peelzym II enzymatic preparation. The process was optimised and the best condition to obtain segments was 1 mL L^{-1} of Peelzym II applied at 67 kPa with two vacuum pulses of 2 min and a subsequent period of 40 min in the enzymatic solution at atmospheric pressure. A better understanding of fruit enzymatic peel removal involves the study of the peeling process in a reactor and this means a detailed study of the evolution of the degradation products in the effluent produced in the enzymatic peel digestion of grapefruit var. *Star Ruby* is one of the purposes of the present work. The influence of temperature on the process is the next aim of the present work.

2. Methods and materials

2.1. Grapefruits

Grapefruits var. *Star Ruby* selected for their large and similar size and shape were purchased in a local fresh fruit market in Lleida, Spain, with average diameter 95.0 ± 8.0 mm, peel mass 69.3 ± 2.5 g and albedo thickness 4.8 ± 0.4 mm, with 8.2 ± 0.3 °Brix in juice and with an acidity of 1.09 ± 0.10 g citric acid/100 mL juice. The average weight of fruits was 387.5 ± 10.3 g.

2.2. Enzyme preparation

The enzyme preparation used was Peelzym II from NOVO Nordisk Ferment, Dittingen, Switzerland. This preparation was selected from among Peezym I, II and IV because it is reported by the manufacturer to have the highest activity. It is also reported that the enzymatic preparation mainly contains polygalacturonases, hemicellulases, cellulases and arabinases (Novo Nordisk Ferment, 1996). Enzymatic activity obtained in an Ostwald 100 capillary viscometer (Stauffer, 1989) at the optimal conditions of 45 °C and at pH 4.5 was 34,100 U/mL for the polygalacturonase activity and 1470 U/mL for the cellulase activity (Pagán et al., 2003).

2.3. Enzymatic digestion

This was carried out in a 5-L stirred-jacketed reactor filled with the buffered enzymatic solution and connected to a thermostatic bath. A batch process at different temperatures was investigated. The reactor was connected to a vacuum pump. Stirring was carried out at low speed by a magnetic stirring rod on the bottom of the reactor in order to avoid friction/abrasion that would cause peel damage. A single grapefruit was digested in each batch in the same way that of orange in a previous work (Pagán et al., 2006). The grapefruit peel was previously scored with a sharp knife so that the cut reached approximately half of the albedo thickness. Cuts were made following marked meridian lines with a distance of 1 cm between them. This distance was considered after studying the width of the spot formed in the albedo impregnated with the enzymatic buffered solution after penetration through a cut. Moreover, the peel was perforated with a thumbtack, punching holes at 1-cm distances. The whole grapefruit peel was extracted very carefully from the fruit by hand by means of four deeper meridian cuts and weighed. The grapefruit segments were covered again with the weighed peel with the joints sealed with electrical tape in a way so as to assure the complete coverage during the experiment. The average surface area of the peel of the grapefruits was 297 cm^2, whereas the covered surface was 60 cm^2, which corresponds to approximately 20.2% of the surface. In fact, the covered surface could have been reduced by using a narrower tape, or cut the chosen tape in half. Nevertheless, on recomposing the whole grapefruit before proceeding to the enzymatic digestion, the segments were much more firmly fixed to the cut pieces of peel with 1-cm wide tape than with the narrower one.

Moreover, with the wider tape there was less risk of enzymatic solution entering the segments, which might produce hydrolysis in these, when the aim was only to quantify the loss of weight of the albedo. The uncovered area of the grapefruits is approximately 80% of the entire surface, and this being almost identical in all the experiments and the peel having the same number of perforations for the entry of the enzymatic solution meant that the experimental errors were kept to a minimum.

The grapefruit peel was later briefly washed with chlorinated water and immersed in a buffered solution. The experiments were started by adding a Peelzym II concentration of 0.067 mL/g L of pH 4.5 buffered 0.1 M citric–citrate solution at 42 °C and finished after a controlled time. This enzymatic concentration and temperature were the optimal obtained from previous experiments (Pagán et al., unpublished). Each experiment was carried out at a constant stirring speed, temperature and vacuum pressure. The vacuum pressure was fixed at 700 mm Hg, as the optimal vacuum found by Romojaro et al. (1996). After each batch, the whole peel was again extracted from the fruit and the tape was removed from the peel. The peel was later immersed in a 0.2% NaOH solution to inactivate the enzymatic activity and dried at 60 °C for 24 h. Finally, the dried peel was weighed again. The reactor effluent were collected after each batch, filtered in a kitchen sieve to remove the large particle and stored at 4 °C for later analysis and ultrafiltration. Blank experiments with no enzymatic preparation were carried out under the same conditions as described above. The results of the experiments were expressed as the peeling response *R* function (Pagán et al., 2006):

$$R = \frac{W_{fb}/W_{0b}}{W_{fd}/W_{0d}} \quad (1)$$

where W_{fb} is the final weight of sample treated in a reactor without enzymatic solution; W_{0b} is the initial weight of sample treated in a reactor without enzymatic solution; W_{fd} is the final weight of sample treated in a reactor with enzymatic solution;