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Surface property modification of vanilla pods (*Vanilla planifolia*) treated with an ultrasound probe to increase the efficiency of solid–liquid extraction

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Vanilla is a flavoring of great culinary value worldwide. The conventional extraction process takes a long time and has high production costs, due to the characteristics of the pod, which contains compounds such as waxes, gums, resins, and fixed oils. This research introduces an ecofriendly methodology to increase the efficiency of solid–liquid extraction on vanilla pods using a sustainable alternative. Ultrasound processing conditions were time (2 min, 4 min, 6 min, 8 min, and 10 min), amplitude (50%, 75%, and 100%), and solvent (0, 60%, and 100% EtOH), and a solid: liquid ratio of 1:10 (pod: solvent) was used. The effect of the pretreatment on extraction efficiency was evaluated as a function of the vanillin concentration (yield). The optimization of the process was carried out with the Minitab 17 software. Surface properties were evaluated in terms of contact angle, adhesion work, and surface energy using the drop method (DropSnake software and LB-ADSA) and the Young and Dupré equations. A surface contact regime was employed to show the induced microstructure and hydrophobic-hydrophilic character after ultrasound pretreatment. Results suggested that the optimal pretreatment was 10 min, 100% amplitude, and 60% ethanol, obtaining an extraction yield of vanillin of 2,703.45 ± 33.25 μg/mL with a significant difference with respect to the control using natural convection (1701.33 ± 23.85 μg/mL, $p > 0.05$, R^2>99). Reductions in the contact angle, in addition to high work adhesion and surface tension values, demonstrated the hydrophilic characteristics of the vanilla pods, and confirmed the modification of surface properties and the opening of diffusion channels related to the increase of the solvent intrusion on the vanilla pod surface after the ecological physical treatment. The results from this work indicate that using ultrasound as a pretreatment in the solid–liquid extraction process might further improve the performance in the extraction of vanillin and reduce the extraction time.

KEYWORDS

ecofriendly methodology, contact angle, impregnation, vanillin, yield extraction

1 Introduction

Vanilla (*Vanilla planifolia*), a tropical orchid of the Vanilla genus, is one of the most popular flavors in the world. Its floral and fruity fragrance with a deep and aromatic body, which makes it unique and universal, has been attributed to the presence of more than 200 compounds, particularly vanillin (C8H8O3 or 4-hydroxy-3-methoxybenzaldehyde), found in a concentration of 1%–2% in cured vanilla pods (Gallage and Birger, 2015). Vanillin is formed from the glucovanillin glucoside by the action of the β-glucosidase enzyme during the vanilla pod curing process, where chemical, biochemical, and enzymatic reactions occur, making this natural extract one of the most appreciated natural flavorings by the food and pharmaceutical industry (Frenkel et al., 2018; Olatunde et al., 2022).

The vanilla extraction process has high production costs and long conventional processing times requiring percolation and maceration, attributed to the diffusion resistance of the extractable material in the structure of the pod due to the presence of waxes, gums, resins, and fixed oils, among others. In order to improve the natural vanilla production and due to the growing global demand for natural vanilla extract, efforts have focused on obtaining vanillin by chemical synthesis and biotransformation (Embuscado, 2019). Ecofriendly technologies for the extraction of interesting metabolites from natural sources, reducing both extraction time and solvent consumption, have been tested by several authors (Capaldi et al., 2023; Cheriyan et al., 2024). Among these is the power ultrasound, based on the propagation of mechanical waves in an elastic medium with frequencies in the range of 20 kHz to 10 MHz. For example, in the case of solid–liquid systems, the cavitation bubbles generated at the interface with the surface of the vegetal matrix collapse, generating microjets directed toward the surface of the solid that are responsible for the breaking of the cell wall of the vegetal tissue, thus releasing its content into the liquid extraction medium as an effect of the high pressure and temperature involved in this process (Bhargava et al., 2021). However, the role played by this mechanism on the structure of the solid and its surface properties has not been systematically analyzed. Zhu et al. (2015) and Samaram et al. (2015) showed that the application of ultrasound not only allows the extraction of metabolites of interest from natural sources, but also that the agroindustry residues increase the potential of this application and reduce its environmental impact. On the other hand, Lavilla and Bendicho (2017) have shown evidence of the advantages that the use of ultrasound has over traditional methods, such as the reduction in the extraction and yield, respectively.

Research concerning the solid–liquid extraction of bioactive compounds from natural sources suggests a dominant mechanism of mass transfer (Gao Q et al., 2015). Castillo-Santos et al. (2017) studied the balance of aromatic compounds in the solid and liquid phases according to mass transfer during solid–liquid extraction. These authors suggested an equilibrium time lower than 40 h for vanilla extraction by maceration (natural convection). Similarly, it has been reported that knowledge of surface properties (hydrophobicity and surface energy) is a determining factor in industrial processes in other areas such as coatings, construction, dental, and ceramic materials (Khojasteh et al., 2016), as well as the inactivation of pathogens in food (Park and Kang, 2017). In addition, the study of surface characteristics is necessary not only in the natural extract process but also in the food industry, considering the role of hydrophobicity in the solid matrix during solvent absorption–diffusion of the extractable material, which allows scaling up of these processes. However, the extent of the effect of these properties on the transfer mechanism in the solid–liquid extraction of the vanilla needs further insight.

Like other bioactive compounds, vanilla extraction is carried out using ethanol:water mixtures as a solvent, taking into account its solubility in solvents with high polarity (Koenig et al., 2015; Plaskova and Mlcek, 2023). Early reports (Gao W et al., 2015; Tarigan and Ebrahimi, 2024) point out that the structure of vanillin clusters is preserved in aqueous solutions containing low percentages of ethanol, showing the repulsion reduction of the vanillin molecule, where the resulting concentration in solid–liquid extraction is dependent on the solvent polarity. The breakup in the multimolecular microstructure of the vanillin is a consequence of the solubility of vanillin due to the hydrogen bond formation between both the water molecules and the other vanillin clusters (González et al., 2018; Levy et al., 2017). Therefore, the objective of this investigation was to study the influence of the surface properties of the vanilla pods (*Vanilla planifolia*) on the efficiency of extraction assisted with probe ultrasound.

According to the principle of solid–liquid extraction, the efficiency of the process depends on the nature of the solid matrix, the properties of the extractable analyte, and its location within the matrix (Mustafa and Turner, 2011). In this context, the mechanism of the solid–liquid extraction can be expressed in a few steps. 1) Initial contact between the solid matrix and the extraction solvent from the extraction system; 2) Intrusion of the extraction solvent through the pores or diffusion channels of the solid matrix; 3) Desorption and solubility of the extractable analyte with the extraction solvent through diffusion channels; 4) The diffusion of the solvent within the extractable material through the pores of the matrix until it comes into contact with the rest of the extraction solvent; 5) Collection and/or separation of the solid and liquid fractions after the extraction time (Pawliszyn, 2003).

Vanillin is the main compound in vanilla. In the vanilla extraction processes, the diffusivity and solubility of the extractable material do not occur by natural convection as in other solid matrices, but rather the mechanism of diffusion is conditioned by the resistance offered by the microstructure (Castillo-Santos et al., 2017). This makes it necessary to focus the efforts on the study of the effect of emerging strategies, such as pretreatment, that allow the opening of the microstructure or diffusion channels of the vanilla pods to improve the extraction process. In this context, some characteristics such as the surface structure, the chemical composition of the surface, and the hydration of the surface are the result of the hydrophobicity of the surface of the solid (Park and Kang, 2017). The study of surface properties, such as contact angle or adhesion work, is an indirect measurement alternative for this purpose.

Because the hydrophobicity of a solid is defined by the adhesion between two condensed phases (solid and liquid), solid–liquid interaction defines the hydrophobic characteristic of solid surfaces in contact with a liquid. Contact angle (θ) is the surface property most used that gives information about the hydrophobicity of the solid surfaces. Contact angles higher than 90° point to a hydrophobic character (low affinity of the solid to the liquid); in contrast, values lower than 90° point to a hydrophilic character (great affinity of the solid to the liquid). Wetting occurs (liquid intrusion into pores or channels or diffusion in the solid) at contact angle values of 0°. Sotoudeh et al. (2023) schematize the stationary interfacial balance of the forces that determine the value of the contact angle of a liquid on a solid surface for the three cases mentioned above. The effect of the roughness of the surface on the hydrophobicity is described by the contact angle. For Wenzel, the liquid partially penetrates the solid forming contact angles less than 90° as a consequence of the surface of the matrix, while in Cassie–Baxter, the liquid is retained due to the resistance of the surface with almost spherical shapes (contact angles near to 180°), and impregnation occurs when the repellency with the surface is minimal (Khojasteh et al., 2016).

2 Materials and methods

2.1 Raw material

The study was carried out with cured vanilla bean pods provided by the company AKIH, from the region of Chinantla Tuxtepec, Oaxaca (17.77499, −96.30347), harvest 2013. The pods were reduced to a particle size of 2 cm.

2.2 Pretreatment with ultrasound

The solid–liquid extraction process was conducted with 5 g of the vanilla pod pieces and 50 mL of ethanol (EtOH) as the solvent at different concentrations: 0, 60%, and 100%, the amplitude was varied in the levels of 50%, 75%, and 100%, and the treatment times were 2 min, 4 min, 6 min, 8 min, and 10 min at a temperature of 25 °C ± 1 °C. The extractions were carried out in a glass container by using an interchangeable tip ultrasonic probe of 7 mm diameter and a constant frequency of 26 kHz, which was submerged in 50% of the corresponding volume (UP-200Ht Hielscher Ultrasound Technology, Berlin, Germany). After the pretreatment, the solid and liquid fractions were separated by filtration to carry out the corresponding analyses.

2.3 Determination of extractable material

2.3.1 Determination of vanillin

The quantification of vanillin in the liquid fraction was performed according to AOAC Method 966.12 (AOAC International, 2012). The preparation of the calibration curve was carried out from a stock solution of 1,000 μg/mL of vanillin (99% purity, SIGMA-ALDRICH). From the above solution, a first set of solutions (12–60 μg/mL) was prepared. Next, two sets of solutions were prepared from the last set (neutral and alkaline by the addition of NaOH 0.1 N). Finally, the absorbency was read at 348 nm using neutral solutions as the target setting through a UV–Vis Spectrophotometer (HACH DR 5000, Colorado, USA) with a line equation for the concentration range of 1.2–6.0 μg/mL of vanillin. For the preparation of the sample (extract), a 1:10 dilution was carried out. Then, two sets of solutions were prepared from the last set (neutral and alkaline by the addition of NaOH 0.1 N) with a dilution factor of 50. The concentration of the sample was determined according to the calibration curve equation and the dilution factor for the absorbency at 348 nm. Vanillin concentrations were determined in triplicate.

2.3.2 Determination of reducing sugars

The glucose analysis in terms of reducing sugars in the liquid fraction was performed by the 3,5-dinitrosalicylic acid (DNS) method (Miller, 1959). The preparation of the calibration curve was carried out from a stock solution of 5 g/L of glucose (99% Purity, SIGMA-ALDRICH). From the last solution, a set of solutions (0.2–1 g/L) was prepared. Next, 0.5 mL of the sample was placed in tubes with the addition of 0.5 mL of 0.2 N sodium hydroxide and 1 mL of DNS reagent (99% purity, SIGMA-ALDRICH). After this procedure, the samples were homogenized, kept in a boiling water bath for 5 min, and then 5 mL of cold distilled water was added. Finally, the absorbency was read at 540 nm using a 0 g/L solution as the target setting with a UV-Vis spectrophotometer (HACH DR 5000, Colorado, USA) with a line equation for the concentration range of 0.2–1 g/L of glucose. A similar procedure was carried out to prepare the sample (extract). The concentration of the sample was determined according to the calibration curve equation and the dilution factor for the absorbency at 540 nm. Glucose concentrations were determined in triplicate.

2.3.3 Determination of total soluble solids

The amount of total soluble solids expressed as °Brix was measured with an analogic refractometer (Atago Pocket PAL1, Tokyo, Japan) by the method of AOAC 932.12, Total solids soluble in fruits and fruit products (AOAC International and Latimer, 2012). All measurements were determined in triplicate.

2.3.4 Determination of surface properties

The surface properties were analyzed systematically in terms of contact angle (θ), surface energy (γ_{SV}), and adhesion work (W_{SL}) of the vanilla pods before and after pretreatment with ultrasound using 0%, 60%, and 100% ethanol (Li and Neumann, 1992).

2.3.5 Contact angle

The contact angle (θ) was measured by the sessile drop method. The drop of the evaluated solvents was deposited on the surface of the vanilla pods, where droplets of hydrophilic and hydrophobic liquid (water and mercury, respectively) were used as controls. A photographic image was obtained from the moment of contact between the drop and the surface of the vanilla pod. Later, the image was digitized through the ImageJ program, and the contact angle was obtained. The experimental measurements were made in triplicate, and the contact angle values are the average of the estimated values from the analysis of the images captured using DropSnake software and the low-bond axisymmetric drop shape analysis (LB-ADSA) method proposed by Stalder et al. (2006). This is a modified version of the sessile drop method that reconciles the

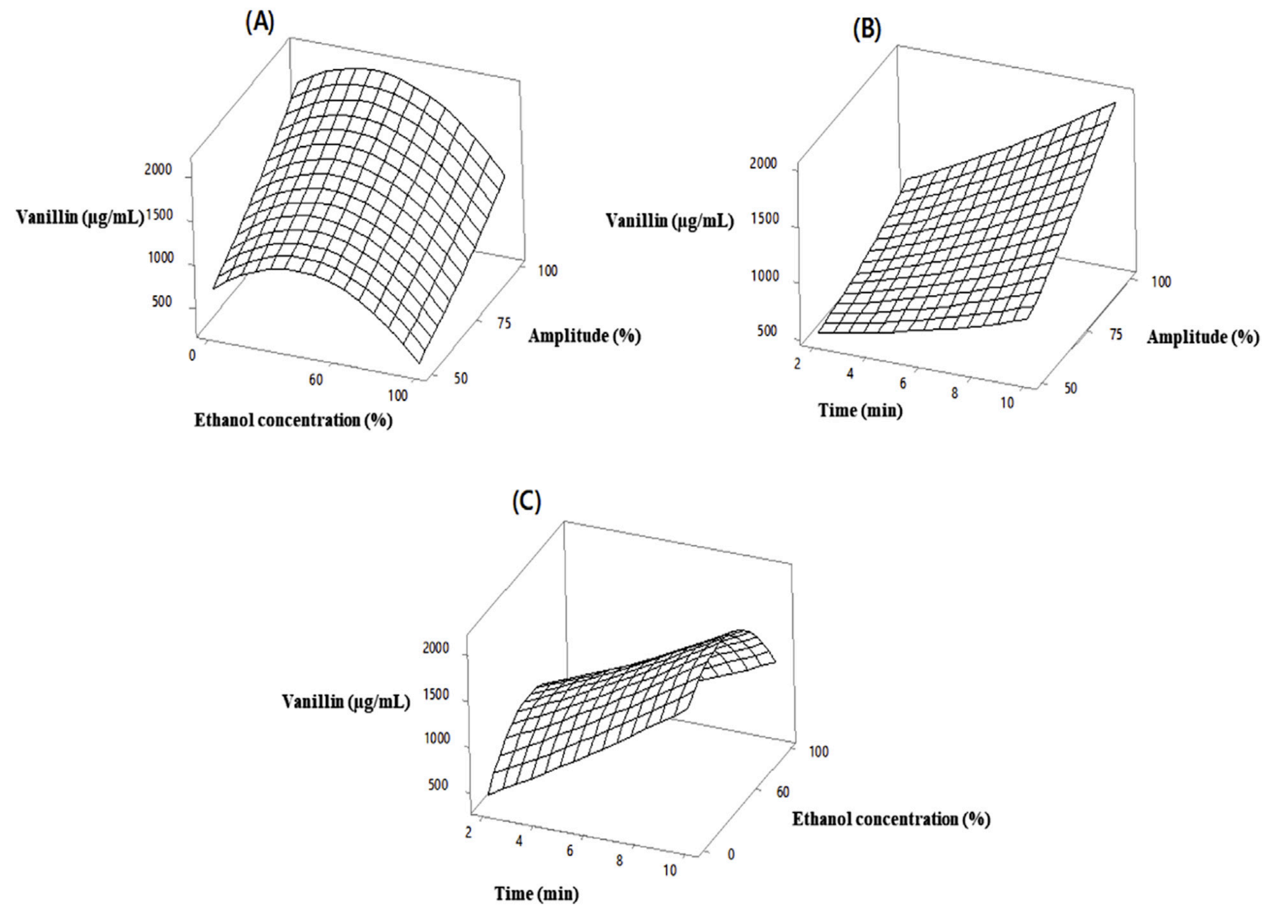

FIGURE 1
Effect of pretreatment with ultrasound on the concentration of vanillin. **(A)** Ethanol–amplitude concentration interaction; **(B)** time–amplitude interaction; **(C)** ethanol time–concentration interaction.

fact that the shape of a drop is global, while its contact angles are local. In essence, this method is similar to the polynomial numerical solution, but due to its elasticity, it takes advantage of the global shape for contour detection and the application of an algorithm to calculate the local contact angles.

2.3.6 Surface energy and adhesion work

Once the values of contact angles of the vanilla pods before and after the pretreatment with ultrasound were obtained, the analysis of the effect of the treatment on the solute–surface interaction, considering the surface energy, and the adhesion work was carried out using the Young–Dupré and Neumann equations (Equation 1).

$$W_{SL} = \gamma_{LV}(1 + \cos\theta) \quad (1)$$

$$\cos\theta = -1 + 2\sqrt{\left(\frac{\gamma_{SV}}{\gamma_{LV}}\right)} \cdot exp\left[-\beta\left(\gamma_{LV} - \gamma_{SV}\right)^2\right] \quad (2)$$

Where γ is the free surface energy (mJm^{-2}), for liquid-vapor (LV), solid-vapor (SV) or solid-liquid (SL) interfaces, θ is the contact angle, W is the reversible adhesion work (mJm^{-2}), and $\beta = 12.47 \times 10^{-5}$ $((m^2\text{–}mJ\text{–}1)^2)$ is a coefficient independent of liquids or solids involved.

2.4 Statistical analysis

Optimization of the experiment was carried out using a multifactorial design, using response surfaces and an analysis of variance (ANOVA) with a Fisher least significant difference (LSD) test and a confidence level of 95%. Minitab version 17 software was used.

3 Results and discussion

3.1 Effect of the application of ultrasound on the extraction of vanillin

The effect of ultrasound on vanillin concentration is shown in Figure 1. The highest concentration level of vanillin was obtained using 60% ethanol as solvent (Figure 1A). This effect was more pronounced with the increased ultrasound amplitude (2,703.45 μg/mL, 1,646.30 μg/mL, and 528.83 μg/mL to 100%, 75%, and 50% of ultrasound amplitude, respectively). It has been attributed to an increased extraction power, taking into account that cavitation bubbles and micro jet formation are directly related to an increase in amplitude (Chemat et al., 2017). In addition, the cellular wall of vanilla pods seems to have a more open microstructure, where the metabolite diffusion in the extraction medium (first vanillin) is apparently increased. In this work, an interaction of time with the ultrasound amplitude is shown in Figure 1B. Results indicated that the concentration of vanillin increased with process time and also with ultrasound amplitude, in that the best process conditions were 10 min and 100% amplitude. These results suggest that both the rate of microstructure opening in vanilla pods and the metabolite migration inside the pore walls and on the extraction solvent were induced by the acoustic cavitation phenomenon (Chemat et al., 2017). The extent of these effects is highly dependent on time and the amplitude of the ultrasound interaction.

Results also indicated the highest increase of vanillin extraction using 60% ethanol with an ultrasound time of 10 min (Figure 1C); obtaining an extraction yield of vanillin of 2,703.45 ± 33.25 μg/mL, which is a significant difference respect to the control carried out by natural convection for 24 h (1701.33 ± 23.85 μg/mL, $p > 0.05$, $R^2 > 99$). This was a clear indication that vanillin affinity and its resulting concentration in the experimental extraction were dependent on the polarity of the solvent tested (polarity indices of 10.2, 6.68, and 4.3 for 0%, 60%, and 100% ethanol, respectively). The breakup in the multimolecular microstructure of the vanillin as a consequence of the solubility of vanillin is increased (24.737, 46.69, 34.25 and 25.93 to vanillin and ethanol 0%, 60%, and 100%) due to the hydrogen bond formation between both the water molecules and the other vanillin neighbor molecules at vanillin clusters (González et al., 2018; Levy et al., 2017). It is possible that more interactions, such as hydrogen bonding, could play a key role in the wetting behavior and subsequently in the yield of vanillin with the use of 60% ethanol, which is approximately twice as high as the yields obtained at 0% and 100%. The structure of vanillin clusters is preserved at low concentrations of ethanol with a decrease of π–π stacking interactions (Gao W et al., 2015; Tarigan and Ebrahimi, 2024), so indicating the repulsion reduction of the vanillin molecule (13.98, 17.24, and 19.42 to 0%, 60%, and 100% ethanol). Vanillin is an organic molecule that exhibits some polarity due to the presence of functional groups such as an aldehyde group and a methoxy group. These polar groups can interact with polar solvents such as ethanol; however, vanillin is predominantly non-polar due to its aromatic structure (Olatunde et al., 2022), which makes it insoluble in water. On this basis, vanillin and 0% ethanol are immiscible (21.959); conversely, vanillin and 100% ethanol are miscible (1.199). Thus, it is clearly shown that vanillin forms a micellar phase in the water-rich environment and a homogeneous ethanol-vanillin phase in the ethanol-rich environment. The vanillin shows high miscibility under water–ethanol equivalent concentrations due to the strong dissolution capability of vanillin in ethanol.

3.2 Effect of pretreatment with ultrasound on reducing sugar and total soluble solids

Extractable material was determined in terms of reducing sugars and total soluble solids as a result of the liberation of glucovanillin from the cellulolytic structure of the vanilla pods during the extraction process. The results of the extractable material are itemized in Table 1. We considered a two-factor design (X_1 EtOH concentration, X_2 time) at three and five levels respectively for the optimal amplitude (100%), as shown previously in Figure 1. From this table, it can be observed that the highest liberation of extractable material was obtained by using 100% ethanol as a solvent in comparison with the other process conditions evaluated. For example, results pointed out the highest sugar reducing liberation with an ultrasound time of 10 min, while for the case of total soluble solids, the sonication time did not make a significant difference. This behavior can be attributed to the increase in ethanol concentration, which promotes the co-extractable constituents, such as sugars, minerals, pigments, protein, fibers, and polyphenols, present in the cellular wall of the vanilla pods (Gao W et al., 2015), because the co-extractable compound concentrations from the solid matrix are correlated with the solvent polarity.

3.3 Surface properties

3.3.1 Contact angle

Contact angles obtained from the drop shape analysis of droplets placed on the vanilla pod surface before ultrasound pretreatment were 96.63°, 57.70°, and 11.31° for 0, 60%, and 100% ethanol, respectively (Figures 2A–C). These contact angles suggest a character from hydrophobic to hydrophilic, with a tendency toward complete wettability with the increase of ethanol concentration tested. These phenomena can be attribute taking into account that both the surface tension (72.75 mNm^{-1}, 42.75 mNm^{-1}, and 22.75 mNm^{-1} for 0, 60%, and 100% of ethanol, respectively) and the interfacial intermolecular forces due the contribution from non-polar and polar components (e.g., van der Waals and hydrogen bonding, respectively) are the responsible for the contact and shape of liquid droplets on the surface (Khojasteh et al., 2016). At the same time, the contact angles show the effect of pretreatment with ultrasound at the tested ethanol concentration, using the treatment that showed the highest yield of vanillin according to the response surface analysis (10 min, 100% of ultrasound amplitude) mentioned above (Figures 2D–F). Similarly, a reduction in the contact angle values of 54.35%, 21.50%, and 12.50% for 0%, 60% and 100% of ethanol, respectively, was observed in comparison with the values obtained in the untreated pods. These results suggest the opening of microstructure in vanilla pods to reduce the resistance to mass transfer and increase solvent penetration. It can be attributed to the effect of cavitation on the formation of microjets that has been addressed previously (Samaram et al., 2015). Additionally, the reduction in contact angle value to 0% and 60% ethanol was related to a decrease in the polarity index (10.2 and 6.68, respectively), allowing a significant difference in the changes obtained on the superficial character after the ultrasound process in vanilla pods (Figure 3).

The contact angle analyses suggest a greater roughness and opening of diffusion channels on surfaces pretreated with ultrasound as a result of the increases in the hydrophilicity of surfaces in the vanilla pods after pretreatment with 0% and 60% ethanol (Elik and Altunay, 2023). A scanning electron microscope

TABLE 1 Design of the experimental matrix and results obtained from the response variables in the solid–liquid extraction of vanilla pods pretreated with ultrasound (amplitude 100%).

Experimental units	Factors		Response variables	
	X_1 EtOH (%)	X_2 Time (min)	Reducing sugars (g/L)	Total soluble solids (°Brix)
1	0	2	0.42 ± 0.00^{m}	0.16 ± 0.05^{f}
2	0	4	0.73 ± 0.00^{k}	0.46 ± 0.05^{f}
3	0	6	0.72 ± 0.00^{k}	0.40 ± 0.10^{f}
4	0	8	1.25 ± 0.00^{h}	0.53 ± 0.05^{f}
5	0	10	1.62 ± 0.00^{f}	0.43 ± 0.05^{f}
6	60	2	0.25 ± 0.00^{n}	17.60 ± 0.10^{de}
7	60	4	0.56 ± 0.00^{l}	17.53 ± 0.05^{de}
8	60	6	1.36 ± 0.01^{g}	17.73 ± 0.20^{de}
9	60	8	1.21 ± 0.00^{i}	17.30 ± 0.10^{e}
10	60	10	0.84 ± 0.01^{j}	17.32 ± 1.04^{e}
11	100	2	1.66 ± 0.00^{e}	18.06 ± 0.05^{cd}
12	100	4	2.24 ± 0.01^{d}	19.23 ± 0.37^{a}
13	100	6	2.29 ± 0.00^{c}	18.63 ± 0.50^{abc}
14	100	8	2.31 ± 0.01^{b}	19.13 ± 0.23^{ab}
15	100	10	2.47 ± 0.01^{a}	18.50 ± 0.00^{bc}

Values in a column with the same letter are not significantly different ($p < 0.05$).

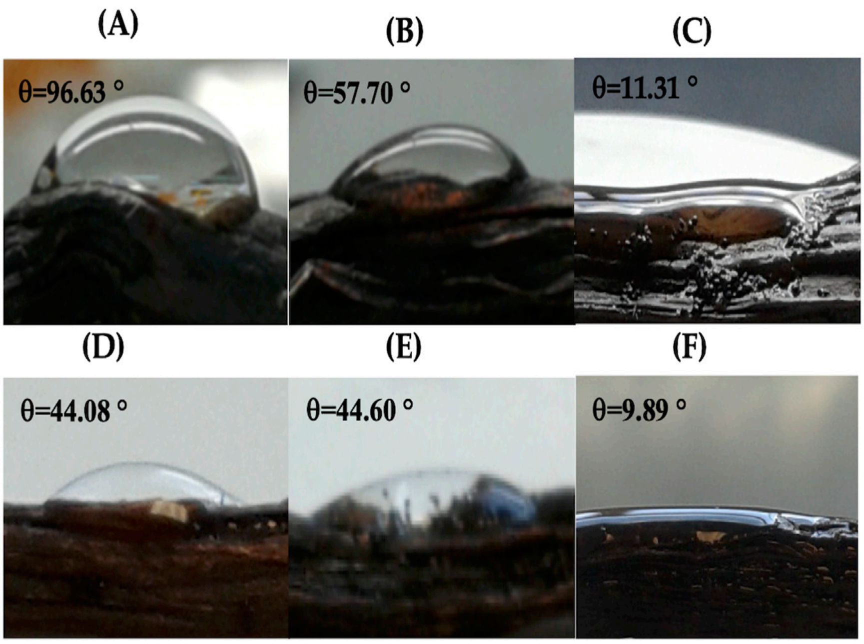

FIGURE 2
Images of the solvent drop on the sheath without pretreatment: **(A)** 0% ethanol; **(B)** 60% ethanol; **(C)** 100% ethanol, and images of the drop of solvent deposited on the sheath pretreated with ultrasound at an amplitude of 100% for 10 min: **(D)** 0% ethanol; **(E)** 60% ethanol; **(F)** 100% ethanol.

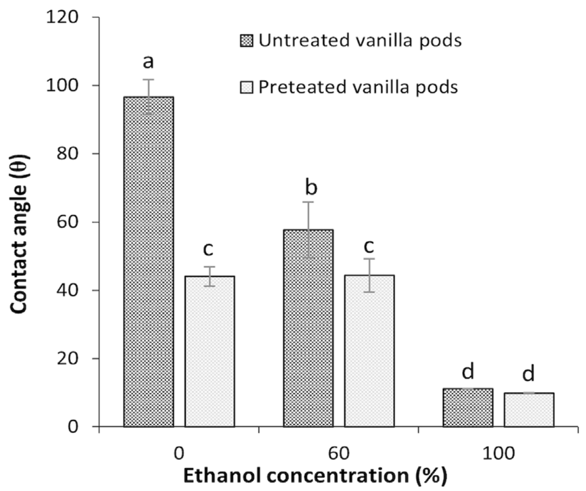

FIGURE 3
Effect of pretreatment on the hydrophobicity in the vanilla pods.

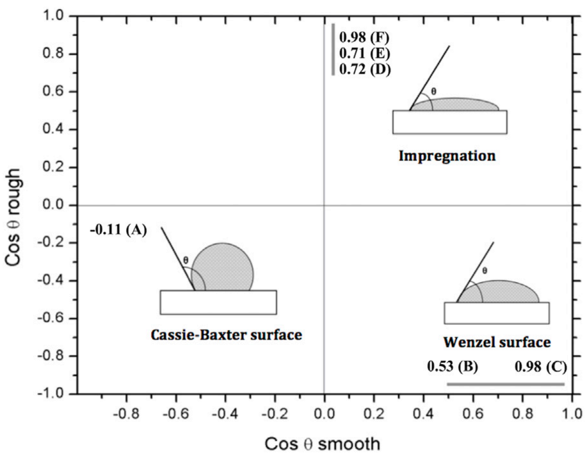

FIGURE 4
Surface contact regime of the vanilla pods without pretreatment in **(A)** 0% ethanol; **(B)** 60% ethanol; **(C)** 100% ethanol; with pretreatment in **(D)** ethanol 0%; **(E)** ethanol 60%; **(F)** ethanol 100%.

(SEM) analysis could reinforce this analysis. When 100% ethanol was used, no changes in the degree of hydrophobicity were observed after ultrasound pretreatment. The above can be attributed to an increase in the affinity at high concentrations of ethanol of some compounds present on the surface of the pods (gums, waxes, resins, and tannins), suggesting the key role of the surface chemical composition in the progression of the wettability of the vanilla pod surface.

Complementary to contact angle measurement, the surface contact regime of the vanilla pods was determined by analyzing the cosine of the contact angles previously obtained according to the Wenzel model as an extension of the Young–Doupré equation (Parvate et al., 2020). Three different surface hydrophobicity regimes can be seen in Figure 4: Wenzel, Cassie–Baxter, and Impregnation. When the surface is hydrophobic, the rough cosine decreases dramatically, according to a greater angle of contact associated with the Cassie–Baxter regime. In contrast to the above, for a hydrophilic behavior, the cosine of the contact angle increases linearly with the roughness, according to the Wenzel regime of Cassie–Baxter. The cosine of the contact angles for the vanilla pods without pretreatment at 0% and 60% ethanol suggested a Cassie–Baxter (A) and Wenzel regime (B). Additionally, the cosine of the contact angles for the pretreated vanilla pods at 0% and 60% ethanol suggested that the surface becomes hydrophilic after the ultrasound pretreatment, increasing the roughening of these (D and E, respectively). This corresponds to the impregnation regime and is related to the improvement of the solvent intrusion on the surface of the pods, confirming the contact angle values ($10^{\circ} < \theta < 90^{\circ}$) mentioned in the previous sections.

In vanilla both pretreated and without pretreatment with 100% ethanol, the analysis of the cosine and the increased vanillin content (1.98–4.63 g of vanillin/100 g of vanilla pods) suggested that before pretreatment, the regime of the surfaces was characteristic of the Wenzel regime (C), while in the pretreated pods, it corresponded to impregnation (F). In other words, the regime was not only related to the increase in roughness, but also, an apparent improvement in wettability and impregnation was observed in the vanilla pods even without pretreatment with 100% ethanol ($0^{\circ} < \theta < 10^{\circ}$), which was attributed to the chemical composition of the surface, the polarity index of the solvent, and the solubility of the vanillin in it, so in this case, an impregnation regimen (C) could not be considered. In other words, the progression of the mode of wettability of the vanilla pod surface through the three different regimes (Cassie, Wenzel, and impregnation) was not only attributed to roughness but also to factors such as the chemical composition of the surface, the polarity index of the solvent and the solubility of the vanillin, and the interrelation of these factors defines the progression of the wettability. Other surface properties that confirm the above statement were determined and are shown in the following section.

3.3.2 Adhesion work and surface energy

Because the contact angle depends on the adhesive and cohesive forces, determining the adhesion work and the surface energy is important to understand the behavior of the surface of the treated vanilla pods. The analysis of the experimental data using Equations 1 and 2 indicated that increases in the adhesion work and surface energy of the solid confirmed the increase of the adhesive forces of the surface of the pods in contact with the liquids tested after the pretreatment with ultrasound, while the opposite effect occurred with the cohesive forces, causing the capillary suction of the solvent to decline and increasing the contact surface (Table 2). It can also be seen in Table 2 that, as with the contact angle, the increase in the adhesion work and the surface energy of the vanilla pods after the pretreatment was dependent on the properties of the liquids evaluated. The greatest increase in adhesion work was observed for 0% ethanol (94.14%) compared to that obtained with 60% and 100% ethanol (11.72% and 0.22%, respectively). Similar results for the contact area between the solvent and the pretreated pods (surface energy) were observed, where the increase was 23.55%

TABLE 2 Surface properties of untreated and pretreated vanilla pods.

EtOH (%)	Contact angle (θ)		Adhesion work (W_{SL}) (mJm^{-2})		Surface energy (γ_{sv}) (mJm^{-2})	
	Untreated vanilla pods	Pretreated vanilla pods	Untreated vanilla pods	Pretreated vanilla pods	Untreated vanilla pods	Pretreated vanilla pods
0	96.63 ± 5.11	44.08 ± 2.84	64.37 ± 6.44	124.97 ± 2.51	101.14 ± 3.21	124.96 ± 3.65
60	57.70 ± 8.17	44.61 ± 4.87	66.82 ± 5.32	74.65 ± 2.67	107.23 ± 6.41	119.42 ± 4.76
100	11.31 ± 0.07	9.89 ± 0.21	45.06 ± 0.01	45.16 ± 0.01	159.89 ± 0.11	165.18 ± 0.23

Yields are shown as mean ± SD (n = 3).

when 0% ethanol was used compared to those obtained with 60% ethanol and 100% (11.36% and 3.30%, respectively).

High surface energy values indicate a greater affinity of the solvent for the solid (Khojasteh et al., 2016), which is desirable for the liquid–solid extraction process. The results of changing the surface properties clearly indicate the opening of channels on vanilla pods after the ultrasound treatment, considering that in all the liquids evaluated, the reduction in the contact angle and the increase in adhesion work and surface energy were observed. The 0% ethanol had a greater effect on surface energy results than 60% and 100% ethanol, but not on vanillin extraction efficiency (1.98 g of vanillin/100 g of vanilla pods), which could be attributed to the significant formation of free radicals during the ultrasound pretreatment. It does not have the same intermolecular vanillin–hydrogen bonding interactions as 60% and 100% ethanol, which play a key role in the higher wetting behavior and the lower yield of vanillin. Makino et al. (1983) indicated that during the application of ultrasound with solvents, the formation of free radicals of OH and H atoms occurs in the gas phase of the cavitation of the bubbles, and that the degree of formation of these radicals depends on the presence of oxygen, as well as the acid–base properties of the participating chemical species. In this context, it is important to point out that with 0% ethanol, there is a higher probability of formation of free radicals (OH) during the cavitation by ultrasound, considering that the dissociation occurs due to the acid–base properties of the water and that this, in turn, has properties of a donor and an electron acceptor. On the other hand, in the aqueous environment for ethanol and water, there is a greater number of molecules in aggregate for the latter than for ethanol (Koenig et al., 2015), creating a greater action of water on the surface of the pods. In the case of ethanol at 60% and 100%, the probability of the formation of free radicals during cavitation decreases because it depends to a greater degree on electrophilic substitutions.

4 Conclusion

The results from this work give further insight into the effect of surface properties of vanilla pods on the extraction yield of vanillin by determining the applicability of different operation conditions for ultrasound-assisted extraction of vanillin. It was shown that the application of probe ultrasound for 10 min, with 100% amplitude and 60% ethanol as the solvent, obtained the highest extraction yield of vanillin. Analysis of the extraction process indicated that the solvent has a higher effect on both the transport of extractable material and on the surface properties of the vanilla pods. The extent of these effects is highly dependent on properties of the solvent concentrations evaluated, that is, interfacial tension and polarity index, which define the mechanisms of the impregnation, adsorption, intrusion, solubility, and diffusion of the compounds during solid–liquid extraction. The surface analysis suggests that diffusion channels open in the vanilla pods as a result of the pretreatment with ultrasound. Both the reduction of the contact angle (21.49%) and the increase of the adhesion work (12.28%) indicated a lower resistance of the vanilla pod structure and, consequently, a higher diffusion of the extractable material during the extraction process.

Considering the higher resistance of the vanilla pods, results of this work point out that the application of ultrasound is an ecofriendly pretreatment that could be a sustainable alternative for the extraction of vanilla pods because it improved the yield of vanillin. Additionally, it was demonstrated that the hydrophobicity of the solid matrix plays a decisive role in the adsorption of the solvent on the surface and the diffusion of the extractable material, defining the efficiency in the solid–liquid extraction processes, and that this is dependent on the roughness of the surface and the solvent evaluated. The results of this study could increase the potential of pretreatment with ultrasound in the food industry to obtain natural extracts from other natural sources. Its applicability might further improve with knowledge of the surface characteristics for the extraction of each bioactive compound, especially if scaling is desired.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

KV-G: Conceptualization, Project administration, Supervision, Validation, Writing – original draft, Writing – review and editing. MA-G: Data curation, Formal Analysis, Investigation, Methodology, Resources, Supervision, Writing – original draft. LO-M: Writing – original draft, Writing – review and editing. BE-G: Data curation, Formal Analysis, Investigation, Methodology, Resources, Writing – review and editing. KB-R: Data curation, Software, Visualization, Writing – review and editing. GA-V: Conceptualization, Methodology, Supervision, Validation, Writing – review and editing. EV-S: Conceptualization, Investigation, Project administration, Resources, Supervision, Writing – review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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