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Study of Adsorption Isotherms and Equilibrium for Removal of Tannins from Cashew Apple Juice with Ion Exchange Resin

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Abstract

Studies of equilibrium isotherms and fixed-bed breakthrough curves were performed, with the purpose of assessing condensed tannin removal for obtaining cashew apple juice clarified with ion exchange resin. Batch equilibrium isotherms and the modeling of equilibrium were evaluated. For the fixed-bed study, two systems were used: standard solution (catechin + vitamin C + sucrose) and cashew apple juice. The influence of the presence of vitamin C and sucrose on the removal of catechin and the concentrations of cashew apple juice tannins were also assessed. Within the evaluated models, Sips and Freundlich presented the best adjustments, with concave curve, while the Sips model presented the best fit to the experimental data. The breakthrough curve in fixed-bed demonstrated that the juice with the highest amount of initial tannins favors a greater resistance to mass transfer during the ion exchange process between tannins and Tanex resin.

Keywords: Isotherms of Adsorption; Equilibrium; Ion Exchange Resin; Clarified Cashew Apple Juice

Introduction

Cajuína is an undiluted and unfermented beverage, derived from the edible part of the pseudo-fruit and obtained by heat treatment and a clarification process [1]. The low astringency and the absence of turbidity are the main characteristics of cajuína, also called clarified cashew apple juice. This beverage is a completely Brazilian product, produced in the Northeast region of the country [2]. Cashew apple juice has a high content of vitamin C [3,4], and when obtained through clarification, this beverage stands out for having neither added preservatives nor sugar, thus becoming a product with great potential for exportation. However, to maintain the characteristics of this drink until its consumption can be challenging. In this sense, the removal of condensed tannins from cashew apple juice, with a consequent reduction in astringency, elimination of turbidity, and manufacturing quality is essential for its acceptance by consumers and for consumption with quality [5].

Literature shows various studies of ion exchange resin application in food industries[6-10]. One of the main advantages of using ion exchange resins is the removal of undesirable products in the processes, to obtain a better-quality product [11,12]. Studiescarried out by Edwin Veras [11] reported the behavior of pH in passion fruit juice when the juice was treated with ion exchange resins. Recently, Akyildiz et al. [13] evaluatedthe behavior of pH and acidity in orange juice to determine the effect of ion exchange resins on the quality attributes and ability of some resins to reduce the acidity of this juice.

The equilibrium relationships in ion exchange are similar to adsorption isotherms, where the separation is based on the interactions between adsorbent-adsorbed [14]. To understand the ion exchange process, it is necessary to conduct studies assessing the adsorption through adsorption isotherms, thus obtaining information on the distribution of solute adsorbed between the liquid and solid phases at several equilibrium concentrations. Data obtained in the adsorption isotherm study are specific to each systemand their determination should be performed considering each application [15]. In addition, the adsorption process is also used to improve the quality of the products studied.

There are different models in literature describing the behavior of adsorption isotherms using ion exchange resin [16-23]. Among the models most used for the adsorption assessment are the Langmuir and Freundlich models [24]. In general, equilibrium adsorption studies are carried out with ion exchange resins in order to find the maximum adsorption capacity, the concentration of ions present in a solution, as well as to determine the model that best represents the experimental adsorption data [25].

Another way to evaluate the separation process with ion exchange resin is by assessing the behavior of mass transfer and removal of matters in the fixed-bed. Several studies report the use of ion exchange resins in fixed-bed, which is applied to the environment through the removal of heavy metals in aqueous media and the removal of contaminants in wastewater [22, 26], and is further used in the food industry, for removal of substances that give an undesirable color to wine [12], removal of acidity in passion fruit juice [11] and removal of sugars in cashew apple juice [27]. The advantage of fixed-bed studies is to be able to evaluate the effects of the initial and final concentration on the breakthrough curves, as well as the mass transfer effect in the bed, as well as studying the efficiency of the resins [26].

For real use in industrial scales an ongoing analysis is necessary, which can be done through studies in the fixed-bed. In this sense, this work aims to evaluate the removal of condensed tannins that interfere in the drink quality through the evaluation of ion exchange isotherms equilibrium. The study evaluated the use of different models (Freundlich, Langmuir, and Sips) and their adjustments to the fixed-bed breakthrough curves. In addition, an analysis of possible interferences in this removal of tannins with constituents present in cashew apple juice was performed.

Materials and Methods

Materials

The materials used in this work were Tanex resin (batch 4711T/09/2, Purolite), NaOH(Vetec, lot 1009504, cod 00113708), and reagents with detailed information given in Table 1. The cashew pseudo-fruit were bought in the local market from two producing regions in Northeast Brazil: Rio Grande do Norte and Piauí (Table 1).

Table 1: Chemical sample used in this work

Chemical name	Chemical formula	Molecular weight / $g.mol^{-1}$	CAS no.	Source
Acetone PA	C_3H_6O	58.08	67-64-1	Vetec
Vanillin PA	$C_8H_8O_3$	152.15	121-33-5	Vetec
Hydrochloric acid PA	HCl	36.46	7647-01-10	Prochemiu
(+) – catechin hydrate	$C_{15}H_{14}O_6$ x H_2O	290.97	225937-10-0	Sigma-Aldrich, C1251
Methanol PA ACS	CH_4O	32.04	67-56-1	JT Bake Solusorb
Lentils sodium hydroxide PA. ACS	NaOH	40.00	1310-73-2	Vetec
Phenolphthalein PA	$C_20H_{14}O_4$	138.32	77-09-8	Neon
2-6-dichlorophenol-indophenol (DCFI)	$C_{12}H_6Cl_2NNaO_2$ * 2 H_2O	326.11	620-45-1	inLab
L (+) ascorbic acid PA ACS	$C_6H_8O_6$	176.12	50-81-7	Vetec-Sigma Aldrich
Metaphosphoric acid PA	HPO_3	79.98	37267-86-0	Vetec
Sucrose PA A.C.S.	$C_{12}H_{22}O_{11}$	342.24	57-50-1	Synth

[a]SP:spectrophotometer, [b]TL: Titulation, [c]Reference: used as a reference for suga

N^d = uninformed

Ion exchange resin

The ion exchange resin used in this study was Tanex resin, which is characteristically a macroporous strongly basic resin type 1 (ammonia quaternary), with styrene matrix and acrylic crosslinked with divinylbenzene containing chloride ions (Cl^-) as mobile counter ions. Tanex ion exchange resin has bead particles of 0.3-1.2 mm in diameter and 0.75 mm in size, with an exchange capacity of 0.6 eq/L in its physical properties. The choice of Tanex resin is related to the efficiency of the removal of condensed tannins based on previous studies to remove tannins to obtain clarified cashew apple juice [28].

In the ion exchange process, the Tanex resin is not regenerated prior to the first useas recommended by the supplier.

Preparation of the cashew apple juice

The cashew apple juice was prepared in laboratory using cashew pseudo-fruit at an adequate ripeness stage. After the purchase, the cashew pseudo-fruits arrived at the laboratory where they were selected, washed in running water, separated from the chestnut, and manually pressed to obtain the raw juice. Then, the raw juice was filtered in cotton cloth to obtain the integral cashew apple juice. After this step, the obtained juice was packed in glass containers and kept at -18 °C for further analysis.

Content of condensed tannins

Tannin extraction: For extraction of condensed tannins present in cashew apple juice, acetone of 70% was used as solvent. The preparation of the solvent for the analysis followed the methodology described by Agostini-Costa et al. [29]. The acetone was completely evaporated at 40 °C using a vacuum rotating evaporator of 700 mmHg (Solab,SL 126, Piracicaba / SP, Brazil) for 15 minutes, and the aqueous residue was diluted with methanol in a 25 mL flask.

Determining of Condensed Tannin Content: After extraction, the condensed tannins in the cashew apple juice extract were determined by the vanillin reaction according to the method described by Broadhurst and Jones [30] and modified by Agostini-Costa et al. [29]. For this analysis, 5 mL of freshly prepared vanillin reagent solution, concentrated hydrochloric acid and methanol to the ratio 4:56:83 (m/v/v), respectively, were used. The reading of the absorbance was carried out at 510 nm using a visible UV spectrophotometer (Varian, Cary 50 Conc, São Paulo, Brazil) within a maximum period of 1 hour. The calibration curve was done using (+) – catechin hydrate as standard. The results were expressed in mg of condensed tannins per 100 g of juice. The tests were performed in triplicate. To obtain the percentage of total removal of condensed tannins, eq (1) was used.

$$\%rem = \frac{C - C_0}{C_0}(100) \qquad (1)$$

where % *rem* is the total percentage of condensed tannin removal; *C0* is the concentration of the initial solution (catechin/water), in mg/mL, or initial condensed tannins of the juice, in mg/100g of juice; *C* is the concentration of the final solution after ionic exchange process (catechin/water), in mg/mL, or final condensed tannins of the juice, in mg/100 g of juice.

Physicochemical Analysis

The total soluble solids (°Brix) were determined through direct reading in a digital bench refractometer (Abbe model RTA-101); while the titratable total acidity was determined with 0.1N NaOH titration in juice samples with 1 or 5 g, using phenolphthalein as indicator, the results were expressed in g of citric acid per 100 g of juice; the measurement of pH was performed in samples of 5 mL cashew apple juice previously homogenized for 10 minutes, and determined by a digital pHmeter (MS Tecnopon, mA210, Piracicaba /SP, Brazil) previously calibrated with buffer solution 4.0 and 7.0. These analyses are in accordance with the methodology described by the Adolfo Lutz Institute [31].

To determine the content of vitamin C, a titration method based on the reduction of 2-6-dichlorophenol-indophenol (DCFI) by L-ascorbic acid (AA) was applied using 1% metaphosphoric acid as extractive solution, according to the methodology described by the Association of Official Analytical Chemists (AOAC, 967.21) adapted by Oliveira et al. [32].

Study of equilibrium in ion exchange column in fixed-bed

Studies of equilibrium in continuous systems were performed in an experimental apparatus containing a glass column, of 28.5 cm internal diameter and a height of 37.0 cm, coupled to a peristaltic pump (Tecnopon, model BP-200-D, São Paulo, Brazil). The system used for the ion exchange was comprised of a container for feeding solution, as shown in Figure 1. After the completion of the experiment, the feeding container was replaced by another container with distilled water used for bed washing (Figure 1).

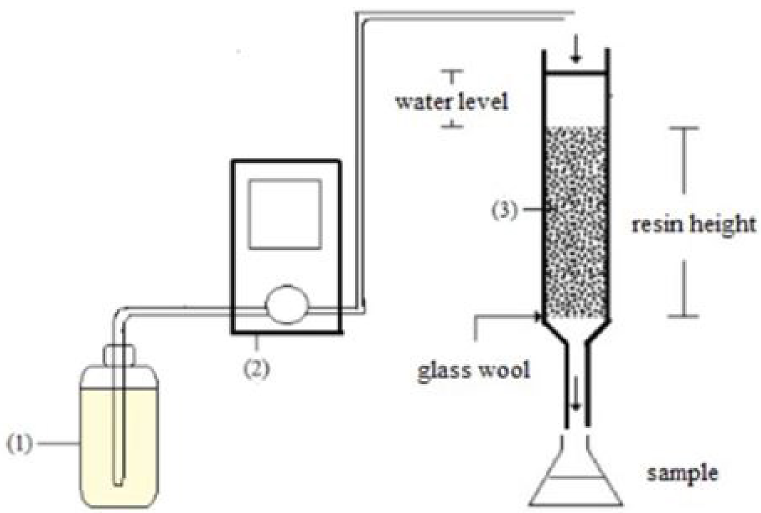

Figure 1: Schematic representation of the ion exchange column, where (1) container for feed solution; (2) peristaltic pump; (3) ion exchange resin

Experiment in fixed-bed column

For ion exchange experiments in fixed-bed, the column was packed with 74 g of the selected ion exchange resin, which corresponded to a height of 20 cm. The packaging was slowly performed using distilled water. The column was fed with feeding solution at a flow of 3 mL/min. This flow was based on previous studies through preliminary tests with a flow of 16 mL/minute, where a preferred path was verified by the column, and also in literature data, where the flow around 3 mL/min provided a larger amount of mass adsorbed by the adsorbent [33,34]. The experiments were conducted at 25 ± 1 °C. Samples of solutions that went through the column were collected at the column outlet (15 to 30 mL) at increasing intervals of 5, 10 and 60 minutes, for a total time of 360 minutes. The samples were kept under refrigeration for 18 hours until the analysis of the samples was analyzed. The amounts of standard catechin, condensed tannins, vitamin C, pH, °Brix and acidity were determined at the inlet and outlet of the column, according to the methodologies previously described. The experiments were performed in duplicate.

Effect of the type of initial solution on ion exchange process carried out in fixed-bed column

In order to study the behavior of the mass transfer through the breakthrough curves and to evaluate the percentage of removal of catechin, condensed tannins, vitamin C, as well as of the pH, °Brix and acidity, a study of the separation process in ion exchange resin in fixed-bed column was conducted. The study was conducted while considering two aspects: (i) to verify if vitamin C and sucrose could influence the removal of catechin(defined as the reference tannin for this study), (ii) and to evaluate how the different concentrations of tannins in cashew apple juice influence the percentage of removal of this compound by the selected resin. For this second aspect, two studies were performed, one using standard solution (A and B) and another using cashew apple juice (1 and 2).

Initially, a standard solution of (+) - catechin hydrate with initial concentration of 0.6 mg/mL (solution A) was used to verify the percentage of catechin removal through the resin selected in ion exchange column in fixed-bed, using a solution containing only catechin.

Then, experiments were carried out using the solution defined as solution B, composed of the standards of catechin + ascorbic acid + sucrose in the proportions 0.6 mg/mL, 1.824 mg/mL and 110 mg/mL (quantity based on the proportion of each in the cashew apple juice), respectively, to evaluate whether there would be interference of ascorbic acid and sucrose in the removal of catechin. Ascorbic acid and sucrose were chosen to represent vitamin C and sugars present in the juice during the catechin removal process.

Based on the results obtained, experiments with cashew apple juice 1 (15 ± 1 mg/100g of tannins) and cashew apple juice 2 (115 ± 1 mg/100g of tannins) were carried out to evaluate the influence of the two different condensed tannins initial concentrations present in the cashew apple juice during the process of removal of this compound. The juices were centrifuged at 3600 rpm for 5 min before undergoing the exchange ion column, to avoid clogging of the bed.

Adsorption Isotherms of condensed tannins

In this study, the adsorption of condensed tannin in cashew apple juice was evaluated using the following models: Freundlich, Langmuir, and Sips (eqs (2)-(4) respectively), since they are the most frequently used isotherms [24].

$$q_e = k_F C_e^{(1/n_F)} \tag{2}$$

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{3}$$

$$q_e = \frac{q_{m_S} k_S C_e^{m_s}}{1 + k_S C_e^{m_s}} \tag{4}$$

where qe is the equilibrium amount of solute adsorbed per unit mass of adsorbent (mg/g), qm is the maximum adsorption capacity (mg/g), kL is the Langmuir constant related to the free energy of adsorption (mL/mg), Ce is the equilibrium concentration of the solute in the bulk solution (mg/mL), kF is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g), nF is the Freundlich parameter, qms is the Sips maximum adsorption capacity (mg/g), k_s is the Sips equilibrium constant (mL/mg), and mS is the Sips model exponent.

Experiments were carried out in batch to evaluate the isotherms that represented the variation of the tannins fixed in the resin according to the remaining concentration of tannins in the solution of equilibrium.

To obtain tannin concentrations in cashew apple juice, dilutions of the whole cashew apple juice were made in distilled water. These experiments were performed with Tanex resin and all dilutions of juice using orbital shaker (Tecnal, TE-422, Piracicaba/SP,Brazil), considering the proportion 1:6 (resin : cashew apple juice, w/w). According to this proportion, 250 mL erlenmeyer containing 30.2 ± 0.3 g of whole cashew apple juice and the dilutions thereof were used with initial concentrations of condensed tannins ranging from 27 ± 3 to 269 ± 2 mg/100 g of tannins and resin (5.0007 ± 0.0003 g). The system resin + juice was inserted into the orbital shaker at a speed of 122 ± 2 rpm, maintaining a constant temperature (25.0 ± 0.1 °C) for 1 hour. After this step, the cashew apple juice samples were separated from the resin through filtration, using a glass funnel with nylon mesh. The samples were put in 50 mL glass containers and then capped and placed under refrigeration for 18 hours. After this period, the juice filtered from the samples was decanted, and the supernatant samples analyzed by spectrophotometry to determine the equilibrium concentration of tannins remained in the juice's supernatant after ion exchange (*Ce*, mg/mL). The amount of tannins removed per resin mass unit in the equilibrium (*qe*, mg/g) was calculated by the mass balance, using eq (5). The experiments were performed in duplicate.

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (5)$$

where *qe* is the amount of tannins in the resin at the equilibrium time (mg/g); *C0* is the initial tannin concentration (mg/mL); *Ce* is the concentration at equilibrium (mg/mL); *m* is the resin mass (g); and *V* is the cashew juice volume (mL).

Results and Discussions

Adsorption isotherms of condensed tannins

Ion exchange equilibrium studies were carried out and isotherm parameters wereestimated for the Freundlich, Langmuir and Sips models. Data were experimentally obtained and fiftted for each model (Figure 2).

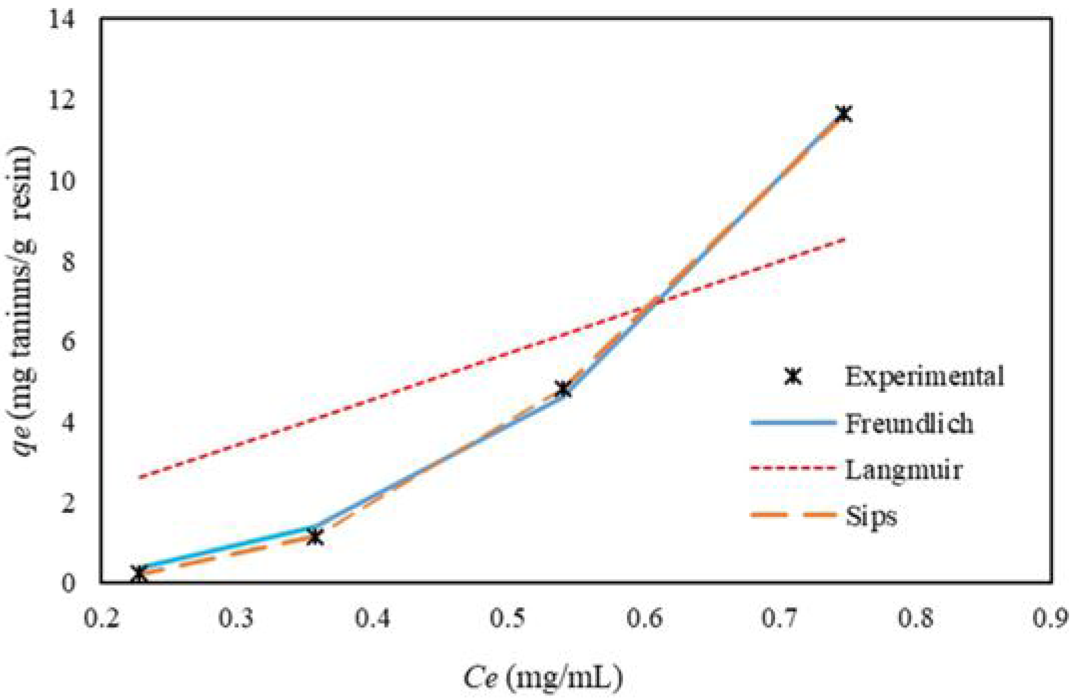

Figure 2: Equilibrium isotherms for the removal of condensed tannins in cashew apple juice by ion exchange with the Tanex resin and fitted isotherms using the Freundlich, Langmuir and Sips models

It is possible to observe from Figure 2 that the Langmuir model did not fit the experimental data, which indicates that ion exchange does not occur in the monolayer. On the other hand, the Freundlich and Sips models present a better fit because they showed concave curves compared to the Langmuir model. According to the classificationof Giles et al. [35], one of the characteristics of an S-type isotherm is the definition of concave curves at low concentrations. This behavior occurs when the adsorbent-adsorbate interactions are weak, and the adsorption is controlled by adsorbent saturation [14, 36]. Among the possible types for concave curve, the shape of the curve observed for this study is in accordance with subgroup S-1, thus indicating that the adsorbent does not clearly show its adsorption capacity. According to Hinz [36], a competitive inhibition reaction that forms complexes within the solution can stop the adsorption of a solute. In our case, the tannins contained in cashew apple juice could be bounded to another component forming a complex reaction. It seems perfectly possible since it is known that one of the most important properties of the tannins is their ability to complex with macromolecules as carbohydrates (sugars). Since the cashew apple juice in aqueous phase is constituted of tannins and a large amount of carbohydrates [37], this fact could promote a complexation reaction.

From the results presented in Figure 2, it was possible to calculate the parameters of each model applied to the ion exchange process between condensed tannins in cashew apple juice and the resin used. These parameters and the adsorption capacity of the resinare shown in Table 2.

Table 2: Equilibrium parameters obtained by the fittings of the isotherm models using ion exchange with Tanex resin at 25.0 ± 0.1 °C

Models	Parameters	Correlations
Freundlich	k_F (mg/g)	27.0 ± 1.5
	n_F	0.35 ± 0.02
	R^2	0.9982
Langmuir	q_m	2102.8 ± 726729.5
	k_L (mL/mg) R^2	0.005 ± 1.889
		0.6799
Sips	q_{mS} (mg/g)	27.4 ± 2.2
	k_S (mL/mg)	2.2 ± 0.4
	m_S	3.8 ± 0.1
	R^2	0.9999

Table 2 shows that Sips and Freundlich's models provided good correlation coefficients (R^2): 0.9999 and 0.9982, respectively. The R^2 values indicate that the experimental data demonstrated a good fit from the proposed models. As the experimental adsorption capacity comes closer to the calculated one, the correlation coefficient comes closer to 1, which was not observed for the Langmuir model (R^2 = 0.6799). This is in agreement with studies carried out by Barros [38]. Still, considering the Langmuir isotherm, it can be verified that the parameter q_m for this isotherm demonstrated considerable error, which means that there is a lack of statistical significance for this data as is shown in Figure 2. Thus, this model is not appropriate to describe the ion-exchange process for cajuína (or clarified cashew apple juice). The Sips isotherm presented the highest degree of correlation with the experimental data, as is evidenced by the R^2 values in Table 2. Furthermore, $m_S > 1$ implies that interactions took place between the components in cashew apple juice. This model obtained a maximum adsorption capacity for the tannins (q_{mS} = 27.4 ± 2.2 mg/g). On the other hand, the Freundlich model also presented a good level of correlation (R^2 = 0.9982), suggesting that multilayers adsorption was possible with a resin adsorption capacity for tannins (k_F = 27.0 ± 1.5 mg/g) close to the one acquired using the Sips model. However, the adsorption intensity (n = 0.35), which was determined following the Freundlich isotherm, was less than 1, indicating non-favorable adsorption.

Breakthrough Curves Analysis

The analysis of the breakthrough curves in fixed-bed was carried out to evaluate the mass transfer of the compounds from solutions A and B, as well as from the cashew apple juices 1 and 2. Table 3 summarizes the initial amounts of catechin, vitamin C, pH, °Brix and acidity for both solutions, A and B, before passing through the column.

Table 3: Chemical and physico-chemical analyzes of solutions A and B before ion exchange

Analysis	Solution A*	Solution B**
Catechin (g/L)	0.62 ± 0.01	0.62 ± 0.01
Vitamin C (mg/100g)	NR	147 ± 5
pH	5.8 ± 0.0	3.1 ± 0.1
°Brix	0.0	11.0 ± 0.1
Acidity (g/100 g citric acid)	NR	0.20 ± 0.00

It can be observed in Table 3 that catechin concentrations for both solutions are thesame (0.6 mg/mL). This suggests that the procedure used to quantify this component (described in section 2.3) presented a good level of precision (0.62 ± 0.01 mg/mL for solutions A and B). For pH and acidity analysis, the difference that was found was related to the addition of 1.824 mg/mL of ascorbic acid to solution B. In contrast, for °Brix analysis, this can be explained by the sucrose addition.

Use of solutions for ion exchange in fixed-bed column

Figure 3 presents the percentage of catechin removal using solution A (catechin only) after going through the exchange ion column at 25 ± 1 °C for 360 minutes.

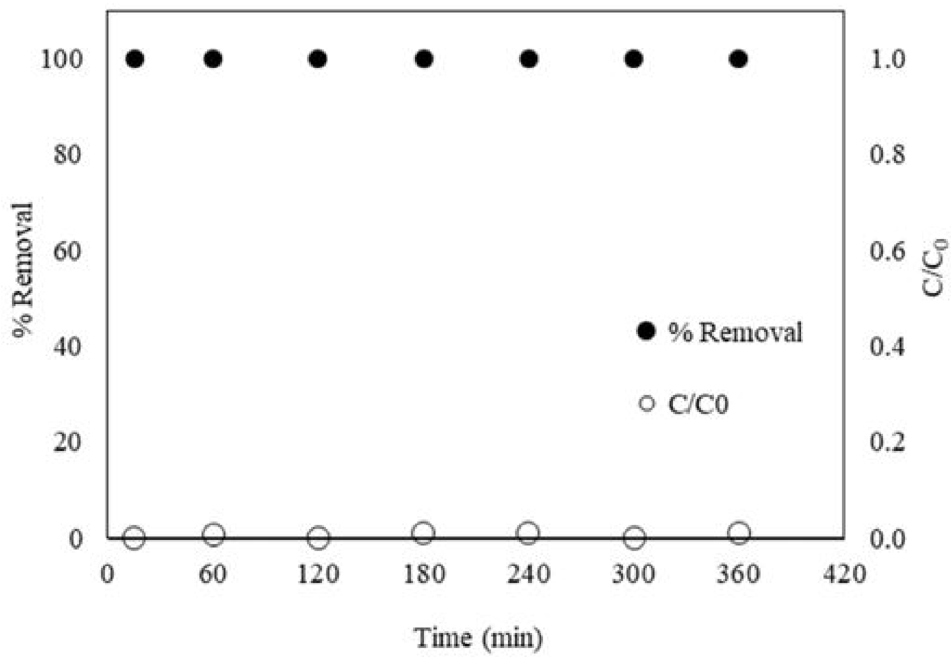

Figure 3: Removal percentage and breakthrough curve for the adsorption of catechin from solution A in a fixed-bed column packed with Tanex resin, as a function of time

Figure 3 shows that the resin in the fixed-bed column has completely removed all the catechin with in the standard solution. This result indicates that the resin was selective with respect to the standard catechin, in line with the manufacturer's specifications. According to this result, it was not possible standard catechin's breakthrough curve. The removal occurred rapidly (< 15 minutes) and was maintained over the experiment (460 minutes). This observation suggests that the standard catechin offered a steady resistance to mass transfer during the ion exchange over the experimental time. The resin's total ion-exchange capacity for the catechin was not reached. In a study carried out by Takemura et al. [39], using a packed bed of ion exchange resin to remove germanium ions. It was observed that the rupture time occurred when the residence time in the bed increased, that is, when the flow rate decreased from 120 mL h^{-1} para to 60 mL h^{-1}.

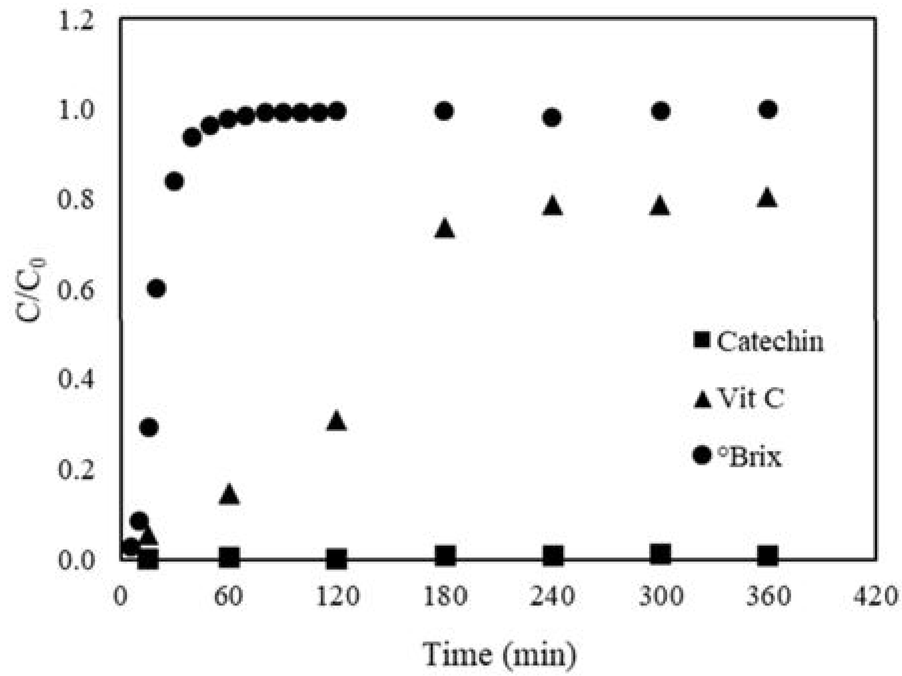

Figure 4: Breakthrough curves for catechin, vitamin C and °Brix using solution B in a fixed-bed column packed with Tanex resin as a function of time

Figure 4 shows breakthrough curves of catechin, vitamin C, and °Brix in solution B, using ion exchange at 25 ± 1 °C, a flow rate of 3 mL/minute in a fixed-bed column.

It is possible to observe from Figure 4 that the catechin in solution B (catechin standard solution + ascorbic acid + sucrose) was entirely removed. The presence of ascorbic acid and sucrose did no influence the removal of the standard catechin by the studied resin. Moreover, the standard catechin mass transfer also presented a steady characteristic. No breakthrough curve was obtained for this component. Thus, catechin contained in both solutions, A and B, showed the same behavior. Differently from what was observed for the catechins, breakthrough curves for vitamin C (ascorbic acid) and sucrose (°Brix) in solution B was achieved. This behavior refers to vitamin C and sucrose could have occurred due to the different maximum capacities that the resin presents for the components in solution B for the studied conditions.

In the breakthrough curve for the adsorption of vitamin C, the bed saturation was not reached, the experiment showed a C/C_0 ratio of about 0.80. There was a trend for stabilization of the final concentration of vitamin C. On the other hand, bed saturation was rapidly reached in the case of the sucrose (expressed by °Brix). As sucrose has moreavailable ions (OH^-) than vitamin C and standard catechin in solution B, this result is completely understandable for the studied conditions. The same flow rate at high concentrations passing through a fixed-bed column is prone to generate slightly sloped breakthrough curves [40,41]. In this study, sucrose is present in solution B (catechin - 0.6mg/mL + ascorbic acid – 1.824 mg/mL + sucrose - 110 mg/mL) with a higher proportion than the other components. This fact could promote a quick mass transfer between the constituents being evaluated. After this period, the sucrose concentration (°Brix) returned to its initial value (11.0 ± 0.1), leading to the complete stripping of the column regarding this compound.

Figures 5 and 6 show the breakthrough curves for pH and acidity in solution B, during ion exchange at 25 ± 1 °C, a flow rate of 3 mL/minute in a fixed-bed column.

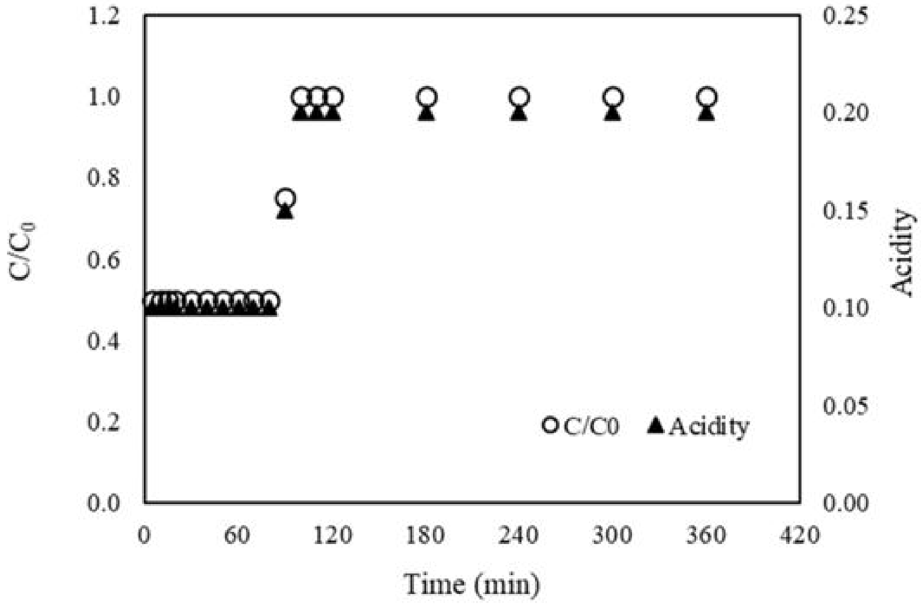

Figure 5: Breakthrough curves for acidity using solution B in a fixed-bed column packed with Tanex resin, as a function of time

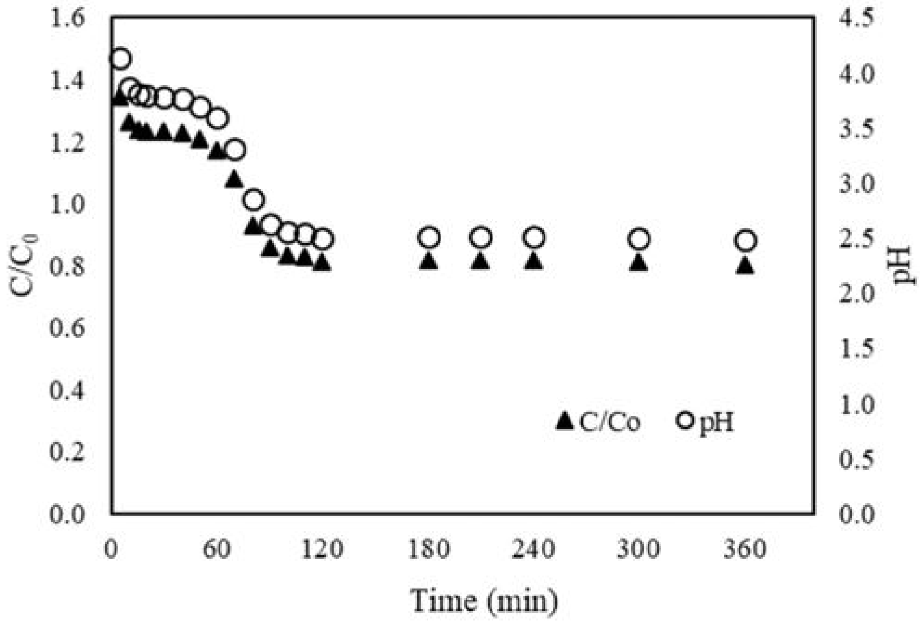

Figure 6: Breakthrough curves for pH using solution B in a fixed-bed column packed with Tanex resin, as a function of time

In Figure 5, it is noticed that the breakthrough curve for acidity exhibited a different profile in comparison to the other breakthrough curves during ion exchange in a fixed-bed column. After 80 minutes, experiments revealed that samples taken from the top of the column presented a reduction of 50% in acidity ($C/C_0 = 0.5 \pm 0.0$). After 100 minutes, the column attained its complete saturation ($C/C_0 = 1.0 \pm 0.0$), which was maintained until the runtime reached 360 minutes. At this time, the final product started to present the same acidity as the feed solution.

The breakthrough curve for pH (Figure 6) also presented a different profile from other curves. It was verified an increase in the pH of the solution at the exit of the column at the beginning of the experiment. pH decreased until attaining 2.6 ± 0.1, a value close to that of the feed solution (3.1 ± 0.1) during the experiment. Concerning the breakthrough curve, it was possible to observe that C/C_0 ratio decreased from 1.35 ± 0.01 to 0.81 ± 0.01, from the beginning to the end of the experiment, respectively. This behavior for pH curve was also found by Veit et al. [42] in their study about biosorptionof chrome (III) using a fixed-bed column. For this study, pH behavior can be elucidated by an ion-exchange mechanism between the ions contained in solution B.

Use of cashew apple juice for ion exchange in fixed-bed column

Different batches of cashew apple juice were used to assess the mass transfer process presented by this product in a fixed-bed column packed with Tanex resin. The removal of tannins and vitamin C was also evaluated. Table 4 presents the results of the chemical and physicochemical analysis for different batches of cashew apple juice centrifuged before the process in a fixed-bed column packed with Tanex resin.

Table 4: Chemical and physico-chemical analyzes of cashew apple juice of different batches before ion exchange in fixed-bed column

Analyzes	Cashew apple juice 1	Cashew apple juice 2
Condensed tannins (mg/100 g)	15 ± 1	115 ± 1
Vitamin C (mg/100 g)	185 ± 6	156 ± 5
pH	4.72 ± 0.01	4.21 ± 0.02
°Brix	11.6 ± 0.1	11.4 ± 0.1
Acidity (g/100 g citric acid)	0.30 ± 0.05	0.35 ± 0.01

The data in Table 4 show that condensed tannin content presented a high degree of variability from one batch of cashew apple juice to another. This means 15 ± 1 mg/100 g in juice 1 and 115 ± 1 mg/100 g in juice 2. Concerning vitamin C content, a concentration of 185 ± 6 mg/100 and 156 ± 5 mg/100 g for juice 1 and 2 were, respectively, verified. Despite this remarkable difference between the batches in terms oftannins and vitamin C, acidity mean values were very close for both cashew juices, 0.30 ± 0.05 in juice 1 and 0.35 ± 0.01 in juice 2. Regarding to the pH and the sucrose (^{0}Brix), it can be verified that there is no meaningful difference between the batches of cashew apple juice.

Figure 7 presents breakthrough curves of condensed tannins, vitamin C, and sucrose in cashew apple juices 1 and 2, during ion exchange with Tanex resin, at 25 ± 1 °C, at a flow rate of 3 mL/min in a fixed-bed column.

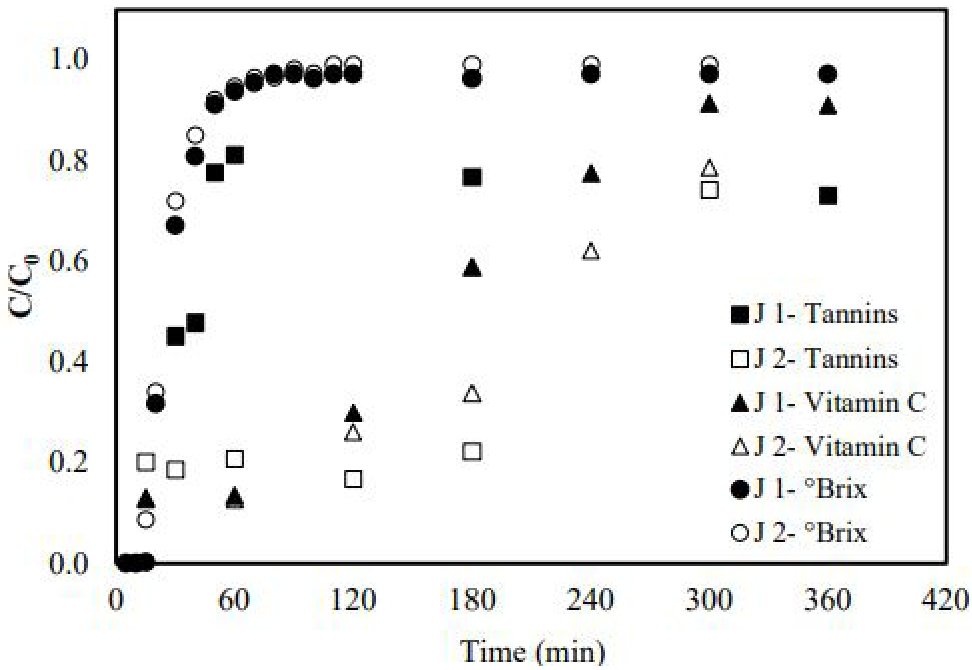

Figure 7: Breakthrough curves for tannins, vitamin C and °Brix in cashew apple juice 1 (J1) and 2 (J2), in a fixed-bed column packed with Tanex resin, as a function of time

When comparing juice 1 to 2 (Figure 7), it is possible to verify that the breakthrough curves presented a different behavior for the adsorption of the condensed tannins. Furthermore, both juices could not reach saturation point in the studied conditions. If the saturation of the fixed-bed column is desired, then an extension of the experimental time would be necessary. Concerning the tannins removal from juice 1, after a runtime of 20 minutes in the fixed-bed column, about 55 ± 1% of this component had been removed. At 60 minutes, this removal decreased to 20 % (C/C_0 = 0.80), maintained until the end of the experiment.

This difference in condensed tannins removal is mostly due to the low content of this constituent in juice 1 (15 ± mg/100 g) about juice 2 (115 ± 1 mg/100 g). On the other hand, the removal efficiency for juice 2 (with high tannins content) was more pronounced than for juice 1 at 60 minutes and reached 80 ± 1% (C/C_0 = 0.20). This result confirms the effect of tannins from cashew apple juice on the ion exchange process, as reported by Vidal and Pereira [27, 28]. They claimed that higher removal efficiencies in condensed tannins were observed for cashew apple juice supernatant concerning a juice submitted to a 50 % dilution. In other words, the higher the condensed tannins contents are in the juice, the higher the removal efficiency will be. This removal efficiency can also highlight the resin affinity with the tannins present in the cashew apple juice. Considering the mass transfer zone, ion exchange in Tanex resin seemed to be more efficient for juice 1 than for juice 2. However, the considerable removal efficiency was verified for juice 2. The results for both cashew apple juices indicate that it is possible to obtain cajuína using ion-exchange resin in a fixed-bed.

Regarding juice 2 (Figure 6), the curve for the condensed tannins presented by this juice reached the breakthrough point (C/C_0 = 0.22) within 180 minutes and reached the exhaustion point (C/C_0 = 0.74) within 300 minutes. Contrary to the results observed for juice 1 - which presented lower initial tannins (15 ± 1 mg / 100 g) and reached saturation within 60 min, faster than juice 2. This is possibly due to the fact that juice 2 had a higher amount of tannins in the solution (115 ± 1 mg/100g), which favor the occurrence of greater resistance in the mass transfer during ion exchange between the tannins and the resin. However, the behavior of the breakthrough curves for condensed tannins in juice1 and 2 was different with regards to the behavior of the breakthrough curve for the standard catechin (Figure 4) in solution B (catechin + vitamin C + sucrose); whose catechin present in the solutions was completely removed by the resin.

One hypothesis could be that the tannins might be interacting with other components in cashew apple juice, different from those in solution B. The tannins may be bound to some compound forming a complex that favors resistance during separation. This complies with the concave shape of subgroup S-1 in the isotherm of equilibrium (Figure 2). Regarding juices 1 and 2, this resistance proved to be lower for juice 1 since the higher amounts of tannins present in juice 2 favored their removal by the resin, thus confirming the effect of tannin concentration on the cashew apple juice in the ion exchange process for obtaining clarified cashew apple juice [28]. Moreover, this result indicates that this resin can also be used to remove tannins when these are present in cashew apple juice in high initial concentrations.

The behavior of the breakthrough curves for the adsorption of condensed tannins from both juices were also compared. Can stated that the curves are different. Possibly, the condensed tannins in cashew apple juices 1 and 2 could be bounded to some compound forming a complex that promotes resistance during the separation. This statement is in accordance with what is described by the concave shape of the equilibriumisotherm in the sub-group S-1 (Figure 2). When considering the resistances between juice 1 and 2, it was observed that the resistance for juice 1 was lower than that for juice 2. This may occur because a higher content of tannins in juice 2 than in juice 1 can favor the removal of this component using resin Tanex. This fact confirms the effect of tannins concentration in the cashew apple juice on the ion exchange process to obtain the clarified cashew apple juice [28]. Moreover, it indicates that such resin can also be used to remove tannins from cashew apple juice with high initial contents of this compound.

The breakthrough curve for the adsorption of vitamin C from juice 1 did not present a saturation point; likewise, this was observed for the condensed tannins in the same juice. After a runtime of 300 minutes, it was possible to achieve a removal efficiency of around 9 % in terms of vitamin C concerning the initial concentration. Thislow removal means an advantage for the final product (cajuína) since most of the vitaminC was preserved in juice. The results obtained for juice 1 endorse the fact that cajuina canbe produced with high vitamin C content by using ion-exchange resin in a fixed bed. In addition, a runtime of 180 minutes will make it possible to maintain low concentrations of tannins in juice to produce cajuína.

When the breakthrough curve for the adsorption of vitamin C from juice 2 is observed, it can be implied that the curve describes a similar profile to the one described by vitamin C in juice 1. This indicates a specific characteristic of the Tanex resin concerning vitamin C in cashew apple juice. Although the juices presented differences for the amounts of vitamin C (juice 1: 185 ± 6 mg/100 g and juice 2: 156 ± 5 mg/100) before passing through the fixed-bed (Table 4), this result indicates that a deviation of almost 20% between the amounts did not influence this component removal by the Tanex resin.

The mass transfer zones (Figure 7) show differences between the breakthrough curves for adsorption of both: vitamin C and condensed tannins from juice 1. As can be seen in Table 4, there is a considerable difference between the initial concentration of vitamin C (185 ± 6 mg/100 g) and condensed tannins (15 ± 1 mg/100 g) in juice 1. This represents that at the beginning of the experiment, the condensed tannins (in low concentrations) presented a lower resistance to the mass transfer in the fixed bed than the vitamin C. This finding also suggests the formation of complexes with the sugars in cashew apple juice during the tannin's separation. The vertical behavior at the beginningof the curve indicates that vitamin C was in higher concentration than condensed tannins. As a result, significant resistance to mass transfer was promoted into vitamin C onto theTanex resin in fixed-bed. In the case of juice 2, a similar behavior was noticed between the breakthrough curves for the adsorption of these components (vitamin C and condensed tannins) under such conditions.

Another point of interest is that the breakthrough curves for the adsorption of vitamin C from juice 1 and 2 are similar to that obtained when solution B was passed through the fixed-bed column (Figure 4). This may be explained by the values of vitamin C initial concentrations in both juices, which are close to the vitamin C concentration (147 ± 5 mg/100 g) initially contained in solution B (Table 3).

It is interesting to notice in Figure 7 that breakthrough curves for the adsorption of sucrose (^{o}Brix) from juices 1 and 2 were the only ones to present signs of resin saturation, which did not take place for condensed tannins and Vitamin C. Moreover, the breakthrough curves for the adsorption of sucrose from both juices describe a similar profile to that obtained for the adsorption of sucrose from solution B (catechin + vitamin C + sucrose). This result is probably due to the high proportion of sugar in cashew apple juice in relation to the other constituents. In a study carried out by Azevedo and Rodrigues[37], they detected a considerable amount of sugar in the juice when compared to the amounts of condensed tannins and vitamin C. This study confirms that when the same flow rate at high concentrations is applied to a fixed-bed column, this can promote a quick mass transfer as well as bed saturation, which is shown for solution B. This also indicates that the amount of sugar in the bed inlet will not interfere with cajuína quality since Tanex resin continues to remove condensed tannins, an undesirable component, and maintains the initial concentration of sugars after bed saturation, expressed in ^{0}Brix.

Figures 8 and 9 show the breakthrough curves for the acidity and pH in cashew apple juice 1 and 2, during ion exchange with Tanex resin, at 25 ± 1 °C, at a flow rate of 3 mL/minute, in fixed-bed column.

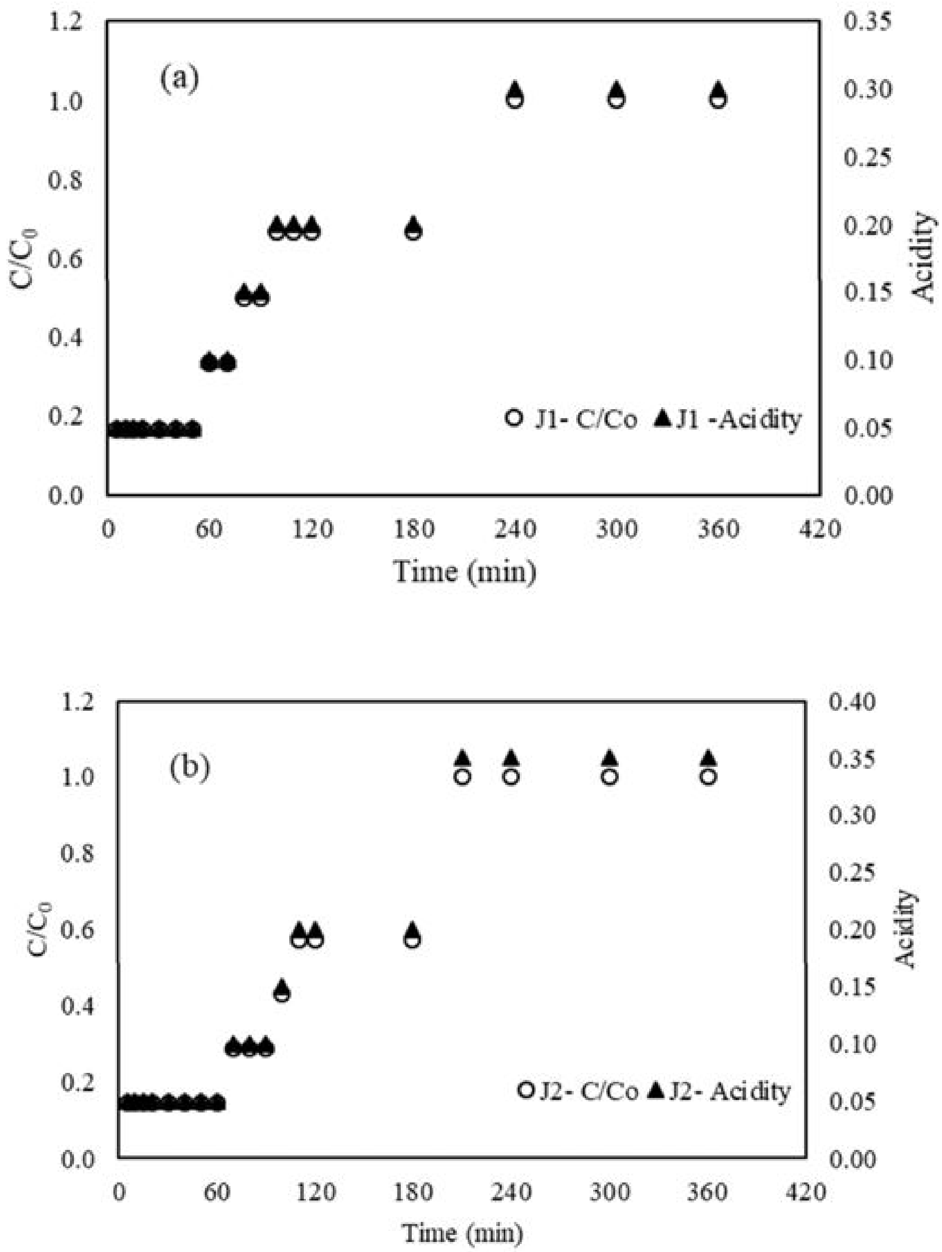

Figure 8: Breakthrough curves for acidity in both juices J1 (a) and J2 (b), in a fixed-bed column packed with Tanex resin, as a function of time

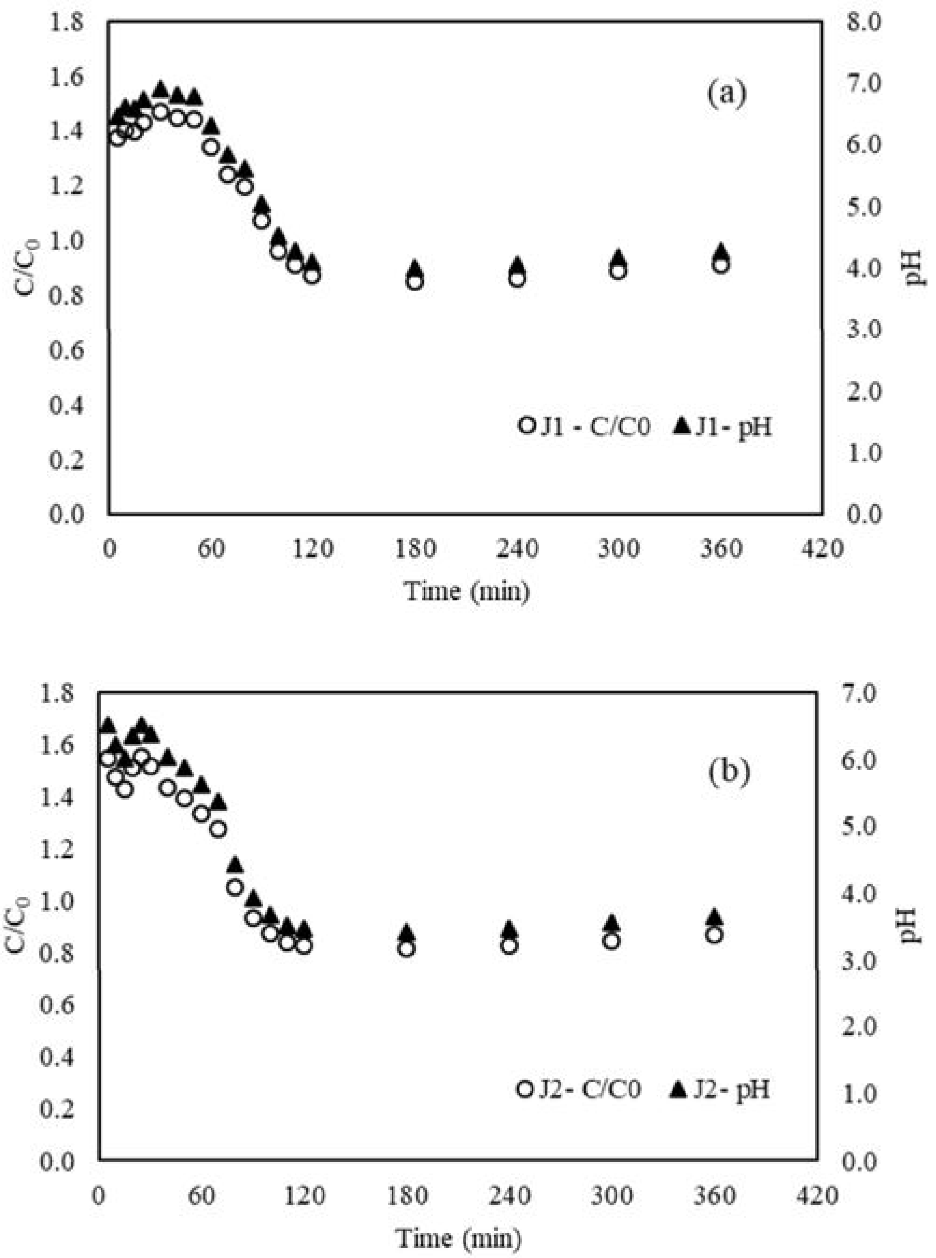

Figure 9: Breakthrough curves for pH in both juices J1 (a) and J2 (b), in a fixed-bed column packed with Tanex resin, as a function of time

The breakthrough curve for the acidity during the ion exchange (Figure 8) exhibited a different shape when juice 1 and 2 were compared and a similar shape if solution B behavior is considered. At a runtime of 180 minutes, it was possible to verify that the resin had reached its saturation ($C/C_0 = 1$), i.e., equilibrium was attained, and juice 1 (Figure 8a) presented its same initial degree of acidity (0.3 ± 0.05 g/100g of citric acid). The same behavior was perceived for the acidity in juice 2 (Figure 8b). The bed attained its equilibrium at 180 minutes. The final product presented the same degree of acidity from the initial solution (0.35 ± 0.01 g/100g of citric acid). As can be observed in Table 3, a slight difference between the acidities of juice 1 and 2 had no apparent effect on the ion-exchange process using a fixed-bed column. Askyildiz et al. [13] used weak base anion exchange resins in the deacidification of orange juice and found a reduction (23.08%) in acidity.

As discussed before, for solution B, the profile described by the breakthrough curves for pH can be attributed to the ion-exchange mechanism among the ions found in cashew apple juices 1 and 2. The breakthrough curves for the pH in juice 1 and 2 (Figure 9) also exhibited a different shape when compared to the other curves and a similar shapewhen solution B behavior is considered. For juice 1, at the beginning of the experiment, it can be stated that the pH increased at the column outlet in the first 60 min (6.51± 0.01, Figure 9a). Over time this pH decreased until it reached 4.25 ± 0.03, a value near to that observed for the feed solution (4.72 ± 0.01). Juice 2 showed similar behavior to what was observed for juice 1 and solution B. For this juice (Figure 9b), the pH values decreased over the experimental time until they reached a value of 3.65 ± 0.02, near the value observed for the feed solution (4.21 ± 0.02).

Akyıldız et al. [13] observed that pH values of orange juice increased by up to 23.08% (3.33 ± 0.06 to 4.10 ± 00.1) when they evaluated the pH of the juice passed through a column of ion exchange resins with a flow rate of 10 mL/min. And also observed a reduction in acidity in the same proportion. The same was reported by EdwinVera et al. [11] when they treated passion fruit juice in ion exchange resins that increasedthe pH from 2.93 ± 0.03 (unprocessed) to 3.3.

Conclusions

In this work, a process of tannin removal from cashew apple juice was assessed using catechin and cashew apple juice, with the purpose of analyzing the process in a fixed-bed column. Among the assessed models, Freundlich and especially Sips presentedthe best fitting for the experimental data. The Langmuir model was not recommended foruse for this system. The fixed-bed column studies indicated that the presence of vitamin C and sucrose did not influence the removal of catechin contained in solution B during ion exchange and that Tanex resin was highly selective for catechin. For two different concentrations of initial tannins in cashew apple juice (high and low tannin content), it was found that both juices promoted appropriate conditions to obtain cajuína, although agreater resistance is verified in the mass transfer; which confirms the affinity of Tanex resin with the condensed tannins. Given those mentioned above, the fixed-bed process using ion exchange resin allowed us to assess the effects of initial and final concentrations on the breakthrough curves and the mass transfer to the main components contained in cashew apple juice. Furthermore, the results of this study indicated that such a process could be considered an alternative for the production of clarified cashew apple juice or cajuína, applying technological innovations to obtain a product within the quality standards, enabling a smooth control process and the standardization of the final product.

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References

1. Brazil, Ministry of Agriculture, Food and Beverage. 2000. Technical Regulation for the Fixation of Identity and Quality Patterns for Fruit and Soup of Fruit or Sauce. Normative Instruction Nº 01; 07 January, Brasília-DF, Brazil.

2. Silva Neto RM, Abreu FAP, Paiva FFA (2003) Cajuína: how to produce with quality. Ed. SEBRAE, Terezina-PI, Brazil.

3. Nascimento RF, Aquino FWB, Amorim AGM, Prata LF (2003) Evaluation of the Thermal Treatment on the Chemical Composition and Quality of "Cajuína" beverage. Food Sci Tech-Brazil. 23: 217-21.

4. Vidal RHL (2016) Evaluation of the process of obtaining cajun by ion exchange resins (Original Title: Evaluation of the process of obtaining cajuine by ionic exchange resins). 136 f. PhD thesis, Department of Chemical Engineering, Federal University of Rio Grande do Norte, Natal-RN, Brazil.

5. Silva Neto RM, Abreu FAP, Paiva FFA (2009) Cajun peduncle processing: Cajuína. Document 123. ISSN 1677-1915, Embrapa Agroindústria Tropical. Fortaleza-CE, Brazil.

6. Coca M, García MT, Mato S, Cartón Á, González G (2008) Evolution of colorants in sugarbeet juices during decolorization using styrenic resins. J Food Eng. 89: 429-34.

7. Stella FM (2010) Effect of filtration with ionic resins on the quality of cachaça (Original Title: Effect of filtration with ionic resins on cachaça quality). 95 f. Master Thesis, Tecnology Sector, Federal University of Paraná, Curitiba-PR, Brazil.

8. Cavia-Saiz M, Muñiz P, Ortega N, Busto MD (2011) Effect of enzymatic debittering on antioxidant capacity and protective role against oxidative stress of grapefruit juice in comparison with adsorption on exchange resin. Food Chem 125: 158-63.

9. Ohmori K, Nakamura K, Kasahara M, Takabatake R, Kitta K, et al. (2013) A DNA extraction and purification method using an ion-exchange resin type kit for the detection of genetically modified papaya in processed papaya products. Food Control 32: 728–35.

10. Ibeas V, Correia AC, Jordão AM (2015) Wine tartrate stabilization by different levels of cation exchange resin treatments: impact on chemical composition, phenolic profile and organoleptic properties of red wines. Food Res Inter 69: 364-72.

11. Vera E, Dornier M, Ruales J, Vaillant F, Reynes M (2003) Comparison between different ion exchange resins for the deacidification of passion fruit juice. J Food Eng. 57: 199-207.

12. Merelo CL (2009) Study and application of new processes for the Majority of the elaboration of wines tinted in a temperate climate zone. 288 f. PhD thesis, Department of Chemical Engineering and Food Technology, University of Cadéz. Puerto Real, Spain.

13. Akyıldız A, Onür E, Agçam E, Kirit BD, Türkmen FU. 2022. Changes in quality parameters of orange juice deacidified by ion exchange resins. Food Chem., 375: 131837.

14. Limousin G, Gaudet JP, Charlet L, Szenknect S, Barthès V, Krimissa M. 2007. Sorption isotherms: A review on physical bases, modeling and measurement. Appl Geochem. 22: 249-75.

15. Rangabhashiyam S, Anu N, Giri Nandagopal MS, Selvaraju N. 2014. Relevance of isotherm models in biosorption of pollutants by agricultural by products. J Environ Chem Eng. 2: 398-414.

16. Alyüz B, Veli S (2009) Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. J Hazard Mater. 167: 482-8.

17. Vasiliu S, Bunia I, Racovita S, Neagu V. 2011. Adsorption of cefotaxime sodium salt on polymer coated ion exchange microparticles: Kinetics, equilibrium and thermodynamic studies. Carbohyd Polym 85: 376-87.

18. Fontan RCI, Minim LA,Bonomo RCF, Silva LHM, Minim VPR. 2013. Adsorption isotherms and thermodynamics of α-lactalbumin on an anionic exchanger. FluidPhase Equilibr 348:39-44.

19. Zhang Y, Yu X, Wang Q, Jiang Z, Fang T (2015) Adsorption of zinc onto anionic ion-exchange resin from cyanide barren solution. Chin J Chem Eng 23: 646-51.

20. DeboniTM, Batista EAC, Meirelles AJA (2015) Equilibrium, Kinetics, and Thermodynamics of Soybean Oil Deacidification Using a Strong Anion Exchange Resin. Ind Eng Chem 54: 11167-

79.

21. Thakare IN, Jana AK. 2015. Performance of high density ion exchange resin (INDION225H) for removal of Cu (II) from waste water. J Environ Chem Eng. 3: 1393-8.

22. Víctor-Ortega MD, Ochando-Pulido JM, Martínez-Ferez A (2016) Thermodynamic and kinetic studies on iron removal by means of a novel strong-acid cation exchange resin for olive mill effluent reclamation. Ecol Eng 86: 53–9.

23. Kalaruban M, Loganathan P, Shim WG, Kandasamy J, Naidu G, Nguyen T, Vigneswaran VS. 2016. Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidized-bed adsorption studies. Sep Purif Technol. 158: 62-70.

24. Soto ML, Moure A, Domínguez H, Parajó JC (2011) Recovery, concentration and purification of phenolic compounds by adsorption: A review. J Food Eng 105: 1-27.

25. Siu PCC, Koong LF, Saleem J, Barford J, Mckay G. 2016. Equilibrium and Kinetics of copper ions removal from wastewater by ion Exchange. Chin J Chem Eng. 24: 94–100.

26. Guimarães D, Leão VA. 2014. Batch and fixed-bed assessment of sulphate removal by the weak base ion exchange resin Amberlyst A21. J Hazard Mater. 280: 209–15.

27. Luz DA, Rodrigues AKO, Silva FRC, Torres AEB, Cavalcante Jr CL, Brito ES, Azevedo DCS. 2008. Adsorptive separation of fructose and glucose from an agroindustrial waste of cashew industry. Bioresource Technol 99: 2455-65.

28. Vidal RHL, Pereira CG (2015) Ion Exchange Resin Applied to Obtain Clarified Cashew Juice.Separ Sci Technol. 50: 2737-46.

29. Agostini-Costa TS, Lima A, Lima MV (2003) Tannin in cashew apple: vanillin versus butanol acid assay. Quim Nova 26: 763-5.

30. Broadhurst RB, Jones WT (1978) Analysis of condensed tannins using acidified vanillin. J Sci Food Agr. 29: 788-94.

31. Adolfo Lutz Institute (2008) Physico-chemical methods for food. 4th Ed .; São Paulo -SP, Brazil.

32. Oliveira RG, Godoy HT, Prado MA. 2010. Optimization of a colorimetric method to determine ascorbic acids in fruit jelly. Food Sci Tech-Brazil. 30: 244-9.

33. Carpiné D (2011) Recovery of phenylethyl alcohol aroma by batch and column adsorption (Original Title: Recovery of phenylethyl alcohol aroma by bath and column adsorption). 115 f. Master Thesis, Federal University of Paraná, Curitiba- PR, Brazil.

34. Cren EC (2009) Processing of ion exchange resin grease solutions (Original Title: Processing of solution solutions in ion exchange resin). PhD Thesis Department of Food Engineering, Stadual University of Campinas. São Paulo, Brazil.

35. Giles CH, Smith D, Huitson A (1974) A general treatment and classification of the solute adsorption isotherm. I Theoretical J Colloid Interf Sci. 47: 755-65.

36. Hinz C (2001) Description of sorption data with isotherm Equations. Geoderma. 99: 225-43.

37. Azevedo DCS, Rodrigues AE. 2000. Obtainment of high-fructose solutions from cashew (Anacardium occidentale L.) apple juice by SMB chromatography. Sep Sci Technol. 35: 2561-81.

38. BARROS MA (2016) Removal of Cr6 + and Fe3 + ions using ion exchange resins. (Original Title: Cr6 + and fe3 ion ion removal + ionic ion exchange resins). 183 f. PhD thesis, Department of Chemical Engineering, Federal University of Uberlandia, MG-RN, Brazil.

39. Takemura, Morisada S, Ohto K, Kawakita H, Matsuob Y and Fukuda D. (2013) Germanium recovery by catechol complexation and subsequent flow through membrane and bead-packed bed column Hiroaki J Chem Technol Biotechnol 88: 1468-72.

40. Lee JW, Kwon TO, Moon IS (2004) Adsorption of monosaccharides, disacarides and maltooligosaccharides on activated carbon for separation of maltopentaose Carbon. 42: 371-80.

41. Vázquez G, Alonso R, Freire S, Gonzalez-Alvarez J,Antorrena G (2006) Uptake of phenol from aqueous solutions by adsorption in a Pinus pinaster bark packed bed. J Hazard Mater. 133: 61-7.

42. Veit MT, Silva EA, Fagundes-Klen MR, Tavares CRG,

Gonçalves GC (2008) Biosorption of chromium (III) in fixed bed column. Technological studies. 4: 88-104.