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Selective adsorption of limonin and naringin from orange juice to natural and synthetic adsorbents

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Abstract In the majority of citrus juices, bitterness is mainly ascribed to the presence of limonoids (triterpenes) and flavanone glycosides (flavonoids), namely limonin and naringin.

In this study, the selective removal of limonin and naringin from citrus juice by batch adsorption to different materials was investigated. Since the removal of reducing sugars, pigments and vitamin C may also occur, the eventual adsorption of these compounds was also investigated. The following adsorbents were tested: activated diatomaceous earths, granulated activated carbon and synthetic neutral resins (Amberlite XAD-4, XAD-7 and XAD-16). Both Freundlich and Langmuir isotherm models showed a good fit to the adsorption of limonin to the resins used. Concerning naringin adsorption, a good fit of these models was only observed when the XAD-7 resin was used. Sigmoidal profiles were obtained for the adsorption of limonin to granular activated carbon. Unfavourable isotherms were also observed for limonin and naringin adsorption to activated earths. These isotherm adsorption profiles can be explained by a multilayer adsorption phenomenon.

The highest adsorption efficiency for the bitter compounds was observed when synthetic neutral resin, Amberlite XAD-7 was used. The separation factor limonin/naringin varied from 16 (with earths) to 57 (with XAD-7 resin). The adsorption of sugars and pigments to the resins was low. No adsorption of vitamin C was detected for any of the adsorbents tested.

The estimated affinity and separation factors show that the neutral resins tested are adequate for the selective removal of limonin from orange juices. The estimated values of free energy of adsorption, lower than -13.3 kJ mol^{-1} K^{-1}, indicate that a physiosorption process occurred.

Keywords Adsorption · Limonin · Naringin · Orange juice · Activated diatomaceous earths · Activated granular carbon (20–40 mesh) · Synthetic neutral resins

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Introduction

In several citrus juices, bitterness is mainly ascribed to the presence of limonoids (triterpenes) and flavanone glycosides (flavonoids), namely limonin and naringin.

In certain varieties of oranges, lemon and grapefruit, an increase in bitterness is observed in juices after extraction (delayed bitterness), which has restrained the industrial use of those varieties. Delayed bitterness is caused primarily by limonin. The observed phenomenon has been explained by the conversion of the non-bitter precursor, limonoate A-ring lactone, to limonin, catalysed by limonin D-ring lactone hydrolase, under acidic conditions [1]. The threshold for limonin is 6 ppm in orange juice at pH 3.8 [2].

Several techniques have been used to reduce the content of bitter limonoids in citrus juice, such as (i) adsorption [3], (ii) addition of bitterness suppressing agents to the juice (e.g., cyclodextrins) [4], (iii) post-harvest treatment of fruits with ethylene prior to processing [5] or (iv) biodegradation by enzymes or cells [5, 6]. All of these methods have several drawbacks since flavour and other components may be modified, decreasing the quality of citrus juice.

Adsorption is gaining wider acceptance for large-scale separation from liquids [7] due to the low-energy nature of adsorptive separation processes when compared to other operations, namely distillation or solvent extraction from diluted aqueous solutions. Adsorption is

a physical-chemical process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface till the thermodynamic equilibrium of the adsorbate concentration is attained, with no further net adsorption [8, 9, 10]. However, when adsorption is used in debittering processes, major difficulties are related to the need for the removal of limonin, naringin and other bitter compounds from the juices, without removing sugars, carotenoids and vitamin C.

The aim of this study was the reduction of bitter taste in citrus juices by selective adsorption of limonin and naringin, to the following adsorbents: activated diatomaceous earths, activated granular carbon (20–40 mesh) and Amberlite neutral resins (XAD-4, XAD-7 and XAD-16). The adsorbents were tested separately. The optimisation of the ratio (amount of adsorbent/amount of juice) was carried out for every adsorbent tested along the time-course of the adsorption.

In addition, the isotherms were established and the fit of Freundlich and Langmuir models to the experimental data points were evaluated. Affinity and separation factors were also estimated.

Materials and methods

Materials

Oranges of Navel variety were harvested in an orange orchard on the South of Portugal, and stored (–18 °C) until use.

The synthetic neutral resins, Amberlite, XAD-4 (apolar; polystyrene), XAD-7 (slightly polar; acrylic ester) and XAD-16 (apolar; polystyrene) were a gift from Rohm and Haas, USA. These resins Amberlite XAD-4, XAD-7 and XAD-16 had the following characteristics: average pore diameter of 50, 90 and 100 Å; surface area of 725, 450 and >800 $m^2\ g^{-1}$ and a pore volume of 0.98, 1.14 and 1.82 mL g^{-1}, respectively. The wet mesh size was between 20 and 60, for every resin.

The diatomaceous earths (approx. 90% SiO_2) and granulated activated carbons (20–40 mesh) were from Sigma Aldrich.

Limonin (minimum 75%, HPLC), naringin (minimum 95%) and β-caroten (Type I: synthetic, approx. 95%) were from Sigma Aldrich. All other chemicals were analytical grade and obtained from various sources.

Analytical methods

Limonin and naringin were analysed by HPLC in a LC-6 Shimadzu equipped with isocratic pump and an ultraviolet detector, SPD-6A Shimadzu UV, by using a RP-C18 column (Merck). In the case of limonin (λ=210 nm), the eluent was a mixture of 45% acetonitrile and 55% water while for naringin (λ=280 nm) it consisted of 20% acetonitrile and 80% water. For both analysis, the isocratic mobile phase was at a flow rate of 1.0 mL min^{-1}. Naringin was also analysed directly by spectrophotometry at 280 nm.

Total content of sugars was assayed by DNS method [11]. Proteins were analysed by Bradford method [12]. The presence of carotenoids was detected by the absorbance of the juice at 450 nm.

Preparation of adsorbents

Prior to use, the resins were washed with distilled water and dried at 40 °C and kept in a desiccator until use. The granulated carbon was washed with distilled water and dried at 100 °C and kept in a desiccator until use.

Effect of contact time on adsorption kinetics

A mass of 2.5 g L^{-1} of each adsorbent was added to 10 mL Navel orange juice (pH 3–3.5) previously centrifuged at 4000 rpm and filtered by filter paper Whatman no. 1. Adsorption was carried out at 25 °C and 140 rpm, in an orbital shaker. Each experiment corresponded to different adsorption times (0–120 min). At the end of each experiment, the adsorbent was removed from the juice by paper filtration. Limonin was assayed in triplicate.

To evaluate naringin adsorption, different amounts of sorbents were used: activated diatomaceous earths 7.5 g L^{-1}; Amberlite neutral resins, XAD-4 (7.5 g L^{-1}), XAD-7 (2.0 g L^{-1}) and XAD-16 (1.0 g L^{-1}).

A mathematical model was used to simulate the uptake of limonin and naringin against time. The model assumes that adsorption is proportional to the solute concentration in solution and to the fraction of unoccupied surface [13].

$$dC_t/dt = -k_1(1 - q/q_{max}).C_t \quad (1)$$

C_t is the concentration of solute in solution at instant t; q is the concentration or loading of adsorbate on adsorbent at instant t, q_{max} is the maximum capacity of the adsorbent and k_1 is a constant.

This equation was integrated numerically and the parameters for each set of experimental data were estimated using non-linear least-square regression analysis, by minimizing the residual-sum-of squares between the experimental data points and the estimated values by the model, using "solver" add-in from Excel for Windows, version 8.0 SR2. The following options were considered: Newton method; 100 iterations, precision of 10^{-5}; 5% of tolerance and 0.001 convergence.

Effect of adsorbent/juice ratio on adsorption kinetics

Different amounts of sorbents: activated diatomaceous earths 0.3–190 g L^{-1}; activated 20–40 mesh granular carbon 2.5–12.5 g L^{-1}; and Amberlite neutral resins, XAD-4 (2.5–200 g L^{-1}), XAD-7 (2.5–40 g L^{-1}) and XAD-16 (0.3–50 g L^{-1}) were added to 10 mL Navel orange juice (pH 3–3.5) previously centrifuged at 4000 rpm and filtered by filter paper Whatman no. 1. Adsorption was carried out for 2 h, as previously described.

The efficiency of the adsorption was estimated as the ratio (mass of adsorbed compound/ mass of adsorbent).

Establishment of isotherms

Theoretical background

The equilibrium of adsorption, at a given temperature, is usually presented under the form of adsorption isotherms, which are useful for selecting the most appropriate adsorbent and also for predicting the performance of adsorption systems [9].

In the adsorption of biological compounds, isotherms are currently described by the Freundlich or Langmuir models [8, 9, 14].

The empirical Freundlich equation is expressed by:

$$q = k_f.C^n \quad (2)$$

where q is the equilibrium concentration or loading of adsorbate on adsorbent, C is the equilibrium concentration of the solute in the fluid phase; and k_f and n are constants that are characteristic of the adsorption system [9, 14, 15]. The dimensions of k_f depend on the value of C while the exponent n is dimensionless. The k_f parameter increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The n value may vary along the adsorp-

tion process and is related to the adsorption efficiency and also to the energy of adsorption [16, 17]. Favourable adsorption corresponds to n values lower than 1, while values higher than 1 indicates unfavourable adsorption [8, 9, 14].

The Freundlich equation has been widely used since it is a mathematically simple model adequate to describe (i) non-linear adsorption in a narrow range of solute concentration and also (ii) adsorption processes on surface adsorption sites that are energetically heterogeneous. However, this model does not consider a limit in adsorption capacity. Theoretically, the amount of adsorbed solute may become infinite as bulk solute concentration increases [17].

The Langmuir isotherm has the following form:

$$q = q_{\max}.C/(k+C) \tag{3}$$

where k is a constant equal to the inverse of the equilibrium constant [18]. This isotherm model has the following theoretical basis: (i) the adsorbed molecules form a monolayer on the adsorbent surface; (ii) each site for adsorption is equivalent in terms of adsorption energy; (iii) there are no interactions between adjacent adsorbed molecules [9]. This isotherm and the number of sites on the adsorbent are limited [18].

However, for the majority of the adsorption systems, interactions between adsorbed molecules may occur leading to other profiles of adsorption isotherms.

In less common situations, concave isotherms are observed. These are unfavourable isotherms since relatively low solids loading are obtained [14].

Experiments

For the establishment of the isotherms q vs. C, experimental data points were obtained by varying juice concentration at constant adsorbent concentration (activated earths, granulated carbons or synthetic neutral resins). Different initial solute concentrations were obtained by diluting Navel orange juice in distilled water.

For limonin experiments, the following amounts of sorbents were added to 10 mL of aqueous solutions of Navel orange juice: 0.25 g of activated earths, 0.1 g of granulated carbons, 0.125 g of XAD-4; 0.1 g of XAD-7; 0.0625 g of XAD-16. For naringin experiments, different masses of adsorbents were used: 0.33 g of activated earths, 0.5 g of XAD-4; 0.25 g of XAD-7; 0.5 g of XAD-16.

The adsorption reaction was carried out at 25 °C, 140 rpm in an orbital shaker. After a 2 h reaction time, the adsorbent was removed from the solution by filtration and centrifugation at 10000 rpm for 4 min. Aliquots were taken from this juice and assayed for their content in limonin, naringin, sugars and carotenoids. All the experiments were carried out in triplicate.

The adsorbed amounts of limonin, naringin, carotenoids and sugars, q, were calculated from the following equation [19]:

$$q = (C_i - C).V/m \tag{4}$$

where, q is the equilibrium solid phase concentration (mass solute/mass sorbent); C_i is the initial (before adding the sorbent) liquid phase concentration (mass solute / volume solution); C is the equilibrium solute concentration in the aqueous phase (mass solute/volume solution); V is the volume of liquid phase; m the amount of adsorbent used (mass).

The fit of Langmuir and Freundlich models to experimental data was carried out using a non-linear curve-fit program in Excel for Windows, version 8.0 SR2, by minimizing the residual sum-of-squares between the experimental data points and the estimated values by the model.

Calculation of the adsorption affinity and separation factors

The adsorption affinity factors for each compound are defined as the equilibrium ratio q/C and calculated as the slope of the initial linear region of the isotherm q vs. C [19]. It is assumed that, in this region, the number of occupied sites is small as compared to the total active sites, which can be taken as constant and a measure of the affinity for the solute.

The separation factor between two solutes, α, is a measure of selectivity of the adsorbent. This parameter was calculated as the ratio between the affinity values of the individual solutes from the solution [7].

In this study, the obtained affinity and separation factors were estimated from the adsorption data obtained from the orange juice aqueous solutions and not from model solutions of each individual compound, as previously described [20].

Estimation of the adsorption free energy

The adsorption free energy (ΔG^0_{ads}) can be related with the Langmuir constant, k, by the following equation [21]:

$$\Delta G^0_{ads} = -RT \ln k \tag{5}$$

where R is the gas universal constant (8.314 $Jmol^{-1}$ K^{-1}) and T is the absolute temperature.

Results and discussion

Effect of contact time on adsorption kinetics

The uptake of limonin and naringin, throughout the time, to the sorbents tested are shown in Figs. 1 and 2. Adsorption of limonin and naringin increased with contact time. Previous experiments were carried out for 6 h. For every solute/sorbent system tested, no significant variation in residual concentrations of either limonin and naringin in juice was detected after a 1.5–2.0 h contact. Thus, after a 2 h reaction time, a steady-state approximation was assumed.

This is a very important aspect for the orange juice industry, since short contact time avoids degradation phenomena of the juices. Also, continuous adsorption systems can be implemented.

The model of Eq. 1 can describe the adsorption kinetics for limonin and naringin. The estimated parameters are presented in Table 1.

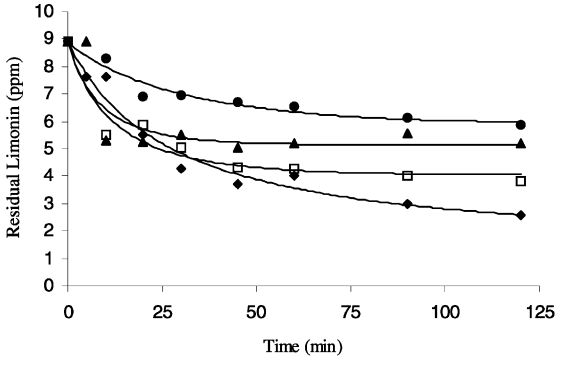

Fig. 1 Time-course of limonin adsorption, at 25 °C, from orange juice to various adsorbents: (*circles)* XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon. Lines are models according to Eq. 1

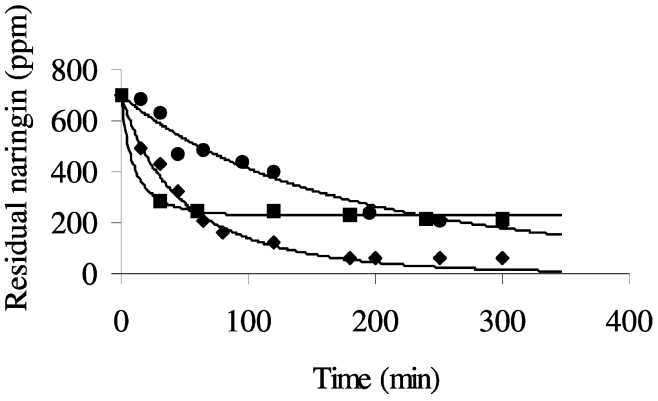

Fig. 2 Time-course of naringin adsorption, at 25 °C, from orange juice to various adsorbents: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin. Lines are models according to Eq. 1

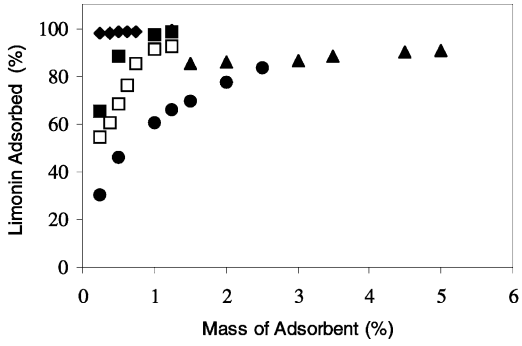

Fig. 3 Effect of ratio sorbent/juice on the removal of limonin from orange juice, at 25 °C, to various adsorbents: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon

Table 1 Estimated parameters for the model fitted to the uptake of limonin and naringin against time

Compound	Adsorbent	k_1 (min^{-1})	q_{max} (mg/g)
Limonin	XAD-4 resin	0.01	2.56
	XAD-7 resin	0.05	3.18
	XAD-16 resin	0.03	2.85
	Diatomaceous earths	0.05	1.50
	Activated carbon (20–40 mesh)	0.05	1.94
Naringin	XAD-4 resin	0.01	34.75
	XAD-7 resin	0.07	15.76
	XAD-16 resin	0.02	24.32

Optimisation of the ratio adsorbent/juice

After a contact time of 2 h, the amounts of limonin and naringin adsorbed to the different sorbents tested are presented in Figs. 3 and 4, respectively. For limonin adsorption (Fig. 3), the best results were obtained with XAD-16 and XAD-7 resins and activated carbon. A removal higher than 95% (m/v) was achieved with low adsorbent loads (less than 1%, m/v). A maximum adsorption of 80% of the original limonin was attained when the XAD-4 resin or activated earths were used at a concentration higher than 2% (m/v).

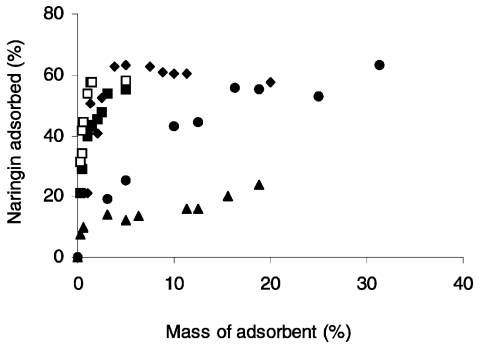

Fig. 4 Effect of ratio sorbent/juice on the removal of naringin from orange juice, at 25 °C, to various adsorbents: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon

The resins adsorbed limonin preferentially over naringin regardless of contact time (Fig. 4), as previously observed by Puri [3]. A plateau was reached for about 65% adsorption of naringin when the resins were used at concentrations higher than 2.5%, 3% and 7.5%, respectively for XAD-7, XAD-16 and XAD-4. The activated earths did not seem to be adequate for naringin removal from orange juices since only 14% of the original naringin was adsorbed.

The adsorption of vitamin C and proteins to the various adsorbents tested showed to be negligible.

With respect to the adsorption efficiency of limonin and naringin to the different adsorbents tested (Figs. 5 and 6), a decrease was observed with the mass of adsorbent used, according to a power equation. This might be due to a total removal of the solute even with low adsorbent concentration.

Shaw and collaborators [22, 4] also attempted the removal of limonin and naringin from grapefruit by adsorption to Amberlite XAD-4. Also, a more effective removal of limonin than naringin from the juice (79% against 47%) was observed. The XAD-16 resin was successfully used for the removal of bitter flavonoids (naringin, narirutin, hesperidin and neohesperidin) from grapefruit juices in a continuous column [23]. Similar adsorption results were obtained with another polystyrene divinylbenzene cross-linked co-polymeric adsorbent resin (Duolite S-861) in debittering lemon, tangerine, grapefruit and Navel orange juices [3]. The preferential adsorption of limonin to these resins over naringin may be partly due to the greater hydrophobicity of limonin as compared to naringin [3]. Debittering with XAD-16 improved the acceptance of grapefruit juices [24].

In addition to neutral adsorbent resins, ion exchange resins were also tested in the removal of acids and bitter compounds from citrus juice [25]. All adsorbent resins tested by Johnson and Chandler [25] were technically

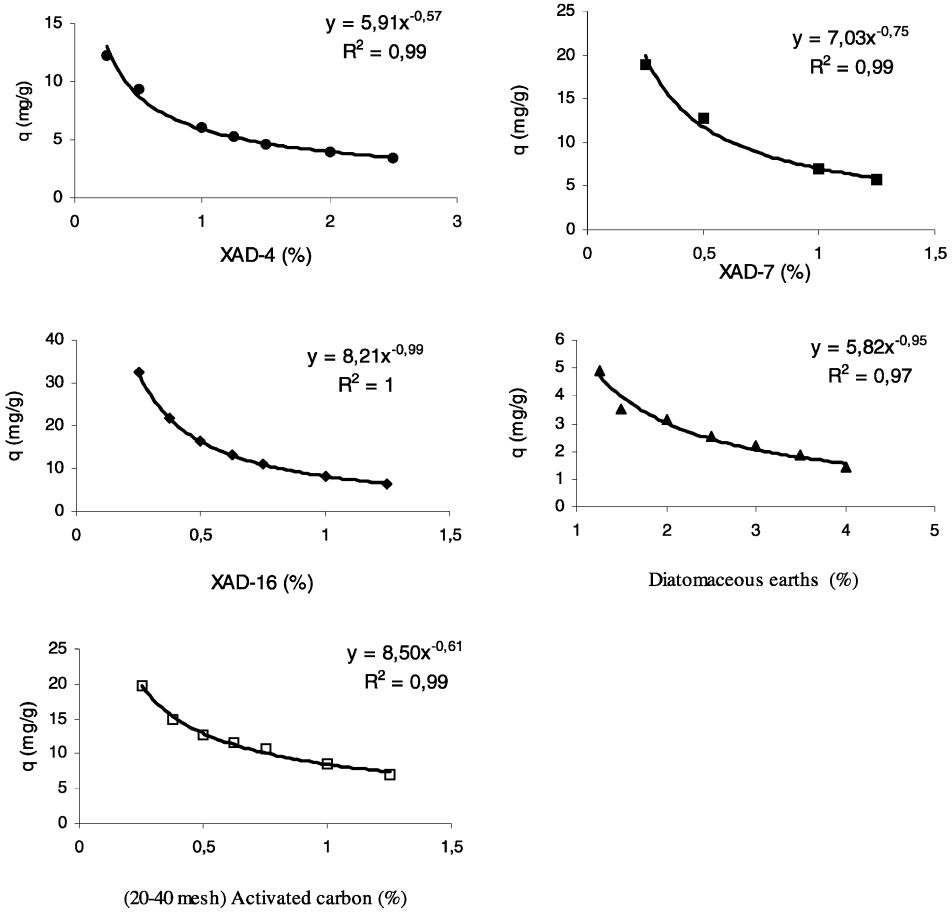

Fig. 5 Adsorption efficiency of limonin to the different adsorbent tested: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon

suitable for debittering grapefruit. With respect to anion exchange resins, the power of adsorption for acids and for limonin and naringin from citrus juices varied widely with the resin.

Adsorption isotherms

Adsorption isotherms of limonin

The adsorption isotherms for limonin to the activated earths, granular carbon and Amberlite neutral resins tested are shown in Fig. 7.

For the cases where Freundlich and/or Langmuir isotherm models could be well fitted to the experimental data points, the estimated parameters of the respective equations are listed in Table 2.

When the XAD-4, XAD-7 and XAD-16 resins were used, the observed profiles suggest a good fit for both Langmuir and Freundlich models to the experimental adsorption data.

For the Freundlich model, k_f values increase with the total adsorption capacity of the adsorbent; n values lower than 1 indicate favourable adsorption while values higher than 1 correspond to unfavourable adsorption [9, 14]. Thus, favourable adsorption of limonin (n lower than 1) was observed for XAD-7, XAD-16 and XAD-4 resins. However, among the resins tested, the XAD-7 resin exhibited a higher performance on the adsorption of limonin from Navel orange juice, since a lower n value, a higher energy of adsorption (related to k_f values) and a lower k value (from the Langmuir model) were estimated (Table 2).

Considerable deviations from the Langmuir and Freundlich models were observed when 20–40 mesh granulated carbon or activated earths were used. In fact, these isotherms exhibited a sigmoid profile corresponding to isotherms of Type IV, according to the BET classification [26]. They consist of stepwise isotherms, where each step corresponds to the formation of a well-defined adsorbed layer in porous solids containing pores in the intermediate or macropore range [26].

A sigmoid adsorption isotherm for limonin from lemon juice on 1% adsorbent cholesterol-talc was also observed [2]. This behaviour was explained by a possible competition between limonin and other less polar molecule [27] as well as by a possible cooperative adsorption [28].

Adsorption isotherms of naringin

The isotherms for naringin adsorption are presented in Fig. 8. When the XAD-7 resin was used, the isotherm

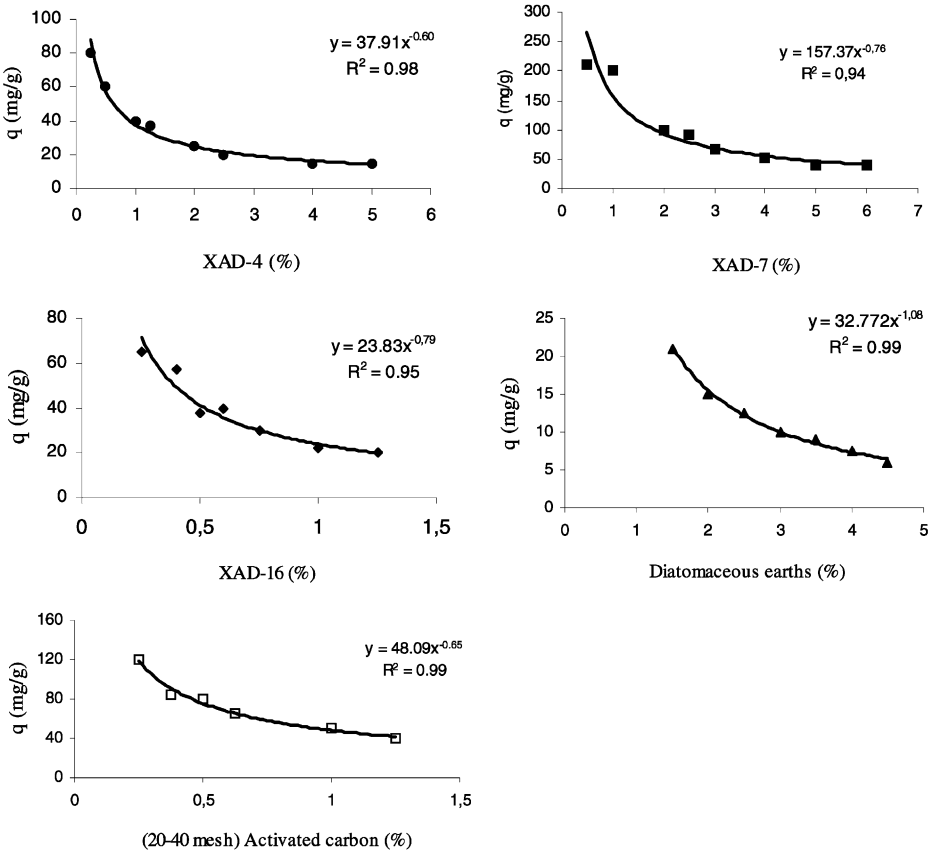

Fig. 6 Adsorption efficiency of naringin to the different adsorbent tested: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon

Table 2 Estimated parameters for Freundlich and Langmuir isotherm models

Compound	Adsorbent	Freundlich model $q=k_f C^n$		Langmuir model $q=q_{max}C/(k+C)$	
		k_f	n	q_{max}(mg/g)	k
Limonin	XAD-4 resin	0.26	0.72	2.72	11.55
	XAD-7 resin	0.89	0.34	2.34	2.46
	XAD-16 resin	0.35	0.69	13.3	75.25
	Diatomaceous earths	1.13	1.06	(a)	(a)
	Activated carbon (20–40 mesh)	(a)	(a)	(a)	(a)
Naringin	XAD-4 resin	0.001	1.34	(a)	(a)
	XAD-7 resin	0.84	0.36	11.6	217.2
	XAD-16 resin	0.004	2.04	(a)	(a)
	Diatomaceous earths	0.001	1.89	(a)	(a)
Reducing Sugars	XAD-4 resin	0.002	1.28	(a)	(a)
	XAD-7 resin	3.77	(a)	(a)	(a)
	XAD-16 resin	(a)	(a)	(a)	(a)
	Diatomaceous earths	(a)	3.21	(a)	(a)
	Activated carbon (20–40 mesh)	0.001	1.75	(a)	(a)
Carotenoids	XAD-4 resin	0.07	0.45	0.22	2.73
	XAD-7 resin	(a)	(a)	(a)	(a)
	XAD-16 resin	0.032	1.22	0.0001	2.35
	Diatomaceous earths	0.55	0.04	0.67	1.03

[a] Data not fitted to the model

profile suggest good fits for both Freundlich and Langmuir models. For XAD-4 and XAD-16 resins and activated diatomaceous earths, the observed isotherms and corresponding estimated parameters for the Freundlich model (Table 3) suggest an unfavourable adsorption of naringin. This may be explained by the occurrence of a multilayer adsorption [14, 26]. A lack of fit of Langmuir model was also observed for these adsorbents (Fig. 8 and Table 3).

Adsorption isotherms of carotenoids

For every neutral resin tested, unfavourable isotherm profiles were obtained for the adsorption of carotenoids

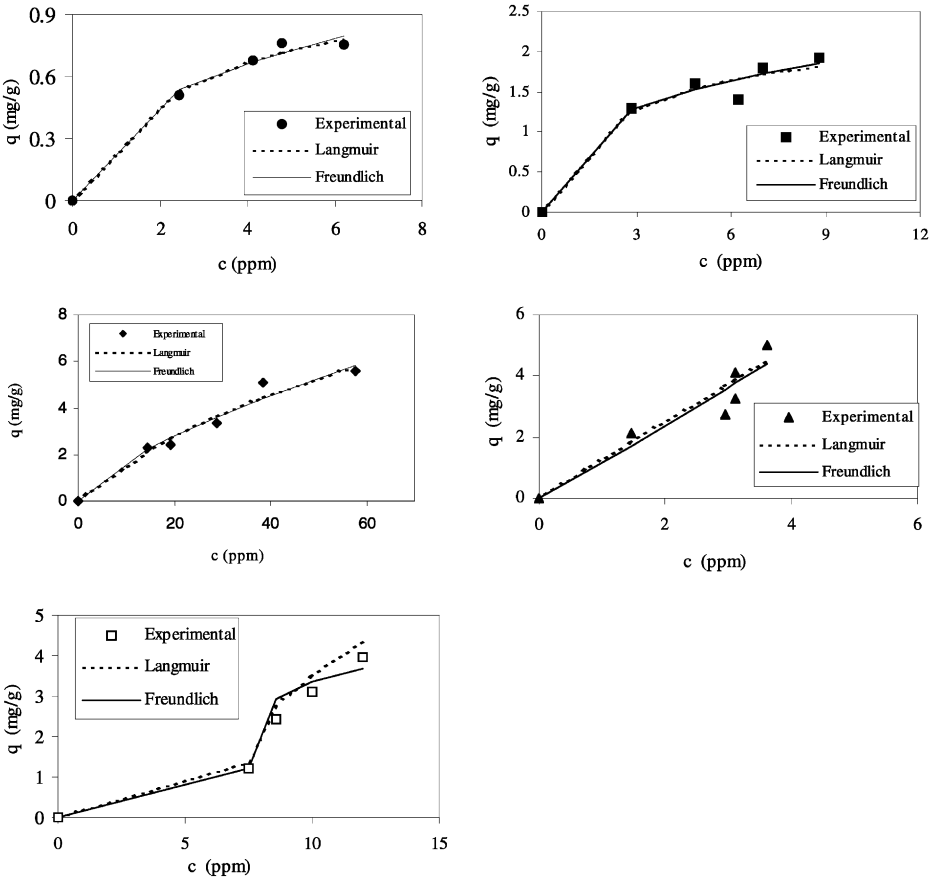

Fig. 7 Adsorption isotherms (Freundlich and Langmuir models), at 25 °C, of limonin from orange juice to the different adsorbent tested: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon

Table 3 Affinity and separation factors for limonin, naringin, reducing sugars and carotenoids, to the different adsorbents

Adsorbent	Affinity factors (mL g^{-1})				Separation factors			
	Limonin	Naringin	Carotenoids	Reducing Sugars	$\frac{\text{Limonin}}{\text{Naringin}}$	$\frac{\text{Limonin}}{\text{Sugars}}$	$\frac{\text{Limonin}}{\text{Carotenoids}}$	$\frac{\text{Carotenoids}}{\text{Sugars}}$
XAD-4 resin	160	3	0.05	0.003	53	5.3×10^4	3.2×10^3	16.7
XAD-7 resin	340	6	0.01	0.004	57	8.5×10^4	4.9×10^4	1.7
XAD-16 resin	130	5	0.06	–	26	–	2.1×10^3	–
Granular carbon (20–40 mesh)	320	–	–	0.001	–	3.2×10^5	–	–
Diatomaceous earths	940	58	0.08	0.002	16	4.7×10^5	1.2×10^4	38.5

(Fig. 9 and Table 3). When activated earths were used, experimental data could be described either by Langmuir or by the Freundlich models.

Adsorption isotherms of reducing sugars

As observed for carotenoids, the adsorbents tested showed a low capacity for the adsorption of reducing sugars (Fig. 10). This may be observed in the isotherm profiles corresponding to unfavourable adsorption (Table 3). These results are rather promising for industrial implementation since the removal of carotenoids and sugars from the juice is negligible.

Affinity and separation factors

For every adsorbent tested, the estimated values for affinity and separation factors (Table 3) show a strong selective adsorption towards limonin. Thus, on the basis of the values for affinity and separation factors, the selective adsorption occurred in the following order: limonin>>naringin>carotenoids≈reducing sugars.

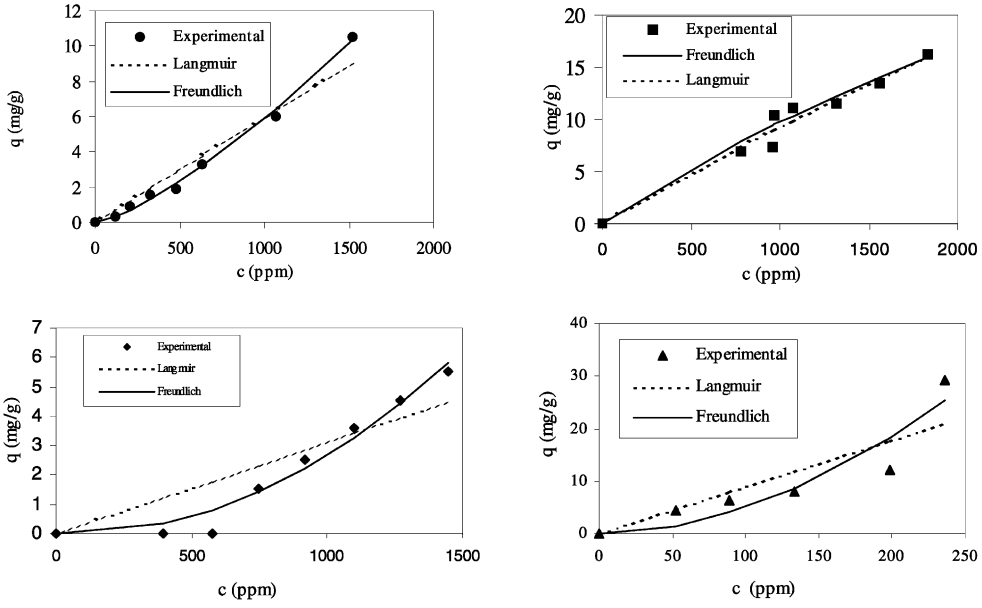

Fig. 8 Adsorption isotherms (Freundlich and Langmuir models), at 25 °C, of naringin from orange juice to the different adsorbent tested: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths

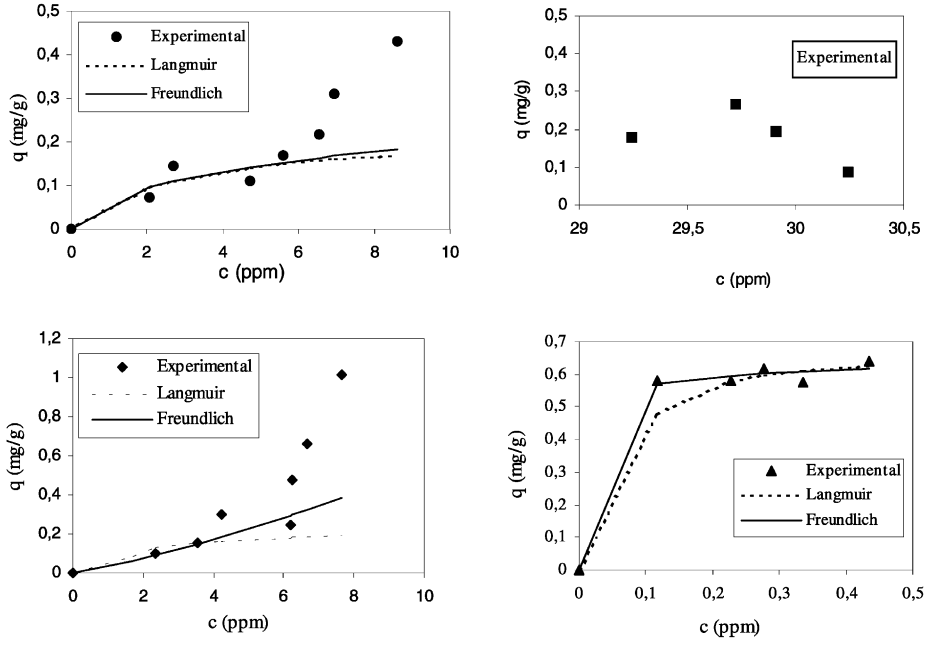

Fig. 9 Adsorption isotherms (Freundlich and Langmuir models), at 25 °C, of carotenoids from orange juice to the different adsorbent tested: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*diamonds*) XAD-16 resin; (*triangles*) activated diatomaceous earths

The highest adsorption affinity for limonin was observed for the diatomaceous earths.

The separation factors indicate that the affinity for limonin ranged from 16 to 57 times greater than the affinity for naringin (with diatomaceous earths and XAD-7 resin, respectively) and from 3–5 orders of magnitude greater than the affinities for the remaining compounds.

Maity et al. [7] and Payne et al. [19] showed that the adsorption of apolar solutes from aqueous solution onto neutral resins (XAD-4 and XAD-7) was due to hydrophobic interactions. This probably explains the better performance of these resins for the adsorption of limonin and naringin (apolar molecules) when compared to the adsorption of carotenoids and reducing sugars.

Table 4 Adsorbed limonin and naringin per unit area of resin

Adsorbent	Limonin	Naringin
	($\mu g\ m^{-2}$)	
XAD-4 resin	7	95
XAD-7 resin	14	70
XAD-16 resin	7	61

In addition, the maximum adsorption of limonin and naringin per unit surface area of resin was calculated, assuming a monolayer adsorption (Table 4). For this purpose, q_{max} values, estimated from Eq. 1 (Table 1), and the reported surface area for the resins used (c.f., materi-

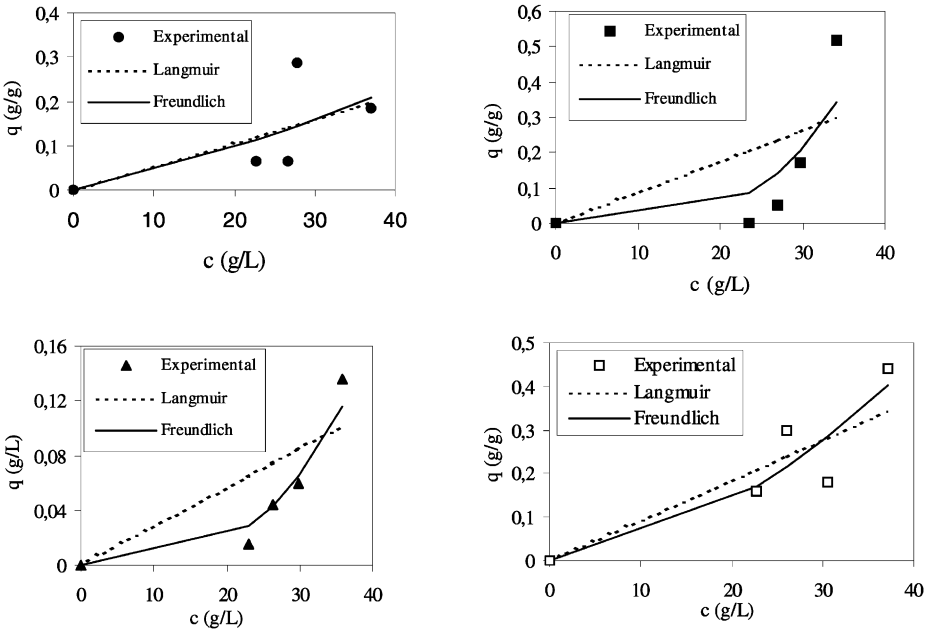

Fig. 10 Adsorption isotherms (Freundlich and Langmuir models), at 25 °C, of reducing sugars from orange juice to the different adsorbent tested: (*circles*) XAD-4 resin; (*solid squares*) XAD-7 resin; (*triangles*) activated diatomaceous earths; (*open squares*) activated 20–40 mesh carbon

Table 5 Estimation of free energy of adsorption

Compound	Adsorbent	ΔG (kJ mol^{-1})
Limonin	XAD-4	–6.06
	XAD-7	–2.23
	XAD-16	–10.71
Naringin	XAD-7	–13.33
Carotenoids	XAD-4	–2.49
	XAD-16	–2.12
	Activated earths	–0.07

als and methods) adjusted to a dry resin basis (i.e., ca. 0.5 g dry resin/g wet resin) [29], were used.

The estimated affinity and separation factors show that the neutral resins tested are adequate for the selective removal of limonin from orange juices.

Estimation of free energy of adsorption

For the systems where the Langmuir isotherm could be fitted to the experimental data (Table 2), free energy of adsorption was estimated by Eq. 5. The estimated values (Table 5) are rather low indicating that a physiosorption process occurred [14].

Conclusions

For every solute/adsorbent system tested, adsorption equilibrium was attained in less than 2 h of contact. A favourable adsorption of limonin to the neutral resins tested was observed. Concerning naringin adsorption, a good fit of both Freundlich and Langmuir models was only observed when XAD-7 resin was used. Sigmoid profiles were obtained for the adsorption of limonin to granular activated carbon. Unfavourable isotherms were also observed for limonin and naringin adsorption to activated earths.

For every resin tested, unfavourable isotherm profiles were obtained for the adsorption of carotenoids. A low capacity for the adsorption of reducing sugars, vitamin C and proteins was also observed for the adsorbents tested. In addition, the estimated values for affinity and separation factors show a strong selective adsorption towards limonin.

The results obtained are rather promising for industrial implementation of the selective removal of limonin from orange juices by adsorption to the neutral resins tested.

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