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Equilibria, Kinetics, and Mechanisms for the Adsorption of Four Classes of Phenolic Compounds onto Synthetic Resins

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The adsorption of five phenolic compounds of four different classes from aqueous batch solutions onto four styrene-divinylbenzene and acrylic resins (EXA 90, EXA 118, XAD 7, and XAD 16) was investigated regarding their equilibria, kinetics and surface-energy heterogeneity, and mechanisms of adsorption. The experimental equilibrium data were very well fitted to Langmuir and Freundlich models ($R^2 > 0.900$). Three kinetic models (pseudo-first-order, pseudo-second-order, and an intra-particle diffusion model) were suitable for describing the experimental data, the pseudo-second-order kinetic model being the best one ($p < 0.001$). The adsorption energy values were low (<19.00 kJ/mol), suggesting a physical adsorption process. Driving forces involved in the adsorption of the phenolic compounds onto the resins were hydrogen bonding, $\pi - \pi$ stacking and hydrophobic interactions.

Keywords adsorption isotherm; adsorption kinetics; adsorption mechanisms; flavonoids; macroporous synthetic resins; phenolic acids

INTRODUCTION

Consumption of foods containing phenolic compounds can reduce the risk of human chronic diseases such as cancer, atherosclerosis, arthritis, diabetes, and other aging diseases (1). Thus, these bioactive compounds have been widely studied in the last decade. In the plant kingdom, phenolic compounds, consisting of over 10,000 compounds, are mainly classified according to their carbon skeleton, i.e., hydroxybenzoic acids (C_6-C_1), hydroxycinnamic acids (C_6-C_3), and flavonoids (flavanones, flavones, isoflavones, flavanonols, flavonols, flavan-3,4-diols, flavanols, and anthocyanidins; C_6-C_3-C_6) (2).

The adsorption of valuable organic compounds from solution is gaining wider acceptance for large-scale separations due to the low-energy nature of adsorptive separation processes when compared to other operations, namely, distillation or solvent extraction from dilute aqueous solutions (3). In addition, adsorption technologies using nonpolar styrene-divinylbenzene (SDVB) copolymers or slightly hydrophilic acrylic polymers have been shown to be applicable for industrial-scale processes because of their high adsorption capacities, ease of recovery of the adsorbed molecules, relatively low costs, and easy regeneration (4). Adsorption is a process that involves the mass transfer of an adsorbate from the fluid phase to the adsorbent surface until a thermodynamic equilibrium of the adsorbate concentration is achieved, with no further net adsorption (5,6).

The non-ionic polymeric macroporous synthetic resins, especially SDVB and acrylic resins, have recently received great attention from the scientific community for their potential in the separation and/or purification of phenolic compounds. They have been used in the reduction of bitterness in juice (naringin) (3,7), in the treatment of waste water from citrus processing (hesperidin) (8), in the partial purification and concentration of phenolic compounds of *Inga edulis* leaves (total phenolics and flavanoids) (9), *Ginkgo biloba* leaves (quercetin and kampferol derivatives) (10), *Spinacia oleracea* leaves (spinacetin) (11), and in the adsorption of pure compounds—cyanidin-3-glucoside (4), hesperidin (12), rutin, naringin, quercetin, naringenin, and tangeritin (13).

This study focused on the comparison of the differences in affinity and intensity of adsorption of three phenolic acids (caffeic, ferulic, and gallic acid) and two flavonoids (catechin and rutin) using several SDVB (EXA 90, EXA 118, and XAD 16) and acrylic (XAD 7) resins. Next, the adsorption kinetics of the five phenolic compounds was determined for the two resins presenting the highest adsorption capacity. Additionally, the energies involved in the adsorption processes were characterised and adsorption mechanisms were proposed.

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MATERIALS AND METHODS

Chemicals

Food-grade macroporous resins Amberlite XAD 7 and XAD 16 (Sigma, Steinheim, Germany), Relite EXA 90, and EXA 118 (kindly supplied by Residion, Mitsubishi Chem. Co., Milan, Italy) were used as adsorbents. The physical and chemical properties of the resins are presented in Table 1. Caffeic acid and catechin (Fluka, Buchs, Switzerland), ferulic and gallic acids, and rutin (Aldrich, Steinheim, Germany) standards (purity $\geq$95%) (Fig. 1) were used in the batch isotherm and kinetics experiments. Citric acid and sodium citrate monohydrate used for buffer solutions and ethanol (96%) were supplied by Synth (São Paulo, Brazil). Ultrapure water was prepared using an Elga Maxima CS system (Elga, High Wycomb, UK).

Experimental Studies

The preconditioning of the adsorbents was performed by an extensive wash (5×20 mL) with distilled water to remove salts and impurities, e.g., Na_2CO_3 and NaCl. The resins were dried at 70°C for 24 h and then cooled in a desiccator at room temperature. Aliquots of 50 mg of dried resin were weighed and immersed in 10 mL of 96% ethanol for 12 h. The ethanol was then replaced with distilled water by washing (5×20 mL). The phenolic compound solutions were prepared in sodium citrate/citric acid buffer (pH 3.50, 0.05 M) in the concentration range of 5 to 500 mg/L, except for rutin, for which concentration ranged from 10 to 250 mg/L. In order to construct the sorption isotherms, 10 mL of these solutions were put in contact with 50 mg of resin in 50 mL amber glass bottles and were saturated with gaseous nitrogen before closing. These bottles were submitted to planetary agitation at 200 rpm for 2 h at 25°C. For the kinetics study, buffered solutions of each phenolic compound (250 mg/L) were kept in contact with the adsorbent in the same conditions and 100 μL were collected after 5, 15, 30, 60, 90, 120 and 180 min.

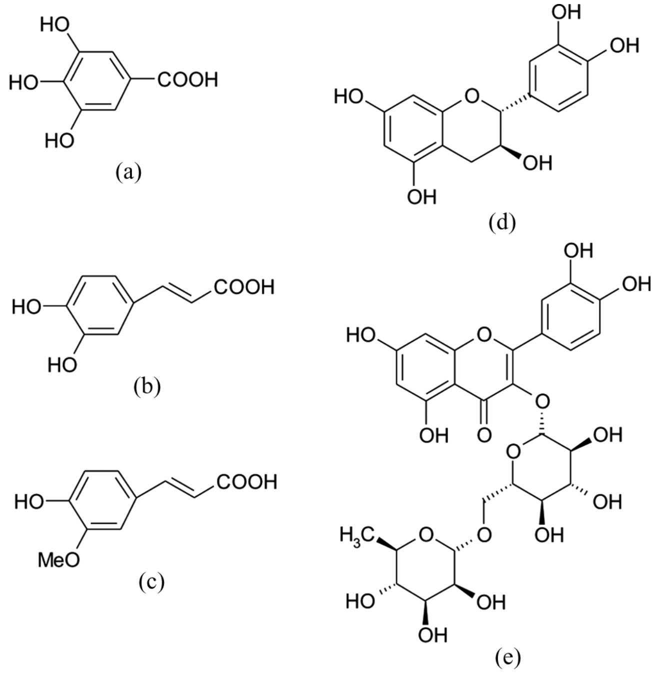


FIG. 1. Chemical structures of phenolic acids and flavonoids: (a) gallic acid, (b) caffeic acid, (c) ferulic acid, (d) (+) catechin, and (e) rutin.

Quantification of Phenolic Compounds

The quantification of phenolic compounds was performed by UV - spectrophotometry using a UV/Visible spectrophotometer (Ultrospec 2000, Pharmacia Biotech, Cambridge, UK). Plots of absorbance against wavelength, with peak scanning between 200 and 400 nm, were made in order to find the maximum absorption wavelength (λ_{MAX}) for each phenolic compound. Calibration curves were set for each phenolic compound using the same buffered solution at λ_{MAX}.

Statistical and Regression Analyses

The experimental data obtained in adsorption isotherms and kinetics studies were analysed by non-linear

TABLE 1
Physical and chemical properties of macroporous synthetic resins

Trade name	Chemical structure	Dipolar moment	Density (g/mL)	Particle size (mm)	Pore radius (Å)	Porosity (mL/g)	Surface area (m^2/g)
[a]EXA 90	[c]SDVB	0.30	1.18	0.25	105	1.30	630
[a]EXA 118	SDVB	0.30	1.04	0.25	90	2.30	1,200
[b]XAD 7	Acrylic	1.80	1.24	0.25–0.84	45	1.14	450
[b]XAD 16	SDVB	0.30	1.08	0.25–0.84	50	1.82	800

[a,b] Alimentary use allowed by the U.S. Food and Drug Administration, Code of Federal Regulations Title 21 and Code of regulation of the Council of Europe, Resolution AP (97) 1, respectively [4, 12].

[c] Styrene-divinylbenzene.

least-squares regression, by minimising the residual sum of squares between the experimental data points and the values estimated by the model, using the STATISTICA 7.1 software (Stat-Soft, Tulsa, OK). The following options were selected: Simplex and quasi-Newton method, 500 iterations, precision of 10^{-5}, a tolerance of 5%, and a convergence criterion of 0.0001.

MODELS

Adsorption Isotherms

Adsorption isotherms are used for describing adsorption equilibria at a given temperature. Experimental data are fitted to mathematical models, e.g., those of Langmuir or Freundlich, which are expressed by Eqs. (1) and (2), respectively.

$$q_s = \frac{Q_M a_L C_S}{1 + a_L C_S} = \frac{K_L C_S}{1 + a_L C_S} \tag{1}$$

$$q_S = K_F C_S^{b_F} \tag{2}$$

where q_s (mg/g) is the mass of adsorbate per mass of adsorbent; Cs (mg/L) is the concentration at equilibrium; a_L (L/mg) and Q_M (mg/g) are the Langmuir constants, K_L is the solute adsorptivity (L/g); K_F (L/g) and b_F (dimensionless) are the empirical Freundlich constants.

Adsorption Kinetics

Adsorption kinetics are used to determine the rate of adsorption processes (14). Three mathematical models were applied to simulate the uptake of phenolic compounds on the macroporous synthetic resin with time: i) a pseudo-first-order Lagergren equation (15,16) (Eq. (3)); ii) a pseudo-second-order model proposed by Ho and McKay (15–17) (Eq. (4)); and iii) an intra-particle diffusion model formulated by Weber & Morris (18) (Eq. (5)).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{4}$$

$$q_t = k_{id} t^{1/2} + C \tag{5}$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively, k_1 (1/min), k_2 (g/mg min), k_{id} (mg/(g min)$^{0.5}$)) are the rate constants of the pseudo-first-order and pseudo-second-order adsorption and intra-particle diffusion models, respectively, and C is a constant related to the thickness of the boundary layer (mg/g).

Surface-Energy Heterogeneity

Dubinin-Radushkevich developed an isotherm model that can provide useful information on the mean adsorption energy, allowing the evaluation of whether physical or chemical adsorption is predominant (19). Consequently, the experimental data were applied to this Dubinin-Radushkevich isotherm model (Eq. (6)).

$$Q_e = Q_{DR} \exp(-K_{DR}\varepsilon^2) \tag{6}$$

where Q_e (mol/ L g) is the adsorption capacity at equilibrium, Q_{DR} (mol/g) is the Dubinin-Radushkevich constant, and K_{DR} (J^2/mol^2) is a constant for the adsorption energy related to the mean adsorption energy, E (Eq. (7)),

$$E = \frac{1}{\sqrt{-2K_{DR}}} \tag{7}$$

where E is the free energy (kJ/mol) of the transfer of 1 mol of adsorbate to the surface of the resin.

The variable ε is the Polanyi potential and is defined by Eq. (8).

$$\varepsilon = RT \ln[1 + (1/C_S)] \tag{8}$$

where R is the gas constant (8.314 J/K mol), T (K) is the temperature, and C_S (g/L) is the concentration at equilibrium.

The representations of phenolic compound structures and their interaction forces with resins were illustrated using the ChemDraw Ultra 11.0 software (Cambridge Soft, Cambridge, MA).

RESULTS AND DISCUSSION

Adsorption Isotherms

Adsorption isotherms were constructed for the five phenolic compounds (caffeic, ferulic, gallic acids, catechin and, rutin) using the four synthetic macroporous resins (EXA 90, EXA 118, XAD 7, and XAD 16). For all isotherms, the data were adjusted to the Langmuir and Freundlich models in order to compare the total adsorption capacities, as well as some qualitative adsorption aspects, such as affinity, favorability, and solute-area interaction. The experimental data obtained for the phenolic compounds studied matched very well to that predicted by both models (Table 2) in the range of studied concentrations; the experimental results are shown in Fig. 2. The Freundlich and Langmuir models yielded similar coefficients of determination (R^2) and significance levels, as shown in Table 2. Thus, both models can be used to describe the adsorption of phenolic compounds onto macroporous synthetic resins.

For adsorption capacities, which were described in terms of Q_M by the Langmuir model, values ranged from 11.42 mg/g (for gallic acid on XAD 16) to 133.90 mg/g

TABLE 2
Estimated parameters for the Langmuir and Freundlich models for the adsorption of phenolic compounds onto macroporous synthetic resins

		Langmuir model				Freundlich model		
Resin	Phenolic compound	Q_M (mg/g)	a_L (L/mg)	K_L (L/g)	R^2	K_F (L/g)	b_F	R^2
EXA 118	Caffeic acid	61.24	0.0538	3.295	0.985***	8.15	0.381	0.978***
	Ferulic acid	117.63	0.0325	3.823	0.992***	8.17	0.540	0.996***
	Gallic acid	27.84	0.0048	0.134	0.929**	0.59	0.576	0.900**
	Catechin	89.14	0.0278	2.478	0.983***	7.69	0.432	0.997***
	Rutin	37.87	0.1389	5.261	0.956***	7.69	0.374	0.966***
EXA 90	Caffeic acid	45.13	0.0230	1.038	0.995***	3.87	0.420	0.953***
	Ferulic acid	107.02	0.0103	1.102	0.954***	3.37	0.592	0.981***
	Gallic acid	24.09	0.0011	0.026	0.981***	0.07	0.765	0.989***
	Catechin	127.72	0.0036	0.460	0.988***	1.43	0.677	0.999***
	Rutin	39.23	0.0259	1.016	0.981***	2.67	0.520	0.992***
XAD 7	Caffeic acid	63.13	0.0168	1.061	0.997***	3.60	0.492	0.979***
	Ferulic acid	95.66	0.0098	0.937	0.997***	2.83	0.591	0.994***
	Gallic acid	37.93	0.0031	0.118	0.995***	0.41	0.660	0.999***
	Catechin	110.00	0.0090	0.990	0.991***	3.36	0.576	0.994***
	Rutin	33.93	0.0307	1.042	0.993***	2.85	0.480	0.988***
XAD 16	Caffeic acid	46.52	0.0244	1.135	0.979***	4.22	0.409	0.904**
	Ferulic acid	103.59	0.0376	3.895	0.996***	8.30	0.501	0.973***
	Gallic acid	11.42	0.0076	0.087	0.985***	0.40	0.511	0.934**
	Catechin	133.90	0.0060	0.803	0.987***	2.63	0.629	0.996***
	Rutin	44.15	0.0680	3.002	0.974***	6.31	0.426	0.987***

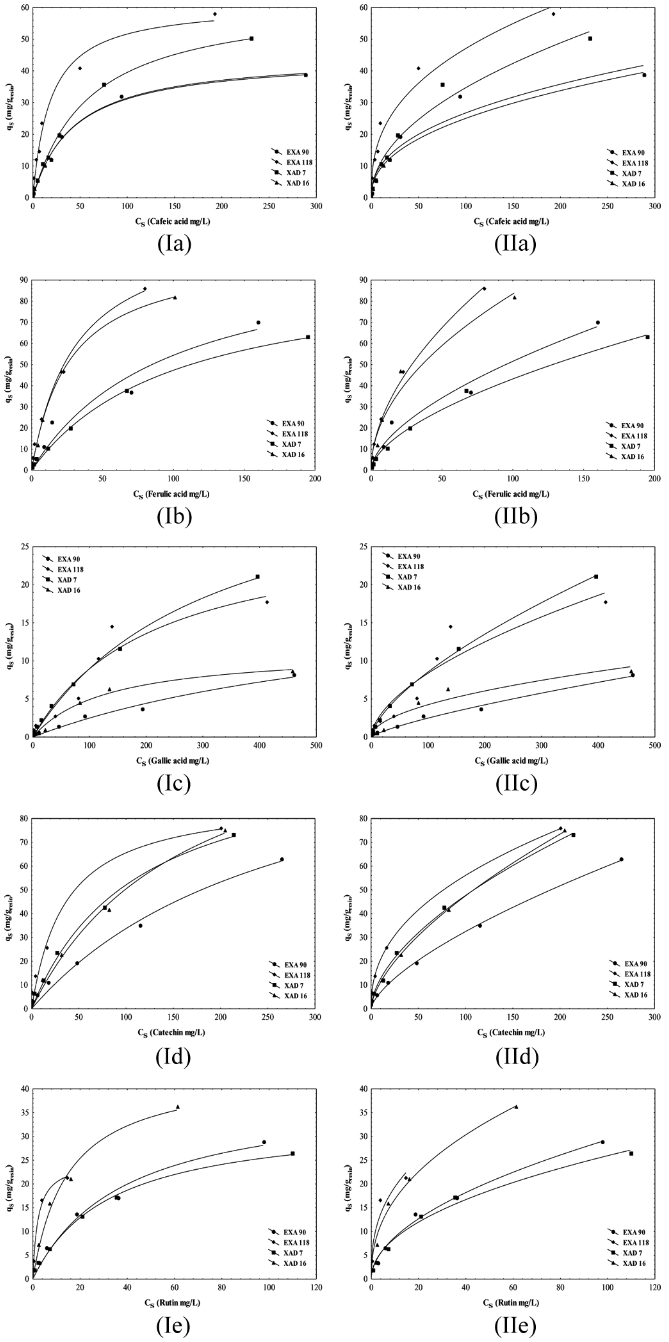
**,***Significant at $p < 0.01$ and $p < 0.001$, respectively.

(for catechin, also on XAD 16). For caffeic acid, similar Q_M values were observed for resins EXA 118 and XAD 7 (61.24 mg/g and 63.13 mg/g, respectively) and for EXA 90 and XAD 16 (45.13 mg/g and 46.52 mg/g, respectively). The same effect also appeared for ferulic acid (107.02 mg/g and 103.60 mg/g, respectively) and for catechin (127.72 mg/g and 133.90 mg/g, respectively). For the a_L, which represents the ratio between sorption and desorption at constant rate, the values ranged from 0.0011 L/mg (for gallic acid on EXA 90) to 0.1389 L/mg (for rutin on EXA 118).

The solute adsorptivity (K_L) is the product of both Langmuir constants (a_L and Q_M), and this value is very important when comparing many solute/solvent adsorption conditions. At higher values of Q_M and a_L, the effectiveness of adsorption onto resins is greater. For example, catechin showed high values of Q_M; with low values of a_L, while, inversely, rutin presents moderate values of Q_M but high values of a_L. The phenolic compounds studied in this work displayed the following order in terms of K_L values: rutin (EXA 118 > XAD 16 > XAD 7 ~ EXA 90), ferulic acid (XAD 16 ~ EXA 118 > EXA 90 ~ XAD 7), caffeic acid (EXA 118 > EXA 90 ~ XAD 16 ~ XAD 7), catechin (EXA 118 > XAD 7 ~ XAD 16 > EXA 90), and gallic acid (EXA 118 ~ XAD 7 > XAD 16 > EXA 90).

The K_F values, which represent adsorption capacity in the Freundlich model, ranged from 0.07 L/g (gallic acid on EXA 90) to 8.30 L/g (ferulic acid on XAD 16). The extent and degree of favorability for adsorption can be expressed by the Freundlich constant b_F, the adsorption being strongly favourable ($b_F \approx 0.1$) to slightly favourable ($b_F \approx 0.9$ to 1.0) (20). According to the b_F values found in this work ($0.374 \leq b_F \leq 0.765$, Table 2), the adsorption of phenolic compounds can be considered favorable for most solute/sorbent combinations. Gallic acid presented the highest b_F values and the lowest K_F values, confirming its weak adsorption.

Values of K_L and K_F clearly demonstrated how the adsorption of gallic acid was poor for all the resins under study. The cinnamic acids used in this study (caffeic and ferulic acids) possess a lateral chain of three carbons (Fig. 1), contributing to their lower hydrophilicity. Ferulic acid, for example, possesses an $-OCH_3$ group on the benzenic ring (position 3), increasing its affinity with non-polar surfaces such as the resins under investigation. This largely



(Ia) (IIa)

(Ib) (IIb)

(Ic) (IIc)

(Id) (IId)

(Ie) (IIe)

FIG. 2. Non-linear regressions of the experimental data obtained for the sorption isotherms of caffeic, ferulic and gallic acids, catechin, and rutin in aqueous solution onto macroporous synthetic resins according to the Langmuir (Ia, Ib, Ic, Id and Ie) and Freundlich (IIa, IIb, IIc, IId and IIe) models (Experimental conditions: Resin dosage = 5 g/L; Temperature = 25°C; Contact time = 2 h; Agitation rate = 200 rpm; pH = 3.5).

explains their high K_L values as compared to gallic acid (a benzoic acid). The degree of hydrophobicity thus seems to be decisive in the adsorption of phenolic compounds using macroporous synthetic resins. Generally, flavonols have a higher solubility in water than flavanols (21). As rutin is a flavonol di-glycoside and catechin a flavanol aglycone (Fig. 1), the former is less hydrophobic, and was expected to have a lower affinity for the resins. Accordingly, rutin presented higher values of K_L than catechin for all resins.

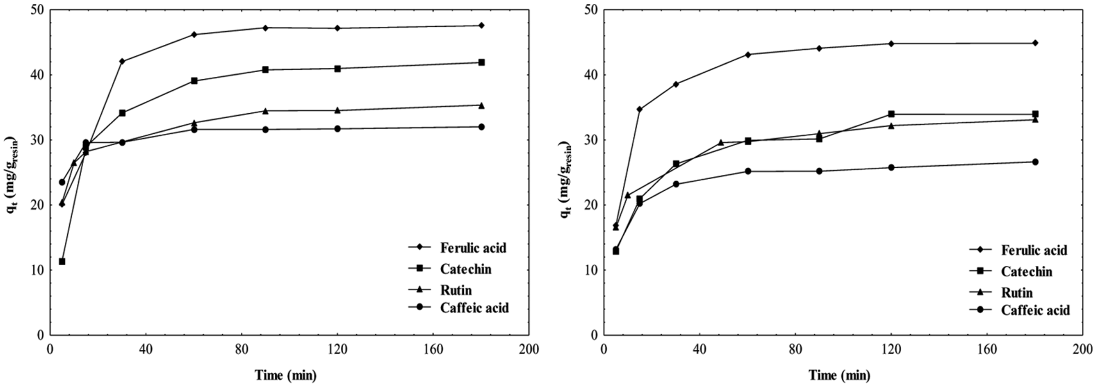
In terms of adsorptive capacity (K_F and Q_M) and solute adsorptivity (K_L), these results are in agreement with other studies using flavonoids. Scordino et al. (4) estimated values of K_F (98×10^{-6} L/g to 8.90 L/g), Q_M (ranging from −188.33 mg/g up to 65.80 mg/g) and K_L (from 0.052 L/g to 6.967 L/g) for cyanidin-3-glucoside (anthocyanin) using 13 resins, including those used in this work. In the recovery of narirutin (a flavanone di-glycoside) using XAD 7, the value of K_F was 7.89 L/g (22). Scordino et al. (12) studied the adsorption of hesperidin (another flavanone di-glycoside) with the same resins as Scordino et al. (4). They found values of K_F ranging between 1.93 and 42.15 L/g, with the best resin being EXA 118.

Ribeiro et al. (3) obtained low b_F values for limonin and naringin using XAD 7 (0.34 and 0.36, respectively), but higher values using XAD 16 (0.69 and 2.04, respectively). Regarding the adsorption of hesperidin, Scordino et al. (12) found higher b_F values using XAD 7 (0.744) than EXA 90, EXA 118, or XAD 16 (0.353, 0.288, and 0.294, respectively). The b_F values obtained by Scordino et al. (4) were higher than those of the present study for all four resins. By contrast, Silva et al. (9) found lower b_F values for total phenolics (0.337 and 0.275 using XAD 7 and XAD 16, respectively) and total flavonoids (0.346 and 0.330 using XAD 7 and XAD 16, respectively), when working with *Inga edulis* leaves extracts. These differences may be due to the fact that the latter authors worked with a multi-component adsorption system (a plant extract), while Scordino et al. used a single compound (cyanidin 3-glucoside).

Finally, regarding the surface area of the resins, most phenolic compounds presented high adsorption capacities (K_L and K_F) when surface areas were higher than 800 m^2/g (XAD 16 and EXA 118). This data is in agreement with Scordino et al. (12).

Adsorption Kinetics

Adsorption kinetics provides information regarding the mechanism of adsorption, which is important for the efficiency of the process. Figure 3 shows the experimental results of the adsorption kinetics for four phenolic compounds on the macroporous synthetic resins EXA 118 and XAD 16, the two resins presenting the highest values of adsorptivities (K_L) in the first step of this study. The experimental data were fitted to three kinetic models in order to determine which model best described the adsorption rate of the phenolic compounds. The models tested were the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models.



(a) (b)

FIG. 3. Adsorption kinetics of phenolic compounds on the synthetic resins EXA 118 (a) and XAD 16 (b). (Experimental conditions: T = 25°C; $C_0 = 250$ mg/L; Aqueous solution at pH 3.5; Agitation rate = 200 rpm).

Figures 3a and 3b reveal that the mass transfer from the liquid phase to the resins was very small after 30 min of contact between the phenolic compounds and the resins EXA 118 and XAD 16, respectively. During this time, the recovery of phenolic compounds from solution was limited to around 63% (EXA 118) and 47% (XAD 16) for caffeic acid, 82% (EXA 118) and 75% (XAD 16) for ferulic acid, 74% (EXA 118) and 56% (XAD 16) for catechin, and 60% (both resins) for rutin. After 60 min, no further variations in mass transfer were detected and a stationary phase was reached with these four polyphenols. EXA 118 showed the highest uptake of phenolic compounds (around 68% for caffeic acid, 93% for ferulic acid, 91% for catechin, and 67% for rutin) within three hours of contact. Ferulic acid and catechin were the phenolic compounds with the highest affinity for the resins. It was not possible to evaluate the kinetics of adsorption of gallic acid, as the affinity for both resins was very low and none of the three kinetic models were appropriate.

Table 3 presents the parameters of the three kinetic models adjusted to the experimental data. The pseudo-first-order model did not show good fit. However, the pseudo-second-order (Fig. 4) model fitted the data reasonably well, whereas the intra-particle diffusion model did not, the majority of the R^2 showing non-significance. The pseudo-second-order model was the best for both resins and the q_e value estimated by the pseudo-second-order model was close to the experimental q_e (data not shown). This suggests that the overall rate of the polyphenolic adsorption process may be governed by several diffusion steps. Ferulic acid presented the highest q_e values (49.98 mg/g of EXA 118 and 46.78 mg/g of XAD 16), confirming the previous results obtained with the Langmuir isotherm (Q_M). Interestingly, the time to reach equilibrium was shorter for caffeic acid (its k_2 value was significantly higher). Bilgili (14) adsorbed 4-chlorophenol using XAD 4 and concluded that the best kinetic model was also the pseudo-second-order model.

Surface-Energy Heterogeneity and Adsorption Mechanisms

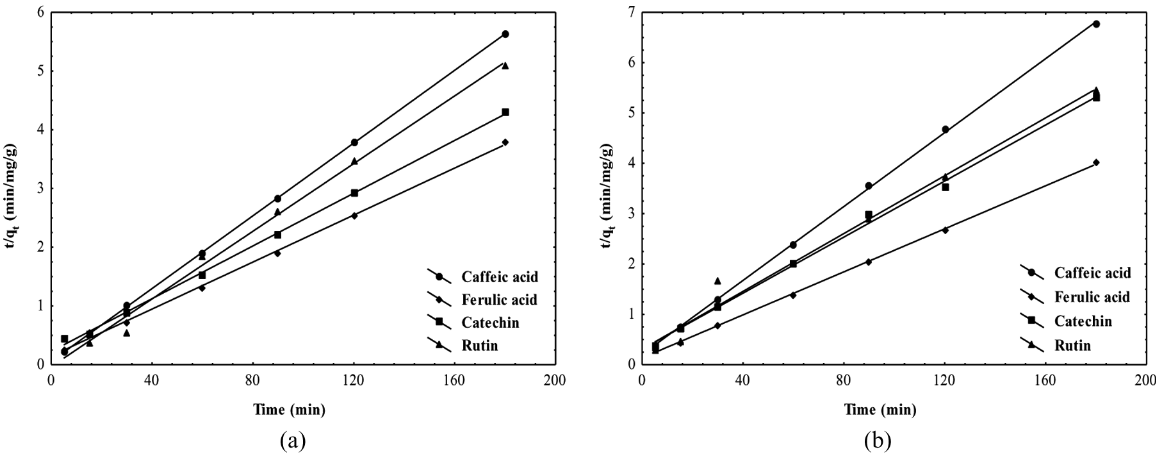
In order to estimate the mean adsorption energies involved in the phenolic adsorption onto resins, the Dubinin-Radushkevich isotherm was applied. Table 4 presents the values of the parameters Q_{DR}, K_{DR}, and E for all phenolic compounds with all the resins studied ($R^2 > 0.90$; $p < 0.01$). The low E values clearly suggest that the adsorption of phenolic compounds onto the resins is a physical adsorption (23).

The adsorption mechanisms of phenolic compounds onto SDVB (EXA 90, EXA 118, and XAD 16) and acrylic (XAD 7) resins were then evaluated. The energy involved in physical adsorption phenomena is a complex cooperation between multiple forces such as hydrogen bonding, hydrophobic interactions, and $\pi - \pi$ stacking interactions (24). Figure 5a depicts the interactions we proposed between gallic acid and XAD 7 resin. Hydroxyl groups of the gallic acid and water molecules act as a hydrogen-bonding acceptor while carbonyl groups from XAD 7 resin act as a hydrogen-bonding donor. In SDVB resins, the interaction between the adsorbate and the adsorbent seems to be predominantly the $\pi - \pi$ stacking type. This interaction is dominated by the dispersion force that arises from the mutual correlation of electrons that belong to interacting monomers (intermolecular correlation effects) (25,26). Thus, taking into account the nature of the macroporous resins (EXA 118, EXA 90, and XAD 16) and the structures of the phenolic compounds, the adsorption mechanisms, as depicted in Figs. 5b, 5c, 5d, and 5e, could be based on $\pi - \pi$ stacking interactions between the aromatic ring electrons in

TABLE 3
Kinetic constants of pseudo-first-order, pseudo-second-order, and intra-particle diffusion models for the adsorption of phenolic compounds onto EXA 118 e XAD 16

Kinetic model	Resin	Compound	Kinetics parameters		
Pseudo-first-order	EXA 118	Caffeic acid	$k_1 = 0.0261$	$q_e = 4.69$	$R^2 = 0.777^{NS}$
		Ferulic acid	$k_1 = 0.0410$	$q_e = 24.93$	$R^2 = 0.913^{*}$
		Catechin	$k_1 = 0.0300$	$q_e = 22.55$	$R^2 = 0.941^{**}$
		Rutin	$k_1 = 0.0265$	$q_e = 13.49$	$R^2 = 0.955^{**}$
	XAD 16	Caffeic acid	$k_1 = 0.0213$	$q_e = 8.97$	$R^2 = 0.867^{*}$
		Ferulic acid	$k_1 = 0.0496$	$q_e = 30.63$	$R^2 = 0.999^{***}$
		Catechin	$k_1 = 0.0660$	$q_e = 49.44$	$R^2 = 0.926^{**}$
		Rutin	$k_1 = 0.0226$	$q_e = 13.50$	$R^2 = 0.894^{*}$
Pseudo-second-order	EXA 118	Caffeic acid	$k_2 = 0.0166$	$q_e = 32.29$	$R^2 = 0.999^{***}$
		Ferulic acid	$k_2 = 0.0027$	$q_e = 49.98$	$R^2 = 0.998^{***}$
		Catechin	$k_2 = 0.0022$	$q_e = 44.54$	$R^2 = 0.999^{***}$
		Rutin	$k_2 = -0.0250$	$q_e = 34.70$	$R^2 = 0.993^{***}$
	XAD 16	Caffeic acid	$k_2 = 0.0065$	$q_e = 27.24$	$R^2 = 0.999^{***}$
		Ferulic acid	$k_2 = 0.0034$	$q_e = 46.78$	$R^2 = 0.999^{***}$
		Catechin	$k_2 = 0.0025$	$q_e = 35.91$	$R^2 = 0.997^{***}$
		Rutin	$k_2 = 0.0027$	$q_e = 34.81$	$R^2 = 0.983^{***}$
Intra-particle diffusion	EXA 118	Caffeic acid	$k_{id} = 0.5988$	$C = 25.40$	$R^2 = 0.635^{NS}$
		Ferulic acid	$k_{id} = 2.3951$	$C = 21.55$	$R^2 = 0.741^{NS}$
		Catechin	$k_{id} = 2.3211$	$C = 16.24$	$R^2 = 0.719^{NS}$
		Rutin	$k_{id} = 1.1766$	$C = 21.73$	$R^2 = 0.831^{*}$
	XAD 16	Caffeic acid	$k_{id} = 1.0165$	$C = 15.03$	$R^2 = 0.739^{NS}$
		Ferulic acid	$k_{id} = 2.0807$	$C = 22.32$	$R^2 = 0.675^{NS}$
		Catechin	$k_{id} = 1.7703$	$C = 13.42$	$R^2 = 0.856^{*}$
		Rutin	$k_{id} = 1.4289$	$C = 16.63$	$R^2 = 0.863^{*}$

*, **and ***significant at $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively. ^{NS}Not significant ($p > 0.05$).



(a) (b)

FIG. 4. Linear plots of the pseudo-second-order kinetic model for adsorption of phenolic compounds on the synthetic resins EXA 118 (a) and XAD 16 (b). (Experimental conditions: T = 25°C; $C_0 = 250$ mg/L; Aqueous solution at pH 3.5; Agitation rate = 200 rpm).

TABLE 4
Parameters for the Dubinin-Radushkevich isotherm equation and the mean adsorption energies (E) of phenolic compounds onto macroporous resins

Resin	Phenolic compound	Q_{DR} (mol/g)	K_{DR} (J^2/mol^2)	R^2	E (kJ/mol)
EXA 90	Gallic acid	2.40×10^{-3}	-2.9×10^{-8}	0.940***	4.12
EXA 118		1.65×10^{-2}	-9.1×10^{-8}	0.910***	2.33
XAD 16		5.12×10^{-3}	-3.8×10^{-8}	0.987***	3.60
XAD 7		1.19×10^{-2}	-5.4×10^{-8}	0.914***	3.02
EXA 90	Caffeic acid	2.11×10^{-1}	-1.0×10^{-8}	0.973***	6.80
EXA 118		3.02×10^{-2}	-4.9×10^{-9}	0.961***	10.01
XAD 16		2.23×10^{-2}	-1.1×10^{-8}	0.976***	6.72
XAD 7		2.71×10^{-2}	-1.2×10^{-8}	0.964***	6.36
EXA 90	Ferulic acid	3.21×10^{-2}	-9.5×10^{-9}	0.901**	7.25
EXA 118		4.67×10^{-2}	-6.3×10^{-9}	0.957***	8.89
XAD 16		4.47×10^{-1}	-6.3×10^{-9}	0.990***	8.85
XAD 7		3.31×10^{-2}	-1.8×10^{-8}	0.962***	5.22
EXA 90	Catechin	2.20×10^{-2}	-4.0×10^{-8}	0.911**	3.54
EXA 118		2.66×10^{-2}	-8.7×10^{-9}	0.957***	7.55
XAD 16		2.61×10^{-2}	-2.4×10^{-8}	0.925**	4.56
XAD 7		2.46×10^{-1}	-1.7×10^{-8}	0.949***	5.29
EXA 90	Rutin	9.90×10^{-3}	-7.1×10^{-9}	0.929**	8.34
EXA 118		8.89×10^{-3}	-1.3×10^{-9}	0.992**	18.98
XAD 16		1.32×10^{-2}	-4.1×10^{-9}	0.961**	11.00
XAD 7		9.33×10^{-3}	-7.5×10^{-9}	0.957***	8.16

**and ***significant at $p < 0.01$, and $p < 0.001$, respectively.

the adsorbate and delocalised π electrons in the basal planes of the resins.

From a chemical viewpoint, various other factors influence adsorption, among them the molecular weight and the position of ring substituents of the phenolic compounds, which contribute to the π-electron delocalisation over the ring (27). This force of interaction has been considered the primary driving force for adsorption in the study of tea polyphenols (24).

Another consideration is that the adsorption process of phenolic compounds here took place in aqueous buffer solution at pH 3.5. The pKa values of these phenolic compounds are higher than 4.2 (28–32), thus all compounds were predominately in their molecular forms, and ionic bonds between resins and phenolic compounds should not have occurred. A possible exception is for gallic acid because it is the most ionizable compound among the studied phenolic compounds, which may explain its lowest adsorption capacity and poor fit in the adsorption kinetics study.

CONCLUSIONS

The characterization of the adsorptive properties of phenolic compounds from different classes is an important step aimed at purifying/concentrating these phytochemicals present in solution. In this study, these properties were characterized qualitatively and quantitatively by different experiments. In general, phenolic adsorption on macroporous resins appeared to be strongly favorable; consequently, high levels of adsorption capacities were achieved using diluted solutions. A short contact time (~30 min) was sufficient to adsorb the phenolic compounds, and these durations could be better predicted using a pseudo-second-order model. The experiments also suggest that the major adsorption mechanisms may be governed by hydrogen bonding (acrylic resin), $\pi-\pi$ stacking interaction (SDVB resin) and hydrophobic interactions. Further studies with mixtures of phenolic compounds should be performed in order to predict the same parameters in a fixed-bed system and to selectively adsorb single components from complex matrices, i.e., natural extracts.

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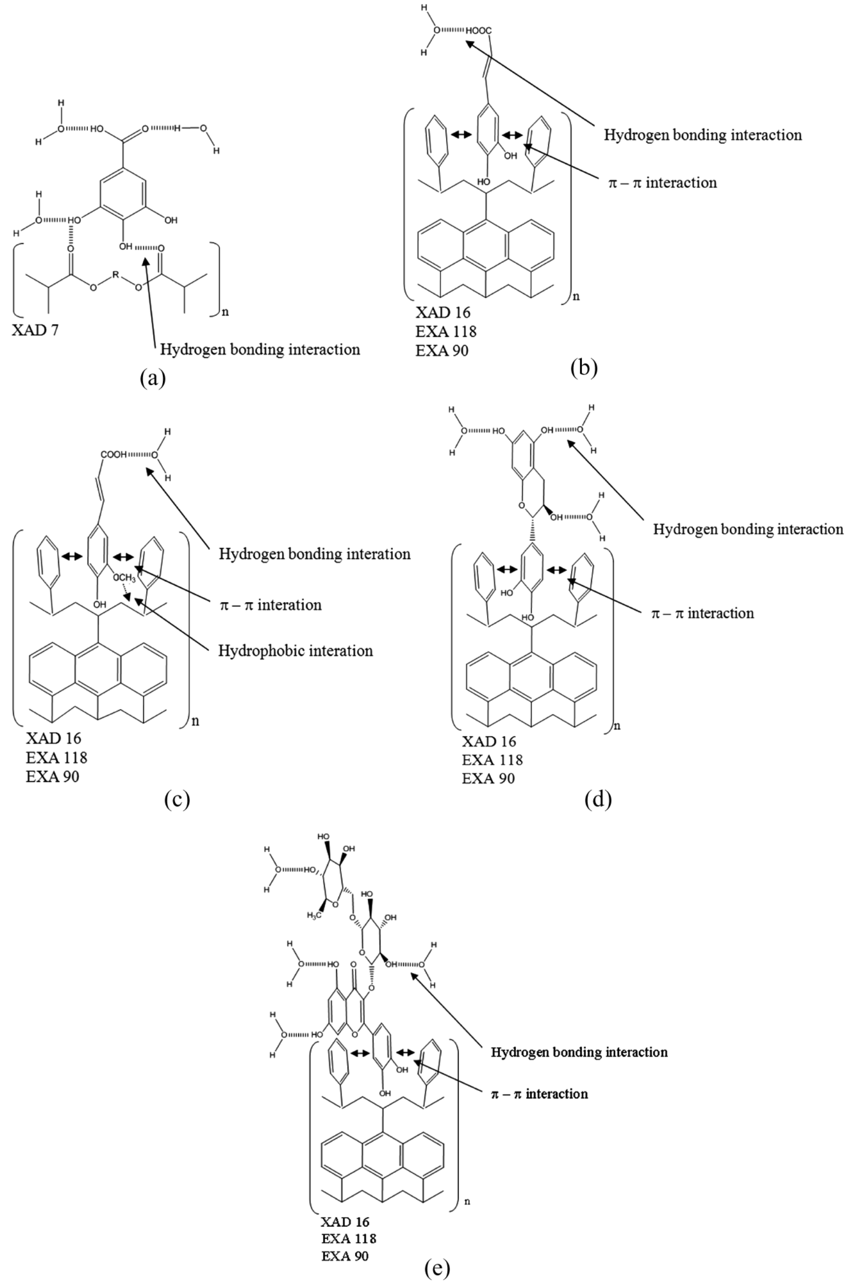

FIG. 5. Schemes for mechanism of adsorption proposed for (a) gallic acid onto XAD 7 resin and (b) caffeic acid, (c) ferulic acid, (d) (+) catechin, and (e) rutin onto XAD 16, EXA 118, and EXA 90 resins.

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