

Structural and thermodynamic factors on the adsorption process of phenolic compounds onto polyvinylpolypyrrolidone

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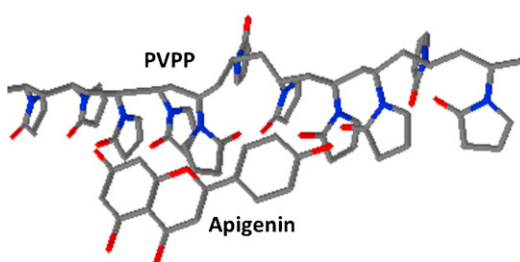
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HIGHLIGHTS

- ▶ Adsorption depends on the PC molecular size, number and availability of its OH groups.
- ▶ The adsorption onto PVPP of some pure PC corresponds to a physisorption process.
- ▶ Adsorption process was spontaneous and enthalpically-driven for C.
- ▶ The adsorption processes were spontaneous and entropically-driven for EGCG and GA.
- ▶ These results implicate potential uses of selective-adsorption of PC.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study we find the possible structural factors that can determine the adsorption process of some pure phenolic compounds (PC) onto polyvinylpolypyrrolidone (PVPP), analyzing their adsorption isotherms by using the Langmuir and the Freundlich theories. In this perspective, the adsorption capacity of short size PC would depend on the number and availability of its hydroxyl groups. To intermediate molecular size PC, the improvement in the adsorption capacity presumably depends on its resemblance with the resveratrol molecule. To large size PC, the adsorption capacity was considerably high due to hydroxyl groups disposed in different spatial orientations with respect to the plane. Thermodynamic analyses showed that adsorption onto PVPP of some pure PC correspond to a physisorption process that was spontaneous and enthalpically-driven for PC like catechin (C) and entropically-driven for PC like epigallocatechin gallate (EGCG) and gallic acid (GA). These results implicate potential selective adsorption uses of PVPP.

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1. Introduction

Compared to porous inorganic materials, polymeric adsorbents generally exhibit a higher stability and selectivity, and are easier to be regenerated. They are also of adjustable functionality, surface area and porosity. Consequently polymeric adsorbents have

been used extensively in the rare precious metal recovery, in the extraction of natural products and in waste water treatment [1,2]. Nevertheless, due to the complexity of the adsorption phenomena occurring at the liquid/solid interfaces, the literature based on aspects related to polymeric adsorbents is still limited [3,4].

Among its several potential applications, polymeric adsorbents have been widely used to adsorb phenolic compounds (PC). The latter use is of relevance to scientists in the fields of chemistry, chemical engineering, botany and pharmacy.

Although many methods and techniques can be employed to isolate and purify PC from natural extracts, including foods, the adsorption based on polymeric adsorbents is the most prominent

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one due to their favorable stability and structural diversity that allows to modulate their adsorption capacity and selectivity [5–12]. To obtain larger adsorption capacity and better selectivity for a specific organic compound, chemical modification of ordinary polymeric adsorbents is often adopted by introducing some special functional groups onto the matrix of the adsorbents [13–15]. These introduced functional groups will modify the chemical composition of the adsorbent surface, and hence improve the adsorption behavior of PC. Some adsorbents that can be copolymerized and functionalized for this propose are polystyrene, acrylamide and polyvinylpyrrolidone [16–25]

The commercial and commonly used resins XAD-4 and XAD-7 presented good properties to the adsorption of PC [26–28]. However, Smith et al. reported that polyvinylpyrrolidone (PVPP) has better adsorption efficiency than XAD-4 [29].

Insoluble PVPP, a highly crosslinked version of polyvinylpyrrolidone, is an inexpensive and excellent adsorbent of PC, and has been widely used in the phenol-stripping of wine, beer, juices and tea infusions [30–33], principally to prevent the haze and the undesirable flavors of these beverages. In this perspective, the study of adsorption isotherms is the one of the basic aspects for the adsorption process and can indicate how the adsorption process is driven, what adsorption mechanism(s) is (are) involved, and also shed light onto the surface properties as well as the degree of affinity of the adsorbents.

Previous works indicate that in general the formation of hydrogen bonds determinates the adsorption of PC onto PVPP [34–38]. However, no studies are available on the existence of a relationship between the structure of pure PC and their capacity to be adsorbed on the PVPP surface. If we consider a complex matrix of PC like wine, tea infusions or fruits juices, we can find cooperative processes between PC and other compounds in solution, which could improve the adsorption capacity of the PC from the matrix. The

presence of a group like galloyl, resorcinol or catechol or the spatial disposition of the hydroxyl groups, or in a simple way, the number of hydroxyl groups, might determine the adsorption process. In fact, all PC have hydroxyl groups capable of forming hydrogen bonds with PVPP and can, therefore, be considered as potential adsorbates. Yet, is such single structural feature, a sufficient condition to secure the adsorption of any PC? Thus, we need to gain understanding on the structural factors and the interactions that can determine the adsorption process. Answering these questions may prove useful to future design of new PVPP-based adsorbents, containing the functional groups needed to increase their adsorption capacity and selectivity toward PC.

In the present work we determined, by means of UV–vis spectroscopy, the parameters of the absorption process of several pure PC onto PVPP. We selected a group of PC (Fig. 1) which comprises gallic acid (GA), methyl catechol (MC), resveratrol (R), piceid (GR), catechin (C), epicatechin (E), epigallocatechin gallate (EGCG), apigenin (AP), genistein (GN), hesperetin (H), quercetin (Q), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tert-butylhydroquinone (TBHQ). These compounds are present in the human diet and are widely used in the food industry due to their proven antioxidant activity or simply as food preservers.

In this study we aimed also at finding the possible structural factors that can determine the adsorption process of each of the mentioned PC onto PVPP, analyzing their adsorption isotherms by using the Langmuir and the Freundlich theories. Moreover we determined the thermodynamic parameters of the adsorption processes of selected pure PC to evaluate the conditions and interactions responsible to improve the adsorption, avoiding the presence of other adsorbates that can change it, like a starting point to understand the requirements to design new and more efficient adsorbents, and to improve the phenol-stripping methods currently used in the food industry.

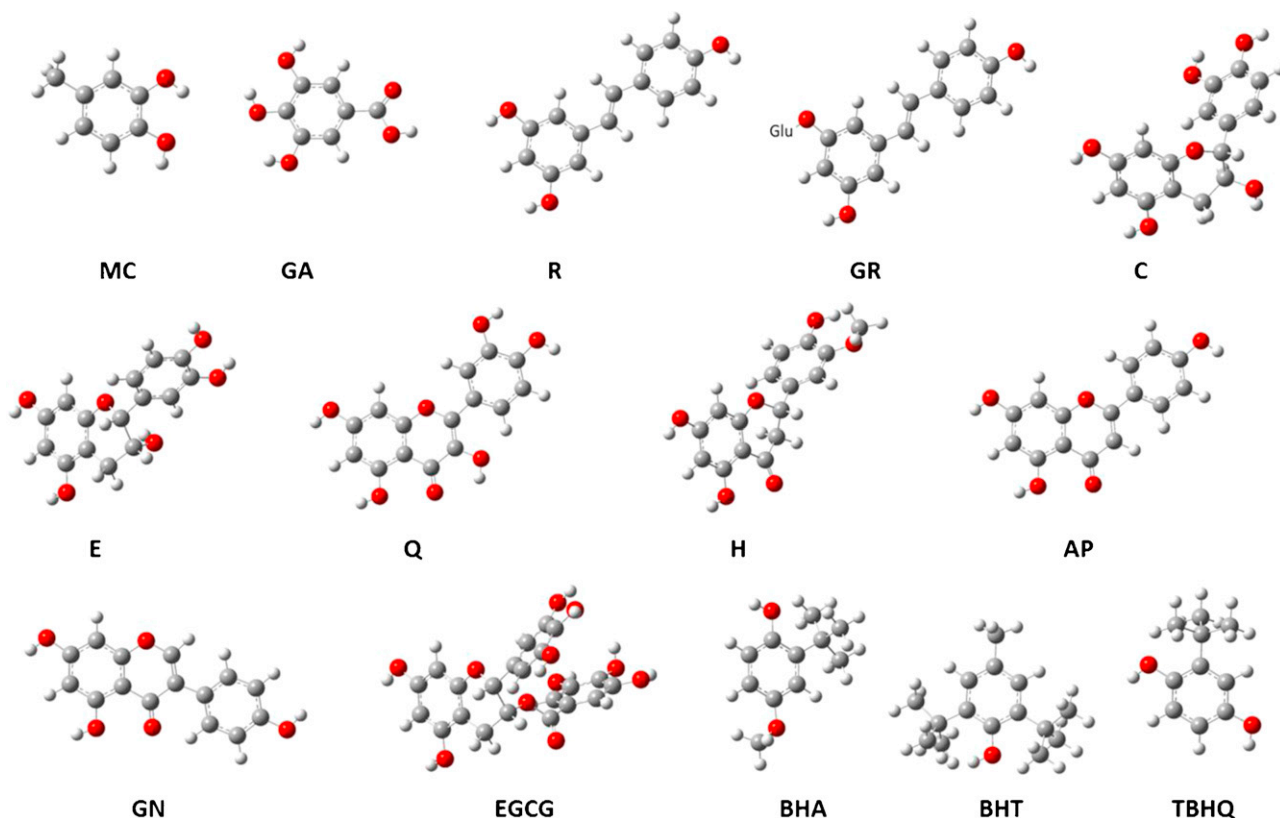


Fig. 1. Molecular structure of PC optimized by a PM3 semiempirical method using *Gaussian98* program.

2. Experimental

2.1. Chemicals

Gallic acid, 4-methylcatechol, resveratrol, piceid, catechin, epicatechin, epigallocatechin gallate, apigenin, genistein, hesperetin, quercetin, butylated hydroxyanisole, butylated hydroxytoluene and tert-butylhydroquinone, all were purchased from Sigma–Aldrich, Inc., St. Louis, MO. Polyvinylpyrrolidone was purchased from BASF Chile S.A. Other reagents were all analytical grade.

2.2. Adsorption of PC onto PVPP in aqueous solution

The reaction medium contained 10 mg of dry PVPP and increasing concentrations of PC prepared in Britton–Robinson buffer solution (0.1 M; pH 4.0) to reach a final volume of 3 mL. In some cases, ethanol aliquots were added to improve the solubility of some PC in the buffer solution. The resulting mixture was transferred to a 4 mL amber flask and equilibrated in a Julabo thermostatic shaking water bath for 4 h at 30 °C, after which the equilibrium was reached. The supernatant was obtained after sedimentation in a Sprout HS microcentrifuge and the absorbance measurements were performed using a Helios Alpha UNICAM spectrophotometer.

PC aqueous solutions which were adsorbed by PVPP were measured and the PC concentration, C_e (mg/L), was calculated based on a standard working curve. To determine the working curve of UV absorbance–PC concentration, the absorbance of the standard PC aqueous solutions, containing various known concentrations was measured under the same conditions of the mixtures with PVPP. The equilibrium adsorption capacity of PC, Q_e (mg/g), was calculated as:

$$Q_e = \frac{(C_0 - C_e)V}{W_{PVPP}} \quad (1)$$

where V is the volume of the PC aqueous solution (L), and W_{PVPP} is the weight of dry adsorbent (g). Adsorption isotherms of PC onto PVPP in aqueous solution were derived accordingly and to reveal the adsorption process, the data were fitted into the Freundlich and the Langmuir equations using Origin Pro 8 SR2 (Origin Lab Corporation, USA).

The Freundlich equation (2) used was:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

where K_F is the Freundlich constant and n is the heterogeneity degree of the adsorbent.

The Langmuir equation (3) used was:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where Q_{\max} is the maximum adsorption capacity and K_L is the Langmuir adsorption equilibrium constant.

2.3. Thermodynamics of selected PC

Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) for the adsorption of some PC onto PVPP were obtained from the equilibrium adsorption constants at different temperatures (20, 25, 30 and 35 °C). ΔG is calculated using the following Eq. (4):

$$\Delta G = -RT \ln K'_L \quad (4)$$

where K'_L is the adsorption equilibrium constant in molar units (M^{-1}) from the Langmuir model, T is the absolute temperature and R is the universal gas constant.

The relation between the K'_L and the absolute temperature can be described by Van't Hoff's equation (5):

$$\ln K'_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

Then ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plot, respectively.

3. Results and discussion

The Langmuir and Freundlich models were used to describe the equilibrium characteristics of adsorption. The Freundlich isothermal model is usually used to describe the multilayer adsorption on a heterogeneous adsorbent surface with different energy sites. In turn, the Langmuir model can be applied for explaining the monolayer adsorption with constant heat onto the adsorbent surface with a finite number of homogeneous sites [37]. The parameters of these two models are listed in Table 1. Results reveal that the isothermal adsorption behavior of pure PC onto PVPP could be described mathematically by these two models because their r^2 values are higher than 0.96. The K_F values are related with the adsorption capacity and indicates that the mayor capacities are obtained for EGCG and R; in descending order EGCG » R > C > GA > E > AP > GR > GN > Q > H > MC. The preservers BHA, BHT and TBHQ have the smallest values and possibly did not be adsorbed by PVPP. Heterogeneous factor ($1/n$) is the lowest for EGCG and is near to 0 indicating that the process is mainly heterogeneous and completely favorable. For GA, AP, C, E, GN, Q, R and GR we see factors greater than 0 and closer to 1, indicating that we would be in presence of a chemisorption process. For H and MC the heterogeneous factors are higher than one and indicate a cooperative adsorption process. This evidence shows the influence of the adsorbates structure on the adsorption process and the possibility of hydrogen bonds formation between their hydroxyl groups and the PVPP carboxyl groups. For example, GA exhibits a galloyl group (Fig. 1) that can be found in several flavonoids and shows mainly chemical contributions due to the

Table 1
Isothermal parameters for the adsorption of phenolic compounds onto PVPP.

	Phenolic compounds													
	GA	AP	C	E	EGCG	GN	H	MC	Q	R	GR	BHT	BHA	TBHQ
Freundlich														
K_F ($\text{mg}^{(n-1)/n} \text{g}^{-1} \text{mL}^{1/n}$)	1.51	1.29	8.49	1.34	101.62	0.51	0.14	0.11	0.29	19.95	0.82	0.02	0.03	0.02
$1/n$	0.75	0.80	0.70	1.14	0.14	1.01	1.34	1.24	0.89	0.97	1.10	1.02	1.18	1.37
r^2	0.998	0.996	0.997	0.992	0.968	0.998	0.993	0.998	0.998	0.998	0.996	0.996	0.983	0.994
Langmuir														
K_L (mL mg^{-1})	7.25	11.80	13.75	0.02	1299.16	0.14	0.01	0.002	9.82	19.27	0.04	0.01	0.002	0.002
R_L	0.56	0.41	0.19	1.00	0.00	1.00	1.00	1.00	0.74	0.26	1.00	1.00	1.00	1.00
Q_{\max} (mmol g^{-1})	0.58	0.28	1.13	–	0.40	–	–	–	0.08	4.62	–	–	–	–
r^2	0.998	0.998	0.998	0.984	0.978	0.998	0.988	0.981	0.999	0.998	0.994	0.990	0.988	0.963

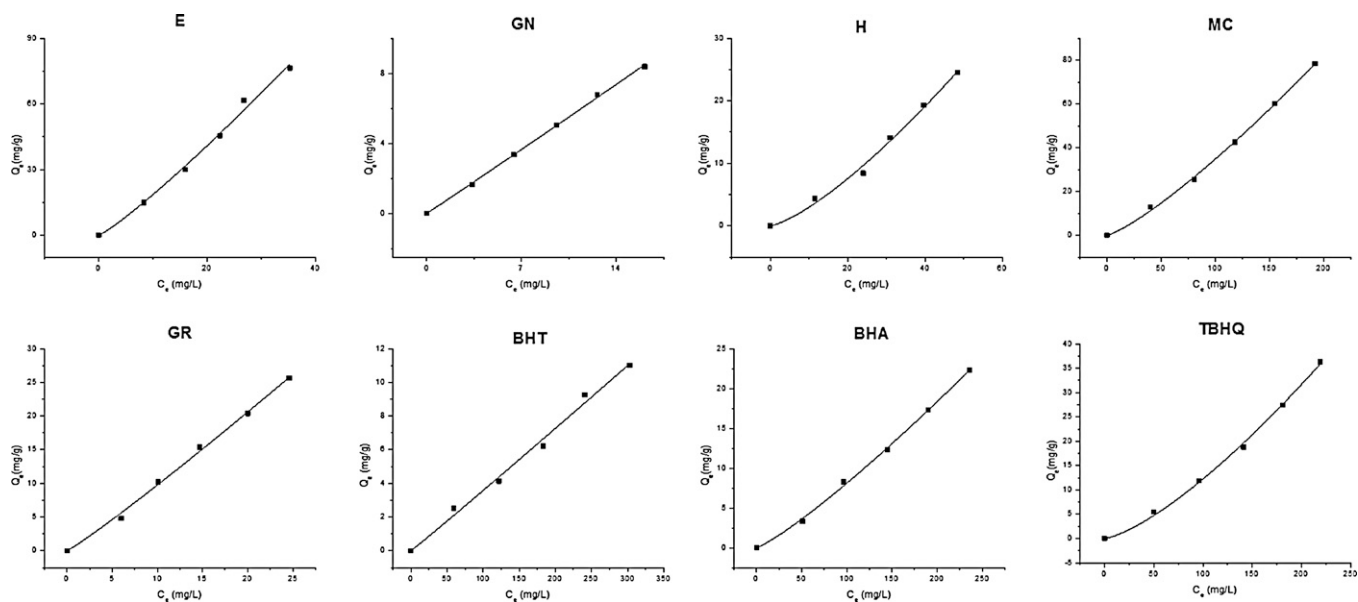


Fig. 2. Experimental adsorption isotherm for some PC onto PVPP at 30 °C. The solid line is the Freundlich isotherm fitting.

possible hydrogen bonds formation with PVPP. MC presents mainly cooperative interactions, possible due to the interaction between MC molecules before the adsorption onto PVPP. In the case of R we can see a chemically-driven adsorption process that has a higher capacity, but when one of the hydrogen atoms of the hydroxyl groups, located on the resorcinol ring, is replaced by one glucose unit (GR) (Fig. 1), the K_F value drastically decreases. In conclusion, the presence of galloyl and resorcinol rings in a molecule produces chemically-driven adsorption processes and increases the adsorption capacity. Moreover the presence of a catechol ring appears to induce to a cooperative-driven adsorption process. So if we compare C and E molecules, similar adsorption processes and capacities

can be expected since they have catechol and resorcinol groups. In fact, both adsorption processes are chemically driven, but the capacity of C is six times higher than that of E only because the disposition of the catechol and the hydroxyl groups located on the carbon 3 of the pyranic ring. Thus, the capacity would depend too on the spatial disposition of the hydroxyl groups in a PC.

AP and GN have resorcinol and phenolic groups, and the difference between both molecules resides on the location of the phenolic ring (Fig. 1). While in AP the ring is located in the carbon 2, in GN the ring is located in carbon 3 of the pyranic ring. Both structures have chemically-driven adsorption processes, however, the adsorption capacity of AP is two times higher than that of GN,

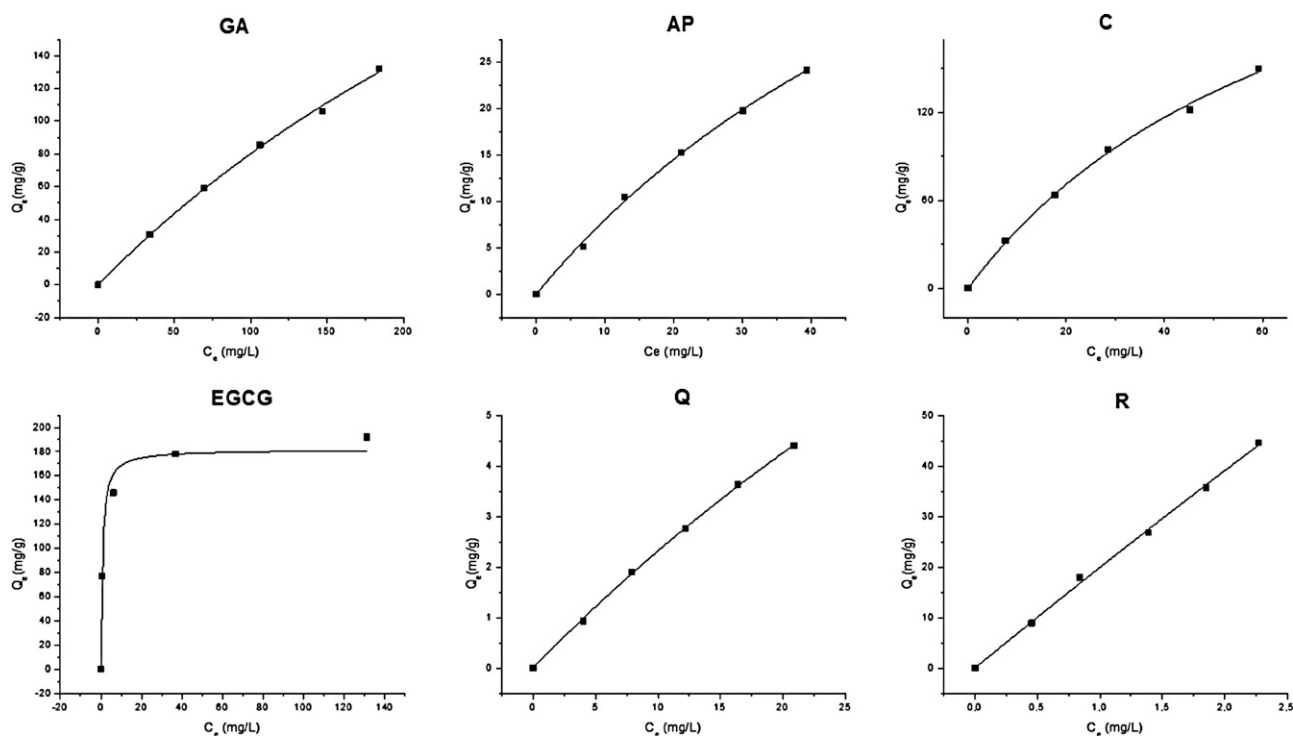


Fig. 3. Experimental adsorption isotherm for some PC onto PVPP at 30 °C. The solid line is the Langmuir isotherm fitting.

Table 2

Langmuir adsorption constants (K_L) at different temperatures and changes of enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) to the phenolic compounds (PC). Moreover shows correlation factor of the Van't Hoff representation (r^2).

PC	T (K)	K_L (mL mg ⁻¹)	r^2	ΔH (kJ mol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	ΔG (kJ mol ⁻¹)
GA	293	6.85	0.96	45.91	154.16	-0.03
	298	5.45				
	303	7.25				
	308	9.98				
C	293	20.02	0.99	-27.11	-77.83	-3.90
	298	16.80				
	303	13.75				
	308	11.70				
EGCG	293	102.18	0.93	161.00	584.18	-13.09
	298	767.39				
	303	1299.16				
	308	3019.90				

possibly due to the similarity of AP with the resveratrol molecule (i.e., distances between resorcinol hydroxyls and carbon 2 phenolic hydroxyl). In the H molecule, the adsorption capacity decreases dramatically with respect to AP, possibly due to the fact that in the former molecule one hydrogen atom of catechol ring was replaced for a methyl group. The latter might account for the change from a chemically-driven to a cooperative-driven adsorption process. In conclusion the hydroxyl groups located in carbon 7 of the resorcinol ring, and phenolic groups located in carbon 2 of pyranic ring, both would improve the adsorption capacity, presumably due to its resemblance with the resveratrol molecule. Finally, it should be noted that in the structure of EGCG (Fig. 1), the resorcinol, galloyl and tri-hydroxyphenyl groups are disposed, each one, in different orientations with respect to the molecular plane. Such spatial disposition would offer multiple adsorption sites to PVPP, explaining the high adsorption capacity as well as the heterogeneously-driven adsorption process featured by EGCG.

As mentioned above, the Freundlich isothermal model is used to describe a multilayer adsorption and describes in a correct way the majority of the adsorption processes of PC onto PVPP seen in this study. Fig. 2 shows that the experimental isotherms of E, GN, H, MC, GR, BHT, BHA and TBHQ can fit into the Freundlich model. However, when observing the shapes of the experimental isotherms of GA, AP, C, EGCG, Q and R (Fig. 3), a compartment described by the Langmuir model can be appreciated. In fact, the Q_e values increase as the equilibrium concentrations of PC increase (with a tendency to reach a plateau). The latter suggests that the maximal adsorption of PC to PVPP took place in a monolayer of the polymer, when the adsorbent surface was saturated, and when all the equivalent adsorption sites were occupied. In fact, the PC that showed the highest capacities and that exhibited mainly chemical contributions to the adsorption process by the Freundlich model were also in agreement with Langmuir model. The parameter K_L is listed in Table 1 for the pure PC and is related with the plausibility of the adsorption process. The high value obtained for EGCG indicates a totally favorable and practically irreversible process. For the GA, AP, C, Q and R molecules, K_L values greater than one indicate that the adsorption process is favorable [36]. The low K_L values obtained for E, GN, H, MC, GR, BHT, BHA and TBHQ, indicate that the processes involved in adsorption of these molecules are unfavorable by the Langmuir model. This contention was corroborated by the separation factor value (R_L) calculated from Eq. (6), listed in Table 1. The R_L values indicate that the isotherm adsorption process would be either unfavorable when greater than one, favorable when greater than zero but lower than one, or irreversible when equal to zero.

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

The maximum monolayer capacities (Q_{max}) were calculated for those PC that presented favorable adsorption processes by the Langmuir model and are listed in Table 1. The high Q_{max} value estimated for R, may relate to its high affinity for PVPP and its short size; in contrast, EGCG exhibited a comparatively low Q_{max} value. The latter could be due to the high affinity and higher size of EGCG, limiting the number of molecules susceptible to be adsorbed onto the PVPP monolayer.

Thermodynamic parameters including the change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are used to describe the thermodynamic behavior of the adsorption process of some pure PC. The PC were selected based on their adsorption capacities and molecular size differences. As show in Table 2, the values of ΔG for GA, C and EGCG were negative, indicating the existence of spontaneous and favorable adsorption processes. The free energy is related to adsorption properties like physisorption when ranged from -20 kJ mol⁻¹ to 0 kJ mol⁻¹, and to chemisorption when ranged from -400 kJ mol⁻¹ to -80 kJ mol⁻¹ [39]. From this view, adsorption of these PC onto PVPP might belong to a physisorption process.

Normally the adsorption process involves negative enthalpy changes and decreases in entropy due to an orderly arrangement on the monolayer surface of the adsorbate molecules in a solid adsorbent. However, the same might not be valid when the adsorption takes place in a complicated solid-solution system [17]. As we can see in Table 2, the most favorable process was seen with the EGCG molecule in concordance with the results discussed above. The positive enthalpy change for EGCG implies an endothermic process reflected in the improvement of the adsorption upon increases in the temperature (Fig. 4). Also implies that the physisorption process could be driven mainly by hydrophobic interactions of association. The latter is corroborated by the positive value of entropy that shows an increment in randomness at the solid-solution interface during adsorption. The results are in concordance with the heterogeneity of the process predicted by the Freundlich model. However, the possibility that other interaction also take place should not be ignored. For instance, interactions due to Van der Waals forces and hydrogen bonds that theoretically can be formed between the hydroxyl groups present in EGCG and the O=C- groups in PVPP. Thus, these interactions might also be responsible for the improvement on the adsorption process. The adsorption process of GA is entropically driven as for EGCG.

The opposite behavior was observed for C, with a negative enthalpy change, due to an improvement of the adsorption process when the temperature decreases (Fig. 4). The result is related to an exothermic adsorption process and reveals that the main interactions that could affect the adsorption are the hydrogen bond formations, which usually have enthalpy values ranging from 8 to 50 kJ mol⁻¹. The negative entropy value reveals the arrangement

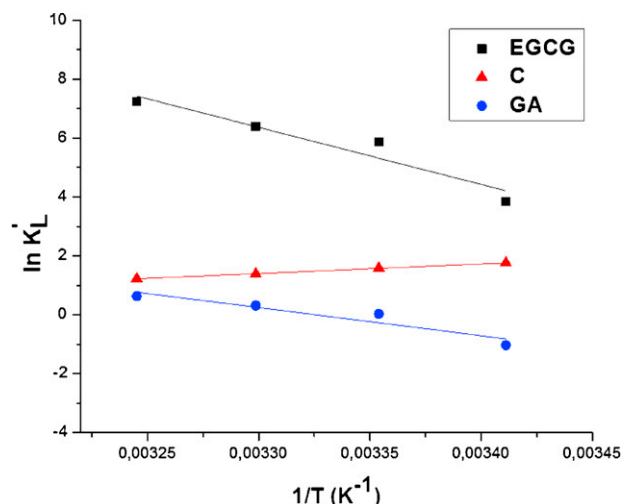


Fig. 4. The Van't Hoff plot for the adsorption process of selected PC onto PVPP.

of the molecule onto the PVPP surface. We can conclude that this process is enthalpically-driven and depends on the possibility to form specific hydrogen bonds at low and moderated temperatures.

4. Conclusions

The adsorption process of pure PC onto PVPP was elucidated using the Freundlich and the Langmuir models. The isotherms were fitted and showed that some structural factors, like hydroxyl groups located in carbon 7 of a resorcinol ring and a phenolic group in carbon 2 of a pyranic ring improve the adsorption capacity of intermediate molecular size PC, presumably, due to its resemblance with the resveratrol molecule. The adsorption capacity was considerably improved for molecules of higher size and hydroxyl groups disposed in different spatial orientations with respect to the plane as in EGCG. In this perspective, the adsorption capacity of short size molecules like GA, MC and some food preservatives, like BHA, BHT and TBHQ, would depend on the number and availability of its hydroxyl groups. These results implicate potential selective uses of PVPP that can discriminate between preservatives and high size PC.

Thermodynamic analyses showed that adsorption onto PVPP of some pure PC correspond to a physisorption process that was spontaneous and enthalpically-driven for C, which mainly depends on the formation of hydrogen bonds with the adsorbent. For EGCG and GA, the adsorption processes were entropically-driven and mainly depend on hydrophobic interactions, complemented and improved with the hydrogen bonds that theoretically can be formed with the hydroxyl groups present in these PC.

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