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Adsorption of complex phenolic compounds on active charcoal: Adsorption capacity and isotherms

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ABSTRACT

Adsorption of polyfunctional phenols encountered in olive oil mill waste waters was carried out on an active charcoal at 293 K. The relation between the structure of the phenol and its adsorption capacity was discussed. Different isotherm equations were considered for modelling the experimental data and their parameters and standard deviations were determined. Freundlich equation was found to provide the best fit except for the catechol.

1. Introduction

Phenols constitute a widespread and important class of water pollutants and are considered as priority pollutants. They are indeed discharged in the liquid effluents from various factories: chemical, petrochemical, paper, wood, metallurgy and cocking plants [1]. They can also originate from diffuse emissions, e.g. roads and pipes tar coatings and from the use of pesticides including their transformation products, e.g. herbicides, fungicides like dinitroorthocresol (DNOC), and pentachlorophenol (PCP). Phenolic compounds are also found in the waste waters of agroindustrial processes like the olive oil mills, tomato processing and wine distilleries [2,3]. The olive oil mill waste waters (OMW) also called alpechin in Spain, contains very high amounts of organic mater (up to 15% by weight), are resistant to degradation and constitutes an important environmental problem due to the content of phenolic compounds, which are antimicrobial and phytotoxic. A process has been proposed [4,5] to reduce the phenolic content of aqueous effluents. It involves as a first step an adsorption–concentration of the pollutant followed by a hydrogenation step. In order to design such a process it is necessary to know the thermodynamic and kinetic parameters of both steps. It is thus important to evaluate the adsorption capacity, isotherm pattern as well as the kinetics of adsorption on the candidate adsorbant for the phenolic compounds to eliminate.

Amongst the phenolic compounds that have been identified in OMW are: hydroxytyrosol, tyrosol, catechol, resorcinol, *o*-vanillin, caffeic acid, elenolic acid, coumeric acid, gallic acid, vanillic acid, ferulic acid, syringic acid, 4-hydroxy-phenylacetic acid, 4-hydroxybenzoic acid, demethyl-oleuropeine, oleuropein, rutin, verbascoside and luteolin-7-glycosid acid [6–10]. The phenolic compounds concentration depends on the kind of oil extraction technology and on the variety of olives used.

A large amount of work has been devoted to the study of phenolic compounds adsorption on activated carbon for water treatment purposes. The development of the investigation on the subjet has been recently reviewed by Dabrowski et al. [11]. Dobbs and Cohen [12] reported an extensive list of isotherm data of several toxic compounds. The effect of selected parameters on the adsorption of phenol on activated charcoal has been studied by Iqbal et al. [13]. Ökzaya [14] compared different isotherm models used to describe the adsorption of phenols on active charcoal. Despite the numerous studies reported in the literature, the attention remained mainly focused upon simple phenols, chlorophenols and nitrophenols. Phenolic compounds with a more complicated structure and/or other functions have received so far little attention. Garcia-Araya et al. [15] studied the adsorption of some phenolic acid on activated carbon. Razmkhar et al. [16] studied the adsorption of

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Nomenclature

a_R	first adsorption constant of the Redlich–Peterson isotherm equation (m^3/kg)
b_R	second adsorption constant of the Redlich–Peterson equation (m^3/kg)
C_e	concentration of adsorbate in the liquid phase at equilibrium (kg/m^3)
C_{ion}	concentration of of the ionic form of the adsorbate in the liquid phase (kg/m^3)
C_{mol}	concentration of of the molecular form of the adsorbate in the liquid phase (kg/m^3)
k_F	adsorption constant of the Freundlich isotherm equation ($(m^3/kg)^{-1/n_F}$)
k_{ion}	adsorption constant of the Langmuir isotherm equation for the ionic form of a weak acid (m^3/kg)
k_L	adsorption constant of the Langmuir isotherm equation (m^3/kg)
k_{mol}	adsorption constant of the Langmuir isotherm equation of the molecular form of a weak acid (m^3/kg)
k_T	adsorption constant of the Toth isotherm equation (m^3/kg)
k_{total}	adsorption constant of the Langmuir isotherm equation (L/g)
m	exponent parameter of the Toth isotherm equation
n_F	exponent parameter of the Freundlich isotherm equation
Q_e	uptake of substrate adsorbed at equilibrium (kg/kg_{AC})
Q_{max}	maximum uptake of substrate adsorbed on AC (kg/kg_{max})
S	specific surface area (m^2/g)

Greek letters

α	ratio of the ionized form to the molecular form of an acidic compound
β	third parameter of the Redlich–Peterson isotherm equation
ϵ_p	internal porosity of the active charcoal
ρ_p	density of the active charcoal (kg/m^3)

Subscripts

e	value at equilibrium
max	maximum value

Superscripts

0	initial value
*	value at saturation

phenolic compounds, amongst them tyrosol, catechol and vanillic acid on yeast in order to remove these compounds suspected to be involved in the browning of white wines. The adsorption of caffeic acid on imprinted monoliths has been studied by Li et al. [17] by frontal chromatography.

In this work, the adsorption equilibria of five phenolic compounds: tyrosol, catechol, veratric acid, vanillic acid and caffeic acid, on an activated carbon has been investigated. These phenolic compounds are present in waste waters coming from agroindustrial activities related to the manufacturing of olive oil, wine, spirits, etc., very common in Mediterranean countries [18] and they have been choosen as model molecules for the study of OMW treatment by adsorption followed by catalytic hydrogenation. This paper is devoted to the thermodynamic study of the adsorption (capacity and isotherms), a second one will be devoted to the kinetic study of the same process (adsorption rate, breakthrough curves).

2. Experimental

2.1. Chemicals

The phenolic compounds were purchased from Aldrich (L'Isle d'Abeau, France) and used as received. The active charcoal Picactif TE80® was kindly provided by Pica (Vierzon, France). Its textural characteristics are reported in Table 1. The distribution of acidic groups at the surface of this material, measured according to the Boehm method [19] by titration with bases of increasing strenght ($NaHCO_3$, Na_2CO_3, NaOH and NaOEt) is also reported in Table 1. Deionized water was used to prepare the solutions of the phenolic compounds.

2.2. Apparatus and tests

In an Erlenmeyer 0.5 g of active charcoal and 10 mL of deionized water were added and shaken for about 5 min in order to degas the active charcoal. Then the solution of phenolic compound (30 mL) were added. The Erlenmeyer was closed and placed in a thermostatic bath at 293 K and magnetically stirred under atmospheric pressure. Samples taken at time intervals are used to estimate the equilibration time. In order to measure the adsorption isotherm, 10 Erlenmeyers were used simultaneously under the same conditions as above, with phenol concentrations between 2 g/L and 15 g/L added to degased suspension of active charcoal. These initial concentrations of phenol were obtained by adding increasing amounts of a concentrated phenol solution and decreasing amounts of water so as to achieve the same total volume of solution (30 mL) in each Erlenmeyer. The solution were analyzed after 48 h to determine the remaining amount of phenol in solution and thus the adsorbed amount, each Erlenmeyer providing one point of the adsorption isotherm. In the case of the phenolic acids, due to their low solubility in water, they were dissolved in a NaOH solution at pH 8. Catechol and tyrosol were dissolved in water leading to solutions with pH of 6.25 and 6, respectively. In order to study the effect of pH upon the adsorption capacity, tyrosol was also dissolved in NaOH solutions of pH ranging between 9 and 13.

2.3. Analysis

The phenol concentration was measured by UV spectrometry using an UV–visible JASCO®UV-980 detector. The wavelenghts at which the measures were carried out correspond to an absorption maximum for each of the studied compounds, they are reported in Table 2.

3. Results and discussion

3.1. Preliminary tests

Before running the experiments to determine the adsorption isotherms, some preliminary experiments were carried out in order to estimate the time necessary to achieve the equilibrium by monitoring the amount of the remaining phenol in solution as a function of time.

Fig. 1 shows the amount of tyrosol remaining in solution at 293 K under atmospheric pressure as a function of time.

It can be seen that after about 5 h, the adsorbed amount is about 90% of the amount adsorbed at equilibrium, while it requires 35–40 h to reach the equilibrium. The equilibration time reported

Table 1
Characteristics of Picactif TE80®

Textural properties		Surface acidic groups (mequiv./gC)	
Specific surface area (S)	1370 m^2/g	Carboxylic acid (COOH)	0.00
Internal porosity (ϵ_p)	0.563	Lactone(–COO)	0.10
Particles density (ρ_p)	966 kg/m^3	Phenol (–OH)	0.40
		Quinone (C=O)	0.02

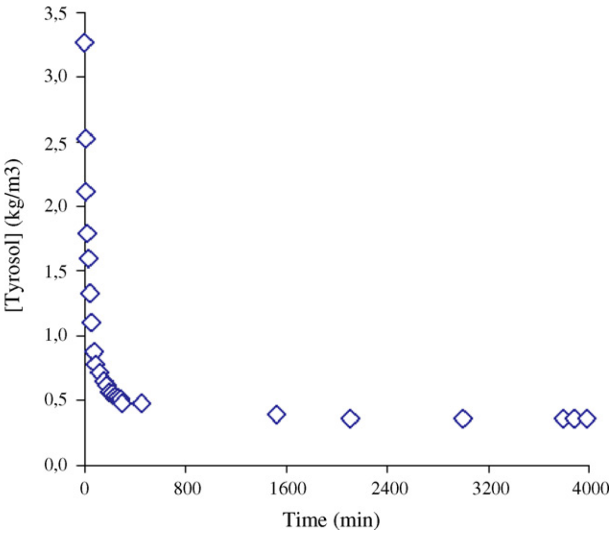


Fig. 1. Tyrosol adsorption in a stirred tank: remaining concentration in solution vs. time.

in the litterature is quite variable, Garcia-Araya et al. [15] report times of about 150 h for the adsorption of phenolic compounds on a commercial active charcoal.

3.2. *Effect of pH*

The effect of pH upon adsorption of phenolic compounds has been observed and related by various authors [25–29] to the degree of ionization of the phenolic sorbate. Indeed at pH $> pK_a$ the compounds are mainly in the form of negatively charged phenoxy ions, while the functional groups of the carbon surface are deprotonated and negatively charged thus the electrostatic repulsion leads to a decrease of the adsorption capacity. On the contrary at pH $< pK_a$ the phenolic compouds are predominantly in the neutral molecular form, while the surface acidity increases favoring the donor–acceptor interaction between the electrons of the aromatic ring and the surface thus leading to an increase of the adsorption capacity. Conversely, at low pH, the phenolic acids are hardly soluble in water. This means that for purification purpose only a narrow range of pH is possible: within this range the phenolic species must be water-soluble, i.e., slightly ionized, but not too much to be adsorbable onto the solid.

Table 3
Adsorption capacity and Langmuir constants for tyrosol as a function of pH

	pH			
	6–6.25	9	11	13
Adsorption capacity (mmol/g_{carbon})	2.89	2.52	1.95	1.94
k_L (m^3/kg)	67.1	24.2	8.1	8.4

This problem has been partially dealt with concerning tyrosol only by carrying out its adsorption at different pH. The results are ported in Table 3.

The variation of the adsorption capacity is explained by the previous discussion considering that for tyrosol $pK_a = 10.12$ [20]. The evolution of the Langmuir constant with the pH can be explained by considering the tyrosol solution as a binary mixture of a molecular and an ionic species. In this case the Langmuir equation becomes [27]:

$$\frac{Q}{Q_{max}} = \frac{k_{Total}C_e}{1 + k_{Total}C_e} \quad (1)$$

where

$$k_{Total} = \frac{k_{mol} + k_{ion}\alpha}{1 + \alpha} \quad (2)$$

$$\alpha = \frac{C_{ion}}{C_{mol}} \quad (3)$$

and

$$pH - pK_a = \log \alpha \quad (4)$$

When the pH is much lower than pK_a, α is close to 0 and k_{Tot} reaches the value of the molecular form k_{mol} while at pH above pK_a, α is large and k_{Tot} approaches the value of the ionic form k_{ion}. Thus for tyrosol, from Table 3 one can derive that $k_{mol} \approx 67\ m^3/kg$ and $k_{ion} \approx 8\ m^3/kg$.

3.3. *Adsorption capacity*

The adsorption capacity of the different adsorbates are reported in Table 4. It may be a difficult task to establish a relation between the chemical structure (cf. Fig. 2) and the adsorption capacity based upon only five compounds but it appears clearly that the adsorption capacity of the acid is much lower than those of the other compounds. This result is surprising considering that :

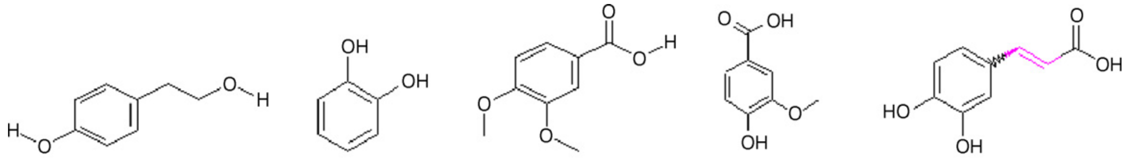
Table 2
Physico-chemical properties of the studied phenolic compounds: UV maximum absorption wavelengths and pK_a values

	Tyrosol	Catechol	Veratric acid	Vanillic acid	Caffeic acid
Wavelength (nm)	225	275	253	253	280
Phenolic pK_a	10.12 [a]	9.85 [b]	–	9.39 [d]	7.82–9.52 [e]
Carboxylic pK_a	–	–	4.44 [c]	4.42 [d]	4.04

[a] Ref. [20].
[b] Ref. [21].
[c] Ref. [22].
[d] Ref. [23].
[e] Estimated from Ref. [24].

Table 4
Adsorption capacity of the phenolic compounds on Active Charcoal TE80®

Adsorption capacity	Catechol	Tyrosol	Veratric acid	Vanillic acid	Caffeic acid
mol/kg$_{AC}$	2.91	2.89	1.1	1.42	1.27
kg/kg$_{AC}$	0.320	0.399	0.200	0.236	0.229
pH	6.25	6	8	8	8



(a) Tyrosol. (b) Catechol (c) Veratric acid (d) Vanillic acid. (e) Caffeic acid.

Fig. 2. Chemical structures of the phenolic compounds studied.

- the formation of donor–acceptor complexes between the aromatic ring and the chemical function at the surface of the adsorbent as evidenced by Mattson et al. [30],
- the presence of carboxy group (electron withdrawing groups) on the aromatic ring, should tend to lower its electronic density and thus ease the acting of the aromatic ring as an acceptor.

Thus one could expect a higher adsorption affinity for the acid function bearing compounds. A possible explanation for the observation, could be that the amount of phenolic compound adsorbed on the active carbon, also depends of the size of the substrate molecule and in this regard, the acids tend to be larger than the catechol or tyrosol thus leading to a lower adsorption capacity for these compounds.

However a similar result is reported by Garcia-Araya et al. [15] after the study of the adsorption of gallic, syringic and *p*-hydroxy benzoic acids on an active charcoal. However dealing with compounds of similar size they argue that the discrepancy observed between the expected order and the one observed was due to differences in solubility rather than to differences in chemical structure (Fig. 2).

3.4. Isotherm determination

The isotherms of the studied compounds are plotted in Fig. 3. Different patterns are observed for compounds with only the phenolic group on one hand and those with the acid functionality on the other hand. Indeed, catechol and tyrosol show a steep beginning of the isotherm while the acids present a much slower increase of the adsorbed amount with the concentration at equilibrium.

3.5. Isotherm modelling

Adsorption isotherms are used to quantify the interaction between the solute and the activated carbon, critical in optimizing the purification process. Some two- and three-parameter isotherm equations summarized in Table 5 are tested in the present work.

- Langmuir, based on the hypothesis of identical adsorption strength of the sorbent is the most widely used two-parameters equation [31,35]. Two ways of evaluating the parameters were used :
  - ○ in the first one the two parameters were let free and estimated independently (entry Langmuir 1, Table 6).
  - ○ in the second one $q_{\max}$ was fixed to the value of the experimental adsorption capacity (reported in Table 4) and k_L was then estimated (entry Langmuir 2, Table 6).
- ○ Freundlich, derived upon assuming an exponentially decaying sorption site energy distribution. It is considered suitable for highly heterogeneous surfaces.
- ○ Redlich–Peterson, a three-parameter equation which incorporates features of both the Langmuir and Freundlich equation. It agrees with Henry's law at low concentration and behaves like Freundlich equation at high concentration.
- ○ Toth, an other three-parameter equation proposed for gas adsorption has been applied for solute adsorption and has been shown to describe adequately highly heterogeneous surfaces [37]. The adsorption capacity has been fixed at the experimental value (cf. Table 4) for the determination of the two other parameters.

The optimized parameters and their standard deviations are obtained from a classical least-square fitting statistical procedure [38] as implemented in Igor® or Gnuplot. The parameters together with their standard deviations are reported in Table 6 and the corresponding curves are shown in Fig. 4.

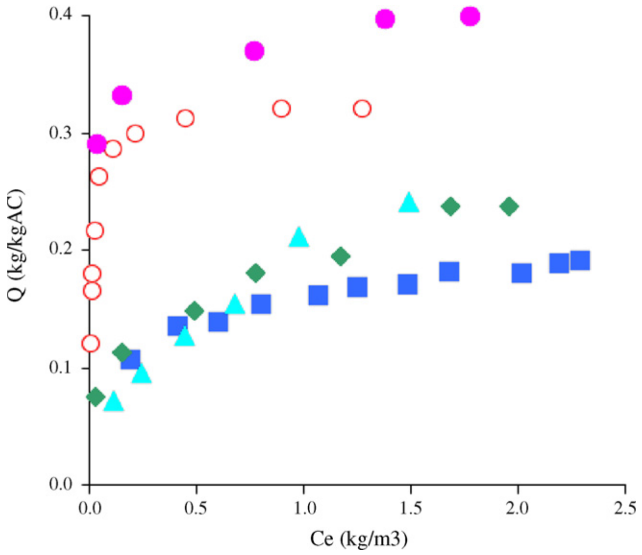


Fig. 3. Adsorption isotherms of phenolic compounds on Active Charcoal TE80® at 293 K: (○) Catechol, (●) tyrosol, (■) veratric acid, (◆) vanillic acid, (▲) caffeic acid.

Table 5
Isotherm equation evaluated

Isotherm type	Equation	Parameters	References
Langmuir	$Q_e = Q_{\max}(k_L C_e/(1 + k_L C_e))$	k_L, $Q_{\max}$	[31]
Freundlich	$Q_e = k_F C_e^{1/n_F}$	k_F, n_F	[32]
Redlich–Peterson	$Q_e = a_R C_e/(1 + b_R C_e^{\beta})$	a_R, b_R, β	[33,25,34,35]
Toth	$Q_e = Q_{\max}(C_e/((1/k_T) + C_e^m)^{1/m})$	$Q_{\max}$, k_T, m	[36,35]

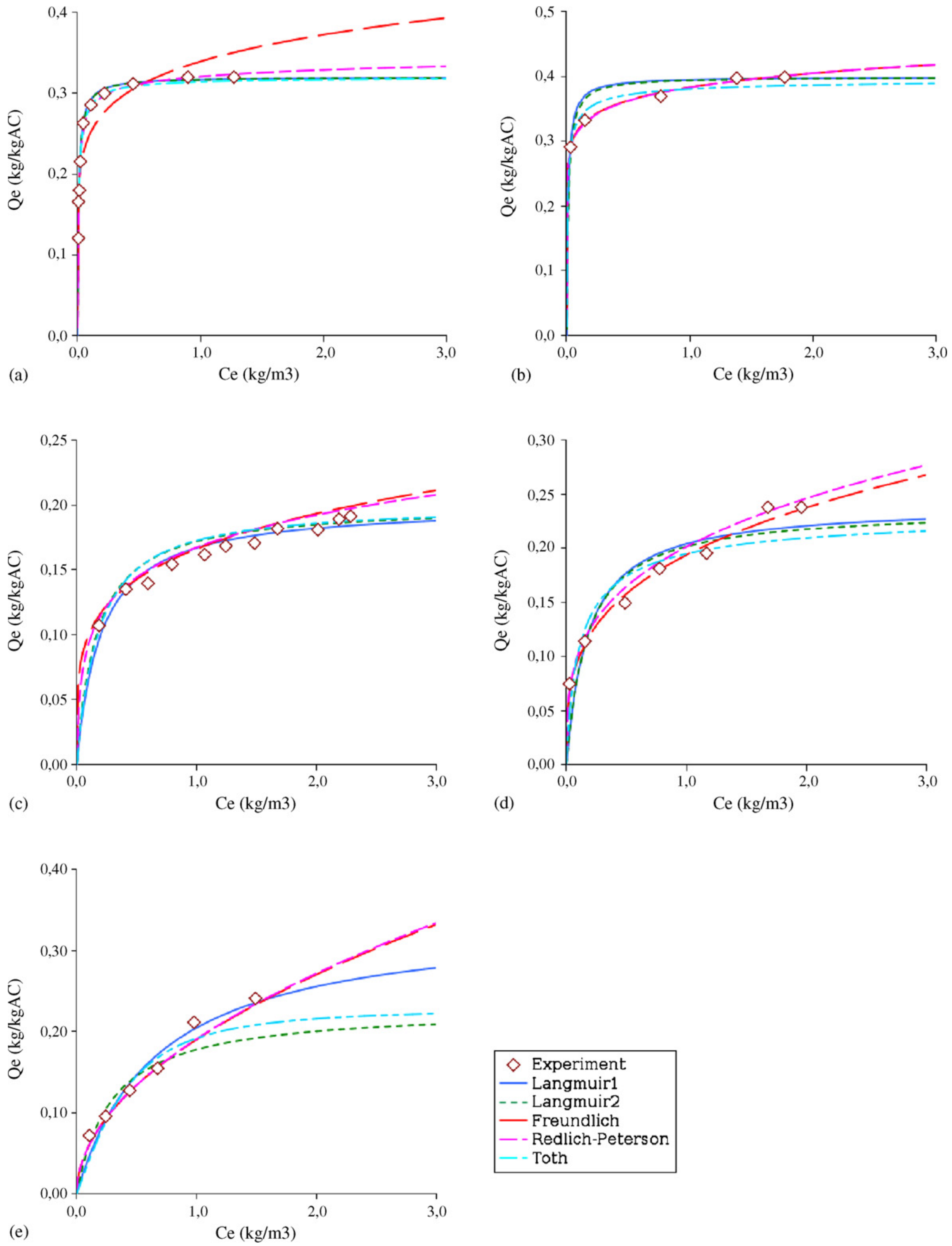


Fig. 4. Comparisonof the experimental data with the different isotherm equations considered for the phenolic compounds studied (a) catechol, (b) tyrosol, (c) veratic acid, (d) vanillic acid and (e) caffeic acid.

Table 6
Estimated parameters for the tested models and corresponding standard deviations (σ)

Equation		Catechol	Tyrosol	Veratric acid	Vanillic acid	Caffeic acid
Langmuir 1	k_L	97.3	86.7	5.03	5.63	1.51
	σ	6.88	64.9	1.43	5.99	1.08
	Q_{max}	0.32	0.39	0.20	0.24	0.34
	σ	0	0.03	0.01	0.05	0.11
Langmuir 2	k_L	94.6	72.8	6.07	5.81	3.46
	σ	5.1	42.6	1.09	6.3	1.17
Freundlich	k_F	0.339	0.383	0.166	0.193	0.190
	σ	0. 05	0.02	0.01	0.03	0.05
	n_F	7.45	12.7	4.56	3.4	1.97
	σ	1.1	1.75	0.42	0.54	0.36
Redlich–Peterson	a_R	36.67	1231	5.25	6042	1121
	σ	11	72000	45.8	205000	31800
	b_R	113.4	3216	30.38	30050	5877
	σ	10.7	75100	55.2	250000	31800
	β	0.97	0.92	0.82	0.71	0.49
	σ			0. 6	0. 6	0. 4
Toth	k_T	62.15	35.17	5.892	6.669	2.768
	σ	9.49	6.43	0.600	1.456	0.662
	m	0.848	0.584	1.059	0.724	1.729
	σ	0.055	0.24	0.127	0.185	0.597

C_e in kg/m^3, Q_e in kg/kg$_{AC}$.

Table 7
Comparison of the adsorption parameter with litterature data

Compound	Q_{max}	k_L	k_F	n_F	References
Phenol	0.236	81.8	11.9	5.26	[39]
4-Nitrophenol	0.227	2530	9.20	3.70	[39]
4-Cresol	0.144	2977	10.1	3.84	[39]
Catechol	0.320	97.3	0.339	7.45	This work
Tyrosol	0.399	86.7	0.383	12.7	This work

In all case, the Toth equation with optimized parameters lead to a curve very close to the Langmuir equation and similarly the optimized Redlich–Peterson equation is often indistinguishable from the Freundlich equation.

The standard deviations reported in Table 6 show that generally the determination of the parameters of the more complex equation are known with a lesser precision than those of the Langmuir or Freundlich isotherm, this is especially true for the Redlich–Peterson equation for which the value of the standard deviation makes the estimated parameters to be meaningless.

Thus it appears that the simplest isotherm equation, Langmuir in the case of catechol and Freundlich for the other compounds, are sufficient to describe the experimental data.

The adsorption of phenolic compounds on the same kind of active carbon (Picactif NC 60) was also studied by Zhou et al. [39]. The values of the adsorption capacities and parameters for the Langmuir and Freundlich equations relative to some of the compounds that they studied are presented in Table 7. The adsorption capacities are of the same order of magnitude, but the other parameters appear to be strongly dependant upon the chemical groups around the aromatic ring. No clear correlation between the adsorption parameters and the sorbate structure can be seen.

4. Conclusion

The adsorption isotherm of some complex phenolic compounds on an active carbon were measured as well as their adsorption capacity. The parameters of different models used to describe the isotherms were determined and the two parameters equations were found to adequately describe the isotherms. It is presently impossible to correlate the adsorption parameter with the structure of the adsorbed molecule. However, acidic phenols exhibit a more progressive isotherm than the non-acidic species.

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