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Activated Carbon Adsorption of Some Phenolic Compounds Present in Agroindustrial Wastewater

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Abstract. Single solute and simultaneous experimental adsorption isotherms of three phenolic compounds: gallic acid, *p*-hydroxybenzoic acid and syringic acid, have been investigated at 20, 30 and 40°C, using a bituminous coal based activated carbon. Regardless of temperature, the capacity of the activated carbon used to adsorb these compounds presented the following order: syringic acid $>$ *p*-hydroxybenzoic acid $>$ gallic acid. The increase of temperature slightly favored the adsorption capacity of the phenolic compounds. In binary and ternary component adsorption, experimental data suggest that interactions between adsorbates improve the adsorption capacity of some of the phenolic acid compounds. On the contrary, at high organic concentrations, adsorbed gallic acid was partially removed from the activated carbon surface because of the presence of the other components.

Keywords: activated carbon, adsorption equilibrium, phenolic acid compounds, gallic acid, *p*-hydroxybenzoic acid, syringic acid

Introduction

Activated carbon, a material with porous structure and large internal surface area, is commonly used as adsorbent for the removal of organic matter micropollutants (i.e. pesticides, phenols, aromatic hydrocarbons, humic substances, etc.) in drinking water treatment (Suffet and McGuire, 1981). Specifically, phenol like compounds are usually target for adsorption studies due to their presence in many water environments and their affinity with the activated carbon surface. Literature reports many works on this subject where the aims are the optimization of the adsorption to develop new adsorbent products and to elucidate the adsorption mechanism (McGuire and Suffet, 1983). Thus, Radke and Prausnitz (1972) observed that adsorptions of *p*-cresol and *p*-chlorophenol onto activated carbon were stronger than other organic compounds such as acetone, 2-propane, etc. Singer and Yen (1981) concluded that adsorptive capacity of activated carbon for phenolic compounds increases with the increasing number of aromatic substituting groups and molecular weight. Costa et al. (1989) also reported the importance of the nature of substituting groups in the aromatic ring to increase the adsorption capacity. Tessmer et al. (1997) pointed up the role of oxygen and surface oxygen complexes onto activated carbons on their adsorptive capacity for phenolic compounds. Ravi et al. (1998) showed the anomalous influence of temperature on the adsorption of some organic compounds, such as phenols, benzyl alcohol, etc.

In this work, the adsorption equilibria of three phenolic acid compounds: gallic acid, *p*-hydrobenzoic acid and syringic acid, on an activated carbon are reported. These phenolic acid compounds are present in wastewaters coming from agroindustrial activities related to the manufacturing of olive oil, wine, spirits, etc, very common in Mediterranean countries (Beltrán et al., 2000a). The concern of these compounds arises from the malfunctions that they may cause in biological treatment units of wastewater treatment plants (Borja et al., 1995). These problems make necessary the application

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of other treatments to aid the biological oxidation of wastewater. In this sense, chemical oxidation (Gómez et al., 2000), activated carbon adsorption (Cotoruelo and Marqués, 1998) or a combination of both (Ince and Apikyan, 2000) have been proposed to remove such biorefractory compounds, like phenols.

Materials and Methods

Reagent grade gallic acid and *p*-hydroxybenzoic acid were obtained from Fluka while syringic acid was purchased to Sigma. Millipore Milli-Q water was used to prepare the aqueous solutions of these compounds. A granular activated carbon, namely Hydraffin P110, was procured from Lurgi (Donan Carbon GmbH & Co. KG, Germany) and used throughout this study. The selection of this activated carbon was in principle made based on the characteristics supplied by the manufacturer. Additionally some selected properties were further determined in the laboratory.

An Autosorb-1 (Quantachrome) gas adsorption system was used to determine the specific surface area (BET) and the micropore volume from the adsorption isotherm of N_2 at 77 K. The volume of pores larger than 1.5 nm width was measured by mercury porosimetry (Pore Master 60, Quantachrome). True and apparent densities were determined using helium and mercury pycnometers (both Quantachrome), respectively.

The FT-IR spectrum of activated carbon was obtained on a Perkin Elmer 1720 spectrophotometer. About 1% of carbon was used on a 0.25 g KBr pellet. The pellet was analyzed immediately after preparation by compression at 10 tonnes for 10 min. in a hydraulic press. The spectrum of a pure KBr pellet was used as background.

Prior to its use in adsorption experiments, the activated carbon was washed with boiling Milli-Q water for 2 hours, then oven-dried at 110°C for 48 hours and eventually cooled down up to room temperature in a dried atmosphere. The equilibria adsorption isotherms for phenolic acids from aqueous solutions on activated carbon were determined at various temperatures in the range 20–40°C using the batch bottle-point method. Different amounts of activated carbon were weighed and suspended into glass bottles (19 mm i.d., 150 mm height) containing 20 ml of organic solution ($0.5\ g \cdot l^{-1}$ phenolic acid, similar concentration to that observed in the agroindustrial wastewaters where these compounds are present (Beltrán et al., 2000b)). The bottles were sealed and placed in an orbital shaker where samples were kept at constant temperature within ±0.1°C.

After the equilibration time was considered to be elapsed, the concentration of phenolic acids in the water was determined by HPLC with a 1100 Hewlett-Packard chromatograph provided with automatic injection, a kromasil 100 C-18 Tracer column (4 mm i.d., 150 mm length), UV-visible detection system set at 280 nm and a Chemstation for data treatment. The analysis was made isocratically with a water/acetonitrile/orthofosforic acid mixture (89.75/10/0.25 by volume) as the mobile phase.

Finally, adsorption isotherms of solutes on activated carbon were obtained from the mass balance of phenolic compounds dissolved.

Results and Discussion

Activated Carbon Characterization

Characterization of the activated carbon used was performed to ascertain its suitability for application as adsorbent in water treatment. Figure 1 shows the experimental isotherm of N_2 at 77 K. It can be seen that corresponds to type II of the BDDT classification, indicative of a porous solid where the adsorbed layer thickness increases progressively with increasing relative pressure which is typical of a micro-mesoporous solid (Brunauer et al., 1940). Figure 2 shows the cumulative pore volume deduced from mercury porosimetry, from which it can be concluded that the activated carbon has also an important volume of mesopores. The

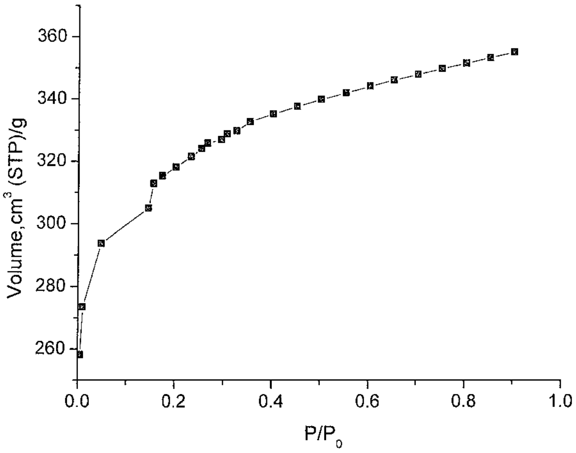


Figure 1. Isotherm of $N_2(g)$ at 77 K on Hydraffin P110 activated carbon.

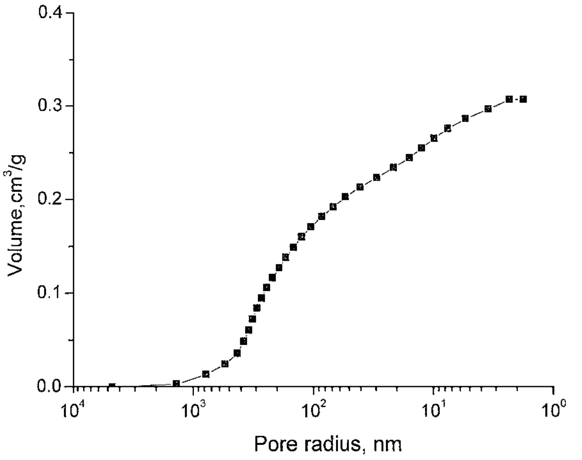


Figure 2. Hydraffin P110 activated carbon pore size distribution.

Dubinin-Radushkevich equation was used to calculate the micropore volume from the N_2 adsorption data. True and apparent densities were determined by helium and mercury pycnometry, respectively. The porosity, ε, and the total pore volume, V_T, were calculated from the apparent and true densities, ρ_a and ρ_t, as follows:

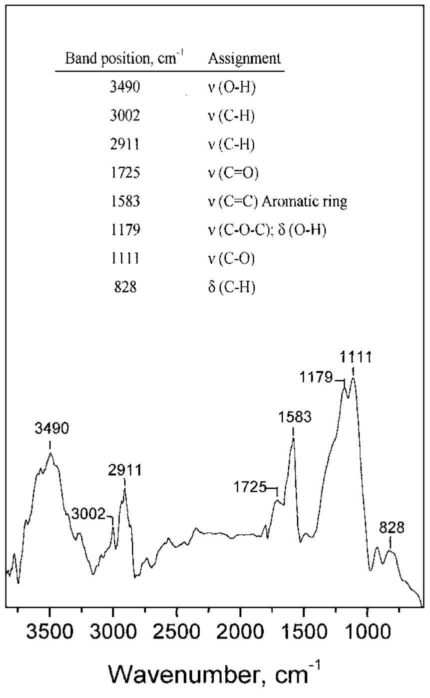
$$\varepsilon = 1 - \frac{\rho_a}{\rho_t} \tag{1}$$

$$V_T = \frac{1}{\rho_a} - \frac{1}{\rho_t} \tag{2}$$

Table 1 summarises the results of the physical characterisation of the activated carbon. Accordingly, the activated carbon possesses a micro-mesoporous structure and a large internal surface area which enables one to choose it for applications as adsorbent in water treatment to remove adsorbates of size like those studied in this work.

Table 1. Hydraffin P110 activated carbon characteristics.

Particle size (mm)	1.6–2.0
True density ($kg \cdot m^{-3}$)	2030
Apparent density ($kg \cdot m^{-3}$)	810
BET specific surface area ($m^2 \cdot g^{-1}$)	967
Porosity	0.601
Total pore volume ($m^3 \cdot g^{-1}$)	7.4×10^{-7}
Micropore volume ($m^3 \cdot g^{-1}$)	4.6×10^{-7}



Band position, cm^{-1}	Assignment
3490	ν (O-H)
3002	ν (C-H)
2911	ν (C-H)
1725	ν (C=O)
1583	ν (C=C) Aromatic ring
1179	ν (C-O-C); δ (O-H)
1111	ν (C-O)
828	δ (C-H)

Figure 3. FT-IR spectrum of activated carbon used.

On the other hand, surface chemistry of activated carbon may influences adsorption. Particularly, it is well reported that the presence of oxygen-containing surface functional groups on activated carbon can determine the mechanism and the extent of phenolic compounds adsorption (Mattson et al., 1969; Vidic et al., 1993). To study the chemical surface of the activated carbon the FT-IR spectrum was recorded as shown in Fig. 3. To exalt adsorption bands a multiple point baseline was used before plotting the spectrum. Also a smooth function was applied to reduce noise. A tentative adsorption bands assignment, which are also presented in Fig. 3, indicates that the activated carbon used contains a numbers of atomic groupings and structures.

From the band assignments it is deduced that some oxygen complexes are present on the carbon surface. Thus, the intense broad band with its maximum at 3490 cm^{-1} is considered to be connected with the adsorption of hydroxyl groups associated by hydrogen bonds. The band at 1725 cm^{-1} has been ascribed to ν(C=O) vibrations in carbonyl groups of ketones, aldehydes or esters. Finally, a great number of ether-type structures both aliphatic and aromatic are likely to be present on the carbon surface (notice the broad band with maximum at 1179 cm^{-1} and 1111 cm^{-1}).

From the standpoint of the adsorption of phenol-like substances, it is highlighted the absence of carboxylic groups onto carbon which are reported to have a negative impact on the physical adsorptive capacity. These groups lead to increased removal of π electrons from the basal planes, which results in weaker dispersion forces (Leng and Pinto, 1997).

The presence of other various oxygen complexes leads one to think that oxidative coupling of phenols which produces polymerization, is not favoured (Vidic et al., 1997). However, carbonyl surface groups can promote chemisorption of phenolic species according to Mattson et al. (1969).

Preliminary Adsorption Experiments

A first series of single solute adsorption experiments was carried out to determine the time needed to reach equilibrium conditions, that it was found to be less than 150 hours. Therefore, this time was chosen for subsequent adsorption experiments since it surely covered equilibrium time for all the conditions applied in this work. Such a long time to reach equilibrium has also been observed for adsorption of phenolic compounds on other commercial activated carbons (Ania et al., 2002).

The pH of water constitutes one of the factors that most influences on the adsorption capacity of compounds that can be ionized (Myers and Zolandz, 1981). Also, acid or alkali species may produce changes onto the carbon surface by reacting with surface groups. These effects may lead to significant modifications of the adsorption equilibrium depending on the pH.

Therefore, a series of preliminary experiments was effected to ascertain the optimum pH for the adsorption of the phenolic acids treated. The maximum adsorptive capacity was found at a pH ranged between 3 and 4. At higher pH values (pH > 4), an important decrease of the adsorption capacity was observed likely due to the increase of the concentration of the ionized organic form which is adsorbed to a lower extent because of its higher solubility in water (Manes, 1981). On the other hand, at pH < 3, the adsorption capacity also lightly diminished with respect to that at pH between 3 and 4. Although chemisorption of phenols is not expected to be of much significance at low temperature (Vidic et al., 1993), it is reported to occur to some extent depending on the nature of activated carbon surface. In this instance, chemisorption would be hindered at low pH because of interference of protons with high electronic density centres of carbon surface, responsible of adsorptive bindings resulting from the formation of bridge bonds with —OH groups of phenolic acids (Nevskaia and Guerrero-Ruiz, 2001) or donor-acceptor complexes as proposed by Mattson et al. (1969). In accordance with these findings, isotherm experiments were carried out at a pH between 3.4 and 3.7, that resulted from the solution of phenolic acids in water without adding any buffering substance.

Finally, once selected pH conditions a number of adsorption experiments were repeatedly carried out to evaluate reproducibility of results. Data deviations in equilibria adsorption isotherms lower than 5% were found in all cases.

Influence of the Nature of the Adsorbate

Single solute adsorption isotherms data at 20, 30 and 40°C of the three phenolic acids studied were plotted in Fig. 4. Regardless of temperature, it can be observed the following sequence for phenolic acids adsorption: syringic acid > *p*-hydroxybenzoic acid > gallic acid. With the exception of the 20°C and 30°C isotherms of gallic, all the isotherms comport with a type L Giles classification (Giles et al., 1960), which means favorable adsorption. However, gallic acid isotherms (20 and 30°C) can be categorized as type S isotherms, which are typical of non-favorable adsorption at low equilibrium concentrations. Both, solubility and chemical structure of organics are factors of prime importance in adsorption. On one hand, it is evident that the more the solubility in water the lower the adsorption capacity of a given compound. Results shown in Fig. 4 comport the above statement since gallic acid was adsorbed to a lesser extent than *p*-hydroxybenzoic acid likely due to their different solubility in water (15 and 8 $g \cdot l^{-1}$ for gallic acid and *p*-hydroxybenzoic acid, respectively).

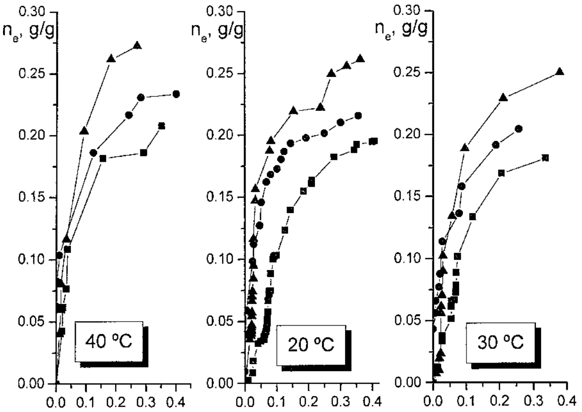


Figure 4. Experimental isotherms of single components on activated carbon: Conditions: 40, 20 and 30°C, pH: 3.4–3.7. ■ Gallic acid, ● *p*-Hydroxybenzoic acid, ▲ Syringic acid.

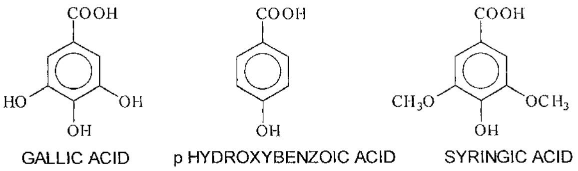


Figure 5. Chemical structures of the three phenolic acids studied.

Similar behaviour was found for the case of syringic acid, the least soluble in water (1 $g \cdot l^{-1}$), which was more strongly adsorbed onto activated carbon than the other two phenolic acids studied.

On the other hand, chemical structures of the three phenolic acids studied are presented in Fig. 5. It should be kept in mind that some substituting groups in the aromatic ring such as carboxylic acids, may act as electron withdrawing groups, thus enhancing the capacity of the aromatic ring to act as an acceptor group. On the contrary, metoxy group and, specially, hydroxyl groups increase the electronic density of the ring (Morrison and Boyd, 1985). Although physical adsorption of phenolic substances onto activated carbon is dominant at ambient temperature, some forces different than the electrostatic ones may also exert some influence on adsorption processes. Thus, Mattson et al. (1969) postulated the formation of donor-acceptor complexes from the interaction between surface carbonyl oxygen groups and the aromatic ring of hydroxyl and nitro-substituted molecules. Vidic et al. (1997) suggested that oxidative coupling of phenols are promoted by basic oxygen complexes of the carbon surface, thereby significantly increasing the adsorptive capacity of activated carbon for phenolic substances. The mechanism of the adsorption is based on the ability of the surface sites to donate delocalized electron pairs and behave as Lewis bases. In both instances, substituting groups of the phenolic acids can play a role. According to the statements above, gallic acid should present the lowest affinity to be adsorbed due to the presence of three —OH groups, followed by syringic acid containing one —OH group and two —OCH_3 groups and, finally, the *p*-hydroxybenzoic acid that only contains one single OH group. As it can be observed from Fig. 4, gallic acid was the phenolic compound studied with the lowest adsorption affinity, likely due to its high solubility and low activation of the aromatic ring. However, syringic acid presented an adsorption capacity higher than that of *p*-hydroxybenzoic acid, which does not corroborate the hypothesis described above. One possible reason could be due to the moderate character of —OCH_3 groups to deactivate the electronic density of the aromatic ring (Morrison and Boyd, 1985). Then, differences in adsorption capacity of syringic acid with respect to *p*-hydroxybenzoic acid may be attributed to differences in solubility rather than to differences in chemical structures. Adsorption isotherm experiments at 30 and 40°C can be discussed in a similar way to that made for 20°C.

Influence of Temperature

Temperature is a major variable in adsorption processes since it affects the solubility of adsorbates and the adsorption equilibrium constant. Figure 6 shows the experimental adsorption isotherms in single solutes on activated carbon at various temperatures. The effect of temperature on the isotherm equilibrium studied was observed to be rather low. This fact has also been reported in literature for the adsorption of several organic compounds present in liquids (Seidel et al., 1985; Ravi et al., 1998). In Fig. 6, it can be observed a slight increase of the adsorption capacity when temperature was risen which is in contradiction with the expected trend of any physical adsorption, because its exothermic nature. The experimental results, therefore, suggest endothermic adsorption processes. Similarly, a priori, anomalous results have also been observed for phenol and substituted phenols and several explanations have been reported in literature. Thus, Costa et al. (1989) attributed the increased phenol adsorption

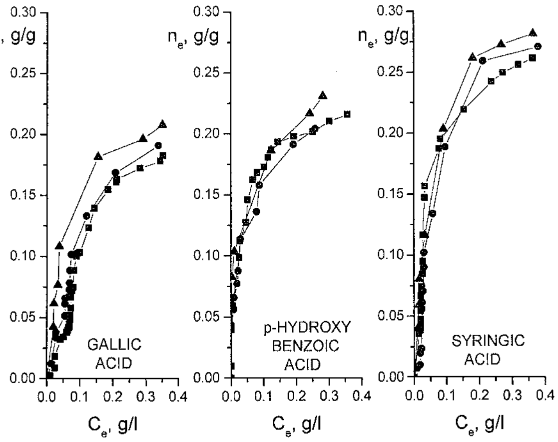


Figure 6. Experimental isotherms of gallic acid, *p*-hydroxybenzoic acid and syringic acid as single components on activated carbon. Effect of temperature. Conditions: pH: 3.4-3.7. ■ 20°C, ● 30°C, ▲ 40°C.

with temperature to the high percentage contribution of micropores to the porosity of the activated carbon used. They reported that an important fraction of these micropores could have a size similar to that of the phenol molecule so that access to these pores would only be possible at certain conditions of temperature at which the phenol molecule could penetrate and diffuse. Seidel et al. (1985) for the case of phenol adsorption and Chiou and Manes (1974) for other compounds (including some phenols), explained the results in terms of the increased packing density of adsorbate molecules in the pores of activated carbon above its melting point. More recently, Ravi et al. (1998) also observed a similar anomalous behaviour on the effect of temperature on the adsorption of cresols, phenol and benzyl alcohol. These authors (Ravi et al., 1998), as first pointed out by Mattson et al. (1969), proposed that the adsorption of compounds they studied was due to an irreversible chemisorption and/or polymerization of adsorbed molecules. This adsorption mechanism would be positively affected by temperature. In the present work, the reasons why temperature presents the effect observed could likely be due to a combination of effects similar to that reported by Costa et al. (1989) and Ravi et al. (1998) according to the micro-mesoporous nature of the activated carbon used (see Table 1) and its surface chemistry discussed above. In any case, more research is needed to clarify the mechanism of adsorption of these phenolic acids onto activated carbon.

Binary and Ternary Multicomponent Adsorption

Binary and ternary mixtures of the three phenolic acid compounds studied were also prepared for isothermal equilibrium determination. Since in a practical case multiple compounds of wastewater are to be adsorbed onto activated carbon, it is convenient to know the effect that the presence of some compound exerts on the adsorption capacity of other compounds.

(a) Adsorption Equilibrium of Gallic Acid. Experimental adsorption isotherms of gallic acid as a single solute of the aqueous phase and in binary and ternary mixtures with *p*-hydroxybenzoic acid and syringic acid are presented in Fig. 7. As can be observed, for aqueous equilibrium concentrations of gallic acid higher than 0.05 $g \cdot l^{-1}$ the corresponding adsorbed concentrations, n_e, in binary and ternary mixtures were lower than those of the single gallic acid adsorption. This negative effect noted on the adsorptive capacity of the activated carbon for gallic acid has also been observed for other compounds (Espínola, 1998; Frick et al., 1981) being likely due to the competition of other solutes for the active centres of the adsorbent surface (notice that in multicomponent adsorption the carbon/compound mass ratio was lower than in single adsorption). In addition, at the highest gallic acid concentrations, the corresponding adsorbed equilibrium concentration slightly decreased with the increasing equilibrium dissolved concentration, a phenomenon already observed in other adsorption systems (Frick et al., 1981). This could likely be attributed to some displacement of gallic acid from the active centres where it was adsorbed because of the presence of the other solutes. Another consequence of this is the reversibility of the process as also reported by Ravi et al. (1998). These authors proposed a multilayer adsorption process in which a fraction of adsorbate remains bonded through electrostatic forces which makes the process reversible. Always at gallic acid concentrations higher than 0.05 $g \cdot l^{-1}$ both binary isotherms of gallic acid were similar so competition of *p*-hydroxybenzoic acid and syringic acid for the available active centres can be considered to be alike. On the other hand, the isotherm curve of the ternary mixture remained below those of the binary mixtures which suggests that the competitive effect of *p*-hydroxybenzoic and syringic acids was limited and it had reached the maximum value.

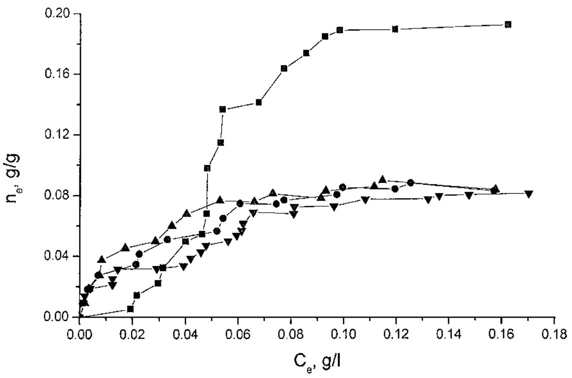


Figure 7. Experimental isotherms of gallic acid as single component and in binary and ternary mixtures with *p*-hydroxybenzoic acid and syringic acid on activated carbon. Conditions: 20°C, pH: 3.4–3.7: Binary mixture initial mass ratio: 1/1. Ternary mixture initial mass ratio: 1/1/1: ■ In single component adsorption, ● in binary mixture adsorption with *p*-hydroxybenzoic acid, ▲ in binary mixture adsorption with syringic acid, ▼ in ternary mixture with *p*-hydroxybenzoic acid and syringic acid.

Finally, at the lowest equilibrium gallic acid concentrations in water when there was an excess of activated carbon relative to the amounts of phenolic acids the isotherms of the binary and ternary mixtures were situated slightly above that of the single gallic acid adsorption. These experimental results suggest that there was not at all competition between adsorbates but interactions between adsorbates favoured the adsorption of gallic acid. Similar results have been reported for other systems (Deryło-Marczewska et al., 1985; Weber and Van Vliet, 1981).

(b) Adsorption Equilibrium of p-Hydroxybenzoic Acid. Figure 8 shows the experimental adsorption isotherm results of *p*-hydroxybenzoic acid as single compound or mixed with the other two phenolic acids in binary or ternary mixtures. In this case, curves of isotherms for binary and ternary mixtures were found to be situated below that corresponding to the single adsorption equilibrium of *p*-hydroxybenzoic acid. Hence, the competitive effects of gallic acid and syringic acid for the available active centres of the adsorbent surface seems to be the main reason of the low adsorbed *p*-hydroxybenzoic acid equilibrium concentration in multicomponent mixtures. It can be highlighted the experimental isotherm of *p*-hydroxybenzoic acid in the presence of syringic acid. Especially for equilibrium concentrations in water higher than 0.05 $g \cdot l^{-1}$, this isotherm presents the lowest values of the equilibrium adsorbed concentration, n_e, which is due to the strong adsorption of syringic acid.

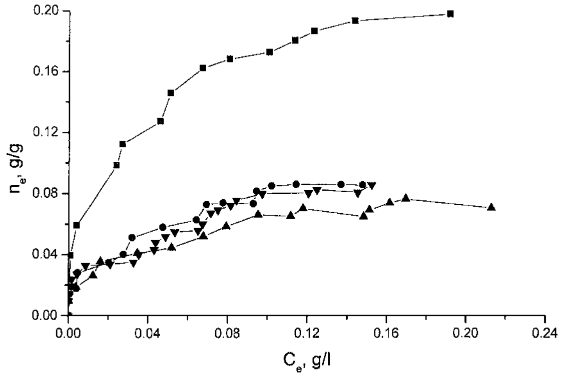


Figure 8. Experimental isotherms of *p*-hydroxybenzoic acid as single component and in binary and ternary mixtures with gallic acid and syringic acid on activated carbon. Conditions: 20°C, pH: 3.4–3.7: Binary mixture initial mass ratio: 1/1. Ternary mixture initial mass ratio: 1/1/1: ■ In single component adsorption, ● in binary mixture adsorption with gallic acid, ▲ in binary mixture adsorption with syringic acid, ▼ in ternary mixture with gallic acid and syringic acid.

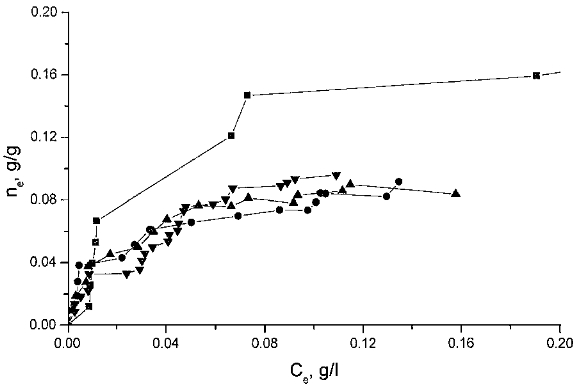


Figure 9. Experimental isotherms of syringic acid as single component and in binary and ternary mixtures with gallic acid and *p*-hydroxybenzoic acid on activated carbon. Conditions: 20°C, pH: 3.4–3.7: Binary mixture initial mass ratio: 1/1. Ternary mixture initial mass ratio: 1/1/1: ■ In single component adsorption, ● in binary mixture adsorption with gallic acid, ▲ in binary mixture adsorption with *p*-hydroxybenzoic acid, ▼ in ternary mixture with gallic acid and *p*-hydroxybenzoic acid.

(c) Adsorption Equilibrium of Syringic Acid. Experimental isotherms of syringic acid obtained from solutions when present alone or in binary and ternary mixtures are presented in Fig. 9. Also in this case, binary and ternary isotherm curves were below the corresponding of the syringic acid in the absence of other phenolic compounds. The isotherm corresponding to the ternary mixture presented adsorbed equilibrium concentrations of syringic acid higher than those corresponding to the binary mixtures and single adsorption. This suggests the development of interaction effects between phenolic acid compounds to improve the adsorption of syringic acid.

(d) Other Aspects Concerning the Multicomponent Adsorption Equilibrium. For comparative reasons the individual isotherms of each phenolic acid obtained from different binary and ternary mixtures are presented in Fig. 10. Although gallic acid presented the lowest adsorption affinity as shown in preceding sections, when it took part of binary mixtures the adsorbed equilibrium concentrations were similar to those of *p*-hydroxybenzoic acid and slightly lower than those of syringic acid. It seems that interaction between adsorbates (Deryło-Marczewska et al., 1985; Weber and Van Vliet, 1981) in binary mixtures favoured the adsorption of gallic acid compared to the adsorption when it was alone in water. Also, in binary mixtures at high gallic acid concentrations adsorbed equilibrium

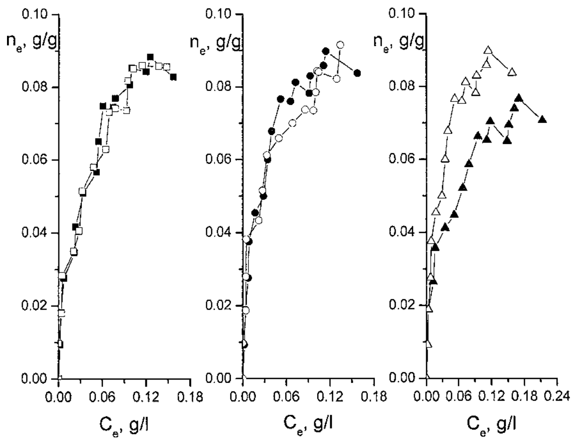


Figure 10. Experimental isotherms of binary mixtures of phenolic acids studied. Conditions: 20°C, pH: 3.4–3.7. Binary mixture initial mass ratio: 1/1. Binary mixtures: ■ gallic acid and □ *p*-hydroxybenzoic acid; ● gallic acid and ○ syringic acid; ▲ *p*-hydroxybenzoic acid and △ syringic acid.

concentrations of this acid decreased which suggests a displacement of adsorbed gallic acid to the aqueous phase. Similar situations have been reported for other compounds like pesticides (Espínola, 1989), halogenated phenols (Álvarez, 1989) and *p*-nitrophenol (Fritz and Schlünder, 1981). On the contrary, the *p*-hydroxybenzoic acid-syringic acid binary system did not show this behaviour. Syringic acid was the strongest adsorbed phenolic acid but it does not seem to exert any effect on *p*-hydroxybenzoic acid to be displaced from the active centres.

Finally, Fig. 11 presents the individual isotherms of the three phenolic acids studied obtained from the ternary mixture. As before, adsorbed equilibrium concentrations of syringic acid were the highest ones. In addition, adsorbed equilibrium concentrations of gallic acid and *p*-hydroxybenzoic acid were similar likely due to the interaction effects among adsorbates. In Fig. 11 it is also observed that for high dissolved equilibrium concentrations ($>0.1\ \mathrm{g \cdot l^{-1}}$) adsorbed equilibrium concentrations of gallic acid and *p*-hydroxybenzoic acid reached a plateau value while that of syringic acid still presented an increasing trend towards higher concentration values.

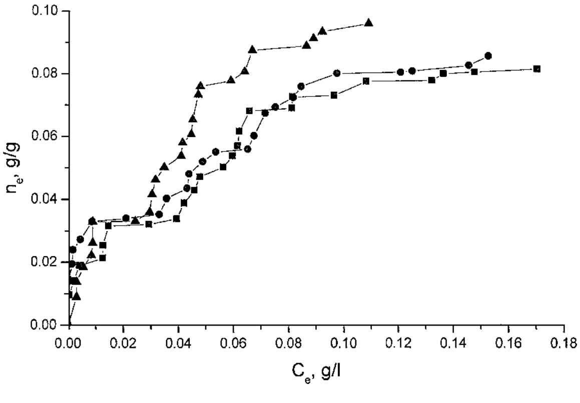


Figure 11. Experimental isotherms of the ternary mixtures of phenolic acids studied. Conditions: 20°C, pH: 3.4–3.7. Ternary mixture initial mass ratio: 1/1/1. ■ gallic acid, ● *p*-hydroxybenzoic acid, ▲ syringic acid.

Conclusions

Main conclusions of this work are:

- High adsorption times are (150 h) needed to reach equilibrium values within the experimental system used.
- Maximum adsorption capacity of the phenolic acids studied was reached at pH between 3 and 4.
- The adsorptive capacity of the activated carbon varied depending on the nature of phenolic acid. In single component aqueous solution the adsorption trend was found to be syringic acid > *p*-hydroxybenzoic acid > gallic acid, regardless of temperature.
- A low significant influence of temperature in the range studied (20 to 40°C) was observed. In any case, adsorption capacity decreased by a little with the increasing temperature, regardless of the phenolic acid adsorbed.
- Interaction effects between adsorbates were noticed to favour the adsorption of one or two components.
- At high dissolved equilibrium concentration, in binary and ternary mixtures, adsorbed gallic acid was likely displaced from the active centres to yield lower adsorbed equilibrium concentrations.
- Adsorption of phenolic acids of agroindustrial wastewater on activated carbon can be an alternative technology to reduce the presence of these compounds which are difficult to be removed by biological oxidation.

Acknowledgments

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References

Ania, C.O., J.B. Parra, and J.J. Pis, "Effect of Texture and Surface Chemistry on Adsorptive Capacities of Activated Carbons for Phenolic Compounds Removal," *Fuel Proccesing Technology*, **77**, 337–343 (2002).

Álvarez, F.J. "Adsorción de Compuestos Fenólicos en Fase Líquida Sobre Carbón Activado. Equilibrio de Mezclas Multicomponentes," Ph.D. Thesis, Universidad Complutense, Madrid, Spain, 1989.

Beltrán, F.J., J.F. García-Araya, F.J. Rivas, P. Álvarez, and E. Rodríguez, "Kinetics of Competitive Ozonation of Some Phenolic Compounds Presents in Wastewaters from Food Processing Industries," *Ozone Sci. Eng.*, **22**, 167–183 (2000a).

Beltrán, F.J., J.F. García-Araya, F.J. Rivas, and E. Rodríguez, "Ozone Remediation of Some Phenol Compounds Present in Food Processing Wastewater," *J. Environ. Sci. Health—A*, **35**, 681–699 (2000b).

Borja, R., A. Martín, V. Alonso, I. García, and C.J. Banks, "Influence of Different Aerobic Pretreatments on the Kinetics of Anaerobic Digestion of Olive Mill Wastewater," *Wat. Res.*, **29**, 489–495 (1995).

Brunauer, S., L.S. Deming, W.S. Deming, and E. Teller, "On a Theory of the van der Waals Adsorption of Gases," *J. Am. Chem. Soc.*, **62**, 1723–1732 (1940).

Chiou, C. and M. Manes, "Application of the Polanyi Adsorption Potential Theory to Adsorption from Solution on Activated Carbon. V. Adsorption from Water of Some Solids and Their Melts, and a Comparison of Bulk and Adsorbate Melting Points," *J. Phys. Chem.* **78**, 622–626 (1974).

Costa, E., G. Calleja, and L. Marijuan, "Comparative Adsorption of Phenol, *p*-Nitrophenol and *p*-Hydroxybenzoic Acid on Activated Carbon," *Adsorpt. Sci. Technol.*, **5**, 213–228 (1989).

Coturelo, L.M. and M.D. Marqués, "Tratamiento de Aguas por Adsorción (I)," *Ing. Quím.*, **349**, 195–200 (1998).

Deryło-Marczewska, A., M. Jaroniec, J. Oscik, and A.W. Marczewski, "Studies of Association Effects in Adsorption from Multicomponent Solutions on Solids," *Chem. Eng. Sci.*, **40**, 917–922 (1985).

Espínola, A. "Equilibrio y Cinética de Adsorción Sobre Carbón Activado de Tres Pesticidas en Disolución Acuosa," Ph.D. Thesis, Universidad Complutense, Madrid, Spain, 1998.

Frick, B., R. Bartz, H. Sontheimer, and F.A. DiGiano, "Predicting Competitive Adsorption Effects in Granular Activated Carbon Filters," in *Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol. 1, I.H. Suffet and M.J. McGuire (Eds.), pp. 229–242, Ann Arbor Science Publishers, Inc., Michigan, 1981.

Fritz, W. and E.U. Schlünder, "Competitive Adsorption of Two Dissolved Organics onto Activated Carbon-I. Adsorption Equilibria," *Chem. Eng. Sci.*, **36**, 721–730 (1981).

Giles, C., T. MacEwan, S. Nakhwa, and D. Smith, "Studies in Adsorption. Part IV. A System of Classification of Solution Isotherms and its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids," *J. Chem. Soc.*, **3**, 3973–3980 (1960).

Gómez, L., A. Urkiaga, M. Gutiérrez, and L. Fuentes, "Fotooxidación de Vertidos Químicos," *Ing. Quím.*, **371**, 211–216 (2000).

Ince, N.H. and I.G. Apikyan, "Combination of Activated Carbon Adsorption with Light-Enhanced Chemical Oxidation via Hydrogen Peroxide," *Wat. Res.*, **34**, 4169–4176 (2000).

Leng, C.C. and N.G. Pinto, "Effects of Surface Properties of Activated Carbons on Adsorption on Behavior of Selected Aromatics," *Carbon*, **35**, 1375–1385 (1997).

Manes, H., "The Polanyi Adsorption Potential Theory and its Applications to Adsorption from Water Solution onto Activated Carbon," *Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol. 1, I.H. Suffet and M.J. McGuire (Eds.), pp 43–64, Ann Arbor Science Publishers, Inc., Michigan, 1981.

Mattson, J.S., H.B. Mark, M.D. Malbin, W.J. Weber, and J.C. Crittenden, "Surface Chemistry of Active Carbon. Specific Adsorption of phenols," *J. Colloid & Interface Sci.*, **31**, 116–130 (1969).

McGuire, M.A. and I.H. Suffet, *Activated Carbon Adsorption of Organics from the Aqueus Phase*, Vol. 2, Ann Arbor Science Publishers, Inc., Michigan, 1983.

Morrison, R.T. and R.N. Boyd, *Química Orgánica*. 5th ed. pp. 599 and 999, Fondo Educativo Interamericano, Tlalpan, México, 1985.

Myers, A.L. and R.R. Zolandz, "Effect of pH on Multicomponent Adsorption from Dilute Aqueous Solution," in *Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol 1, I.H. Suffet and M.J. McGuire (Eds.), pp. 243–272, Ann Arbor Science Publishers, Inc., Michigan, 1981.

Nevskaia, D.M. and A. Guerrero-Ruiz, "Comparative Study of the Adsorption from Aqueous Solutions and the Desorption of Phenol and Nonylphenol Substances on Activated Carbon," *J. Colloid & Interface Sci.*, **234**, 316–321 (2001).

Radke, C.J. and J.M. Prausnitz, "Adsorption of Organic Solutes from Dilute Aqueous Solution on Activated Carbon," *Ind. Eng. Chem. Fundam.*, **11**, 445–451 (1972).

Ravi, V.P., R.V. Jasra, and T.S.G. Bhat, "Adsorption of Phenol, Cresol Isomers and Benzyl Alcohol from Aqueous Solution on Activated Carbon at 278, 298 and 323 K," *J. Chem. Technol. Biotechnol.*, **71**, 173–179 (1998).

Seidel, A., E. Tzscheutschler, K. Radeke, and D. Gelbin, "Adsorption Equilibria of Aqueous Phenol and Indol Solutions on Activated Carbons," *Chem. Eng. Sci.*, **40**, 215–222 (1985).

Singer, P.C. and C. Yen, "Adsorption of Alkyl Phenols by Activated Carbon," in *Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol. 1, I.H. Suffet and M.J. McGuire (Eds.), pp. 167–189, Ann Arbor Science Publishers, Inc., Michigan, 1981.

Suffet, I.H. and M.A. McGuire, *Activated Carbon Adsorption of Organics from the Aqueus Phase*, Vol. 1, Ann Arbor Science Publishers, Inc., Michigan 1981.

Tessmer, C.H., R.D. Vidic, and L.J. Uranowski, "Impact of Oxygen-Containing Surface Functional Groups on Activated Carbon Adsorption of Phenols," *Environ. Sci. Technol.*, **31**, 1872–1878 (1997).

Vidic, R.D., M.T. Suidan, and R.C. Brenner, "Oxidative Coupling of Phenols on Activated Carbon: Impact on Adsorption Equilibrium," *Environ. Sci. Technol.*, **27**, 2079–2085 (1993).

Vidic, R.D., C.H. Tessmer, and L.J. Uranowski, "Impact of Surface Properties of Activated Carbon on Oxidative Coupling of Phenolic Compounds," *Carbon*, **35**, 1349–1359 (1997).

Weber, W.J. and B.M. Van Vliet, "Fundamental Concepts for Application of Activated Carbon in Water and Wastewater Treatment," in *Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol. 1, I.H. Suffet and M.J. McGuire (Eds.), pp. 15–41, Ann Arbor Science Publishers, Inc., Michigan, 1981.