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Evolution of adsorption kinetics and isotherms of gallic acid on an activated carbon oxidized by ozone: Comparison to the raw material

Benoît Cagnon^{a,*}, Olivier Chedeville^a, Jean-François Cherrier^b, Vincent Caqueret^b, Catherine Porte^b

^a Institut de Chimie Organique et Analytique (ICOA, CNRS-UMR 6005), Université d'Orléans, BP 16729, Institut Universitaire de Technologie, 16 rue d'Issoudun, 45067 Orléans-cedex 2, France

^b Laboratoire du Génie des Procédés pour l'Environnement, l'Energie et la Santé (GP2ES-EA21), Conservatoire National des Arts et Métiers, 2 rue Conté, Case Courrier 302, 75003 Paris, France

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ABSTRACT

The evolutions of both adsorption kinetics and isotherms of gallic acid on a commercial activated carbon (AC), initially submitted to ozone in water for 4 h were studied. The microporous properties were investigated by N₂ physisorption at 77 K and the surface oxygen groups created on the surface of the carbon by oxidation were characterized by Fourier Transform Infrared Spectroscopy (FTIR). The studies of the adsorption kinetics and the isotherms of gallic acid on the ozonated and non ozonated AC were carried out at several temperatures (between 5 °C and 50 °C). Four models (pseudo-first order, pseudo-second order, Elovich and the intraparticle model) were used in order to determine kinetic parameters of adsorption. The best results were obtained with the pseudo-second order model. Moreover, a decrease in both the rate constant and the activation energy of adsorption with the ozone exposure time of AC was evidenced. However, no modification appeared in the adsorption mechanism rate limited by the intraparticle diffusion both for ozonated and for non ozonated AC. Two models (Langmuir and Dubinin-Radushkevich) were tested from experimental isotherms and compared. The Langmuir model provided the best correlation under all the temperatures. Results showed that ozonation of AC for 4 and 8 h led to an increase in surface oxygen groups, which can be considered as acid groups, without microporous modification. The adsorption capacity of the oxidized material was increased by a value up to 28% under all the experiments. The Langmuir and the DR models showed that the surface occupied increases and the process of micropores filling proves to be favoured when the AC is oxidized by ozone.

1. Introduction

Industries are subjected to increasingly stringent environmental standards which have led to the development of new wastewater treatment processes. One of the major objectives of water research is to improve the elimination of organic micropollutants, which constitute a health hazard and can modify the organoleptic qualities of water [1,2]. The combined use of ozone (O₃) and activated carbon (AC) is a recent method of wastewater treatment which combines the two effects of ozonation and adsorption on activated carbon and generates hydroxyl radicals (HO•) by interaction between the oxidant and the surface groups of the adsorbent. According to Lei *et al.* [3], this radical formation is due to the reactions of ozone with basic surface groups. Nevertheless, according to Valdés and Zaror [4], acid groups can enhance HO• generation by interactions between O₃ and deprotonated acid surface groups. The latter may lead to the formation of

O₂^{-•} and O₃^{-•} which are a radical promoter. These radicals belong to the most oxidizing species in water and allow the degradation of pollutants that are refractory to the action of ozone alone and/or that are not easily adsorbed on activated carbon [5]. However, the interaction between O₃ and AC could generate chemical and structural modifications in the adsorbent and then could alter its adsorption characteristics. Thus, in order to set up a treatment process based on O₃/AC coupling, it is important to understand and control the modifications of the activated carbon submitted to ozone. Moreover, the use of an adsorption process requires controlling the adsorption kinetics and determining the equilibrium conditions [6].

The aim of this work was to study the effect of ozonation on a commercial activated carbon (PICA 150) on the chemical and porous properties of the material and on its adsorption efficiency. Both the adsorption kinetics and the isotherms of gallic acid, a micropollutant frequently found in agro-industrial wastewaters were performed. Initially, the AC was submitted to ozone for 4 h and 8 h and modifications in the structural and chemical properties were analysed (nitrogen adsorption isotherms at 77 K and FTIR). The adsorption kinetics of gallic acid were carried out at different

* Corresponding author. Tel.: +33 2 38 49 44 31; fax: +33 2 38 49 44 25.
E-mail address: benoit.cagnon@univ-orleans.fr (B. Cagnon).

temperatures (5–50 °C) for the AC submitted to ozone in water for 4 h. Several models (pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion model) were tested and activation energy was estimated in order to understand the adsorption mechanism and the effect of O₃/CA interaction on the adsorption kinetics. Two isotherm models were also tested (Langmuir and Dubinin–Radushkevich) to estimate the ACs adsorption capacity, to determine and calculate the isotherm parameters, the surface occupied and the microporous volume occupied.

2. Materials and methods

2.1. Characterization of the activated carbon

The commercial activated carbon used (Picachem 150) was supplied by Pica (Vierzon, France). The AC was washed before each experiment to eliminate its residual acidity due to its activation treatment. The porosity of the materials was characterized through a conventional nitrogen adsorption isotherm at –196 °C (77 K) by Promes (UPR 8521, Perpignan, France) using a Micromeritics ASAP 2000 M. The sample was previously degassed at 250 °C for 24 h under a residual vacuum of less than 10^{–4} Pa. The nitrogen adsorption isotherm was analysed according to Dubinin's theory [7,8]. Both the specific microporous volume W_0 (cm³/g) and the mean pore size L_0 (nm) were estimated from the linear part of the Dubinin–Radushkevich (D–R) plot [8,9]. The Sing α_s plots [10] were also used to determine the external specific surface S_{ext} (m²/g), assuming that for slit-shaped micropores the specific microporous surface S_{micro} (m²/g) could be estimated using the specific microporous surface and the mean pore size [8]. The mean diameter of particles was determined using a laser granulometer (Coulter LS 230).

The FTIR spectra of the AC before and after ozonation were obtained on a Nicolet iS10 FT-IR spectrometer. The samples were dried overnight at 80 °C before the spectra were recorded.

2.2. Kinetics and isotherms of adsorption

The adsorption kinetics experiments were carried out in Erlenmeyer flasks containing 100 mL of solution with an initial concentration of 1 g/L of gallic acid (Sigma Aldrich) and 0.1 g of activated carbon placed in a thermostated bath at 5, 10, 25, 40 or 50 °C (±0.2 °C). Samples were withdrawn at suitable time intervals.

The adsorption isotherms were carried out in the same experimental conditions with gallic acid initial concentrations ranging from 0.01 to 1 g/L.

In both cases, solutions were stirred by magnetic stirrers. To avoid gallic acid photodegradation, the flasks were kept in the dark. Samples were filtered through a 0.45 μm membrane filter. Gallic acid concentrations were determined before and after adsorption using a UV spectrophotometer (Jasco V-530) at 265 nm. The sorption capacities at t time q_t (g/g) and at equilibrium q_e (mol/g) were calculated from equations:

$$q_t = \frac{C_0 - C_t}{w} \cdot V \quad \text{and} \quad q_e = \frac{C_0 - C_e}{w} \cdot V \quad (1)$$

where C_0 , C_t and C_e represent gallic acid concentration, respectively, in the initial solution, at time t and at equilibrium (mol/L), w is the weight of the adsorbent (g) and V the sample volume (L).

2.3. Ozonation of the activated carbon

Ozonation of the AC was carried out in a batch reactor. 10 g of washed activated carbon were introduced into 1 L of deionised water. Ozone, introduced through a porous diffuser, was produced

from pure oxygen in an ozone generator Labo LOX (Trailigaz). The ozone concentration in gas was 20 g N/m³ (±1 g N/m³) and the gas flow rate was 80 N L/h (±5 N L/h). The AC was recovered by filtration and dried in an oven at 80 °C for 24 h. AC was submitted to ozone for 4 h (P150-4) and 8 h (P150-8). P150-0 corresponds to the initial AC.

3. Theory

3.1. Kinetic models

Adsorption kinetic data were modelled using the Lagergren pseudo-first order [11,12], Ho's pseudo-second order [13,14] and Elovich models [15] to determine the order of the reaction, the rate constant and the activation energy. The intraparticle diffusion model was used to determine the rate controlling step [16,17].

The pseudo-first order model is based on the sorption capacity of the solid phase. Commonly, it is applicable over the first 30 min of the sorption process. The pseudo-first order kinetic equation is expressed as follows:

$$\frac{dq}{dt} = k_1 \cdot (q_e - q_t) \quad (2)$$

where k_1 is the rate constant of pseudo-first order adsorption (min^{–1}), q_e the amount of gallic acid adsorbed at equilibrium (g/g) and t the time (min). The integrated form of this expression is:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (3)$$

The kinetic parameters k_1 and q_e in Eq. (3) can be obtained from the linear plot of $\ln(q_e - q_t)$ versus t .

The pseudo-second order model is also based on the sorption capacity of the solid phase. It is generally used to describe the chemisorption process. The pseudo-second order kinetic equation is expressed as follows:

$$\frac{dq}{dt} = k_2 \cdot (q_e - q_t)^2 \quad (4)$$

where k_2 is the rate constant of pseudo-second order adsorption (g/(g min)). The integrated form of this equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (5)$$

The linear form of the pseudo-second order model enables the values of k_2 and q_e to be determined from the slope and the intercept of t/q_t versus t .

The Elovich equation is another rate equation based on the adsorption capacity. Initially used to describe the chemisorption of gas onto solid phase, it has recently been used to model the adsorption of pollutants from aqueous solution [18]. The Elovich equation is written as:

$$\frac{dq}{dt} = \alpha \cdot e^{(-\beta \cdot q_t)} \quad (6)$$

where α is the initial adsorption rate (g/(g min)) and β the desorption constant (g/g). The integrated form of this expression is:

$$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln t \quad (7)$$

The kinetic parameters α and β in Eq. (7) can be obtained from the slope and the intercept of the linear plot of q_t versus $\ln(t)$.

The intraparticle diffusion model is used to determine the rate limiting step of the adsorption kinetics. It is expressed as:

$$q_t = K_i \cdot t^{0.5} + C \quad (8)$$

where K_i is the intraparticle diffusion rate constant (g/g min^{–0.5}) and C a constant (g/g). Plots may present a multi-linearity

Table 1

Porous properties of activated carbons used (initial (P150-0) and oxidized (P150-4 and P150-8)).

	W_0 (cm ³ /g)	L_0 (nm)	S_{BET} (m ² /g)	S_{ext} (m ² /g)	S_{micro} (m ² /g)	S_{tot} (m ² /g)	Diameter (μm)
P150-0	0.75	2.43	2032	630	617	1247	1042
P150-4	0.75	2.44	2048	674	615	1289	1071
P150-8	0.75	2.49	2000	590	602	1192	1071

corresponding to successive steps in the adsorption phenomenon. The first step, very short, corresponds to a limitation of adsorption by external diffusion. The second step corresponds to a gradual adsorption stage during which intraparticle diffusion is the rate limiting factor. The third step is the final equilibrium in which adsorbate concentration in aqueous solution becomes very weak, thus slowing down the intraparticle diffusion phenomenon. The value of the intercept C indicates whether external diffusion limits the adsorption phenomenon: if the straight line passes through the origin, intraparticle diffusion is the rate limiting factor; otherwise, external diffusion operates simultaneously to control the rate of adsorption [19,20].

3.2. Isotherm models

The Langmuir equation is used for a monolayer adsorption [21]. The linear Langmuir equation determines the maximum amount of adsorption corresponding to complete monolayer coverage of the surface q_m (mol/g):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (9)$$

where C_e is the equilibrium concentration (mol/L), q_e is the adsorbed amount at equilibrium (mol/g) and b is the Langmuir constant (L/mol). The values of q_m and b can be determined from the linear plot of C_e/q_e versus C_e from the slope and the intercept, respectively.

In the case of liquid-phase adsorption, several studies have shown that the adsorption energy can be estimated according to the Dubinin–Radushkevich equation (D–R) [22]:

$$q_e = q'_{\text{DR}} \exp \left[-B \left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^n \right] \quad (10)$$

where q'_{DR} (mol/g) is the limiting amount filling the micropores, B (in mol²/J²) a constant related to the most probable energy of adsorption E (J/mol) ($E = (2B)^{-1/2}$), R the gas constant (8.314 J/(mol K)) and T the temperature (K). As shown elsewhere [23], the value $n = 4$ which leads to a better overall fit for the experimental data was chosen for this study. The D–R isotherm constants (q'_{DR} and B) were determined from the linear plots of $\ln q_e$ versus ε^2 , where $\varepsilon = RT \ln(1 + (1/C_e))$. This linear form of the D–R equation enables the values of q'_{DR} and B to be determined from the intercept and the slope, respectively.

4. Results and discussion

4.1. Structural and chemical properties of the activated carbon

The structural properties of ACs are presented in Table 1. It can be observed that ACs P150-0, P150-4 and P150-8 exhibit the same porous properties. The oxidation by ozone in these experimental conditions (liquid phase) does not appear to modify the porous properties. The particles main diameter of ACs P150-0, P150-4 and P150-8 were close (respectively 1042 μm and 1071 μm).

The FTIR spectra (Fig. 1) show the evolution of the surface group nature for AC submitted to ozone. ACs P150-4 and P150-8 exhibit more intense bands for 1100–1250 cm⁻¹, which may be related to

OH bending vibrations in the carboxyl group (1125 cm⁻¹) and phenol (1175 cm⁻¹). The broad mode at about 3450 cm⁻¹ is indicative of hydrogen bonded OH species. Moreover, these spectra indicate that the contact of AC with ozone leads to the formation of carbonyl groups, since absorbance at 1580 cm⁻¹ (C=O stretching vibration in the carboxyl group), and at 1720–1790 cm⁻¹ (C=O stretching vibration in lactones, quinone, ester and carboxyl functions) increased with ozone exposure time [24]. These analyses show that the ozonation of AC led to an increase in surface oxygen groups, which can be considered as acid groups, without microporous modification. Our results are in agreement with the study by [25] which has shown that oxidation in the liquid phase increases in particular the concentration of carboxyl groups.

This phenomenon was also observed by [26] who showed a progressive decrease in pH_{PZC} due to the formation of acid groups for AC submitted to ozone.

4.2. Kinetic study

It was therefore important to determine the effect of temperature on the adsorption of gallic acid in order to optimize the operating conditions of the O₃/CA treatment process. In order to study the effect of ozone on the gallic acid adsorption kinetics of AC, experiments were carried out with ACs P150-0, P150-4. Moreover, to study the effect of temperature on the adsorption kinetics and to determine the activation energy using Arrhenius's law, experiments were carried out at different temperatures (5 °C, 10 °C, 25 °C, 40 °C and 50 °C). The results presented in Fig. 2 show that the adsorption capacity evolved rapidly initially, and then the curves reached a plateau corresponding to the equilibrium. The time necessary to reach this state was temperature-dependent: the equilibrium state was reached more quickly when the temperature increased. Thus, for the two ACs, equilibrium was reached in approximately 120 min at 50 °C and in 300 min at 5 °C, indicating that the adsorption kinetics of gallic acid was enhanced when the temperature increased.

Kinetic models can be applied to determine the rate constant and the adsorption mechanism. The results presented in Table 2, and Figs. 2 and 3 show that the pseudo-second order kinetic model

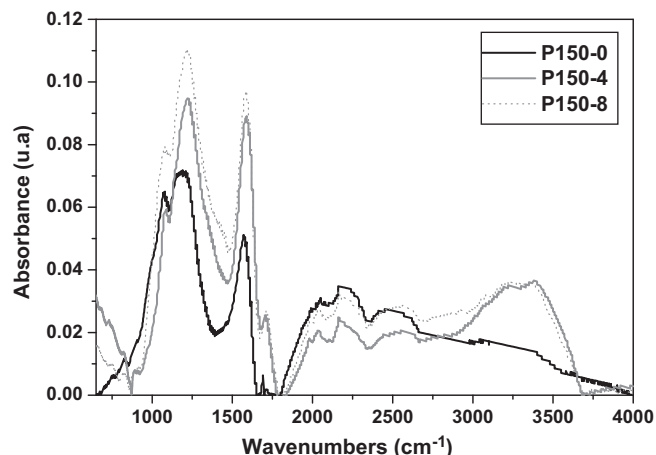


Fig. 1. FTIR spectra of initial and oxidized activated carbons.

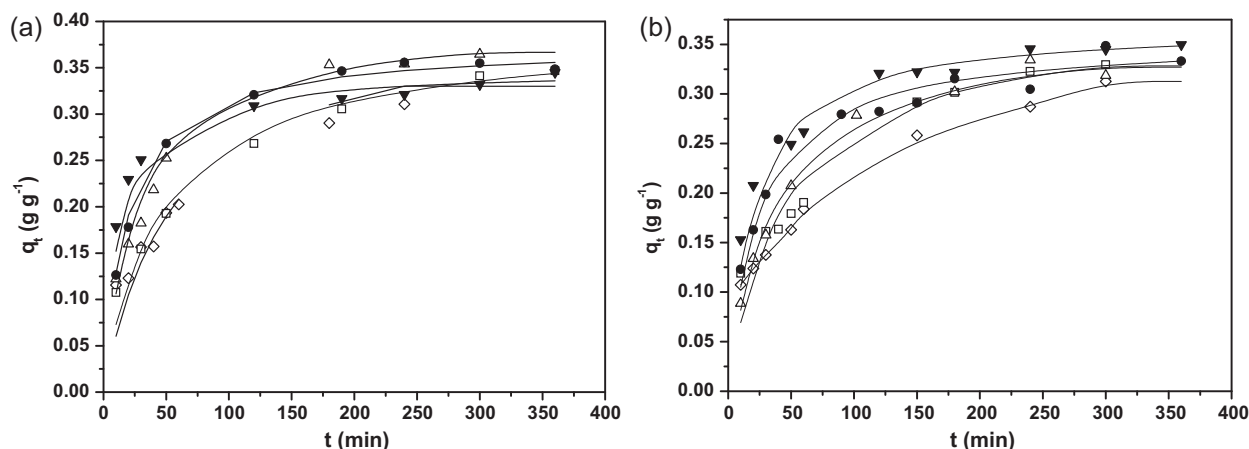


Fig. 2. Influence of temperature on adsorption kinetics of gallic acid on P150-0 (a) and P1504 (b) (5 °C (◇), 10 °C (□), 25 °C (Δ), 40 °C (●) and 50 °C (▼)).

is the most suitable one to describe the adsorption of gallic acid onto these ACs ($r^2 > 0.984$). For P150-0 and P150-4, an increase in temperature induced an increase in the rate constant k_2 : the latter rose from 0.042 to 0.223 g/(g min) for P150-0 and from 0.050 to 0.140 g/(g min) for P150-4 AC when the temperature increased from 5 to 50 °C. Moreover, results show that the adsorption capacity decreased when the temperature increased: q_e decreased from 0.410 g/g to 0.348 g/g for P150-0 and from 0.379 g/g to 0.367 g/g for P150-4 when temperature increased from 5 °C to 50 °C. Adsorption (being an exothermic process) is favoured by a decrease in temperature whereas diffusion (being a kinetic phenomenon) is favoured by an increase in temperature.

The comparison between the results obtained for each AC at 25 °C indicates that the adsorption phenomenon was slower when AC was submitted to ozone. Thus, at this temperature, the rate constant k_2 was 0.090 g/(g min) for P150-0, 0.079 g/(g min) for P150-4 and 0.055 g/g for P150-8. Moreover, the comparison between the results obtained for P150-0 and P150-4 shows that this effect is greater at 40 °C and 50 °C: at 50 °C, k_2 decreased from 0.223 g/(g min) for P150-0 to 0.140 g/(g min) for P150-4 (a decrease of 37%). Several assumptions based on the formation of surface oxygen groups could explain this phenomenon. On the one hand, according to Álvarez *et al.* [27], these oxygenated groups could disadvantage the adsorption of the pollutant. The ozonation of AC may lead to a decrease in π -electrons from the carbon surface which attenuates the dispersive interaction with gallic acid. On the other hand, according to Valdés *et al.* [26], these oxygen groups can obstruct the entry of the micropores and thus decrease the adsorption capacity of AC. The preceding results show that, under the operating conditions used, the ozonation of AC led to a

modification in its chemical properties without modification in its structural properties. The increase in the acid surface groups of AC following its ozonation could decrease its affinity with gallic acid and thus explains the decrease in the adsorption kinetics. In order to determine the activation energy of adsorption E_a (J/mol), data were fitted with Arrhenius's equation (Eq. (11)):

$$k_2 = A \cdot e^{(-E_a/R \cdot T)} \quad (11)$$

where A is a pre exponential factor (g/(g min)), R is the gas constant ($R = 8.314 \text{ J/(K mol)}$) and T is the temperature (K). In both cases, the activation energy was positive, meaning the existence of an energy barrier. The activation energy of the initial AC ($E_{aP150-0} = 25.2 \text{ kJ/mol}$ with a $r^2 = 0.975$) was higher than for AC submitted to ozone ($E_{aP150-4} = 17.1 \text{ kJ/mol}$ with a $r^2 = 0.994$), confirming the modification in the nature of the interactions between AC and gallic acid. The decrease in activation energy could be explained by a decrease in the hydrophobicity of AC submitted to ozone. Ozonation led to increase the oxygen surface groups which could favour interaction between AC and water. Thus, the water could be adsorbed preferentially by the oxygen surface groups and lets the solute fills the microporous volume not occupied by water, making the adsorption time of gallic acid longer: hence, k_2 and E_a for P150-4 are lower than those of P150-0. Our results are in agreement with Fernandez *et al.* [28] who have shown that the process of micropores filling proves to be favoured when the AC contains oxygen surface groups for phenol adsorption.

According to Lazaridis and Asouhidou [16] an activation energy lower than 25–30 kJ/mol could mean that the adsorption phenomenon is intraparticle diffusion rate controlled.

Table 2
Kinetics parameters for adsorption kinetics of gallic acid on the activated carbons used at different temperatures.

T (°C)	Pseudo-first order			Pseudo-second order			Elovich		
	q_e (g/g)	k_1 (min ⁻¹)	r^2	q_e (g/g)	k_2 (g/(g min))	r^2	α (g/(g min))	β (g/g)	r^2
P150-0									
5	0.333	0.008	0.863	0.410	0.042	0.984	0.033	12.8	0.939
10	0.303	0.012	0.974	0.385	0.061	0.996	0.026	14.0	0.986
25	0.220	0.015	0.819	0.400	0.090	0.996	0.034	13.0	0.984
40	0.270	0.019	0.994	0.375	0.139	0.999	0.055	15.2	0.963
50	0.133	0.008	0.950	0.348	0.223	0.998	0.188	23.7	0.977
P150-4									
5	0.258	0.006	0.993	0.379	0.050	0.989	0.238	14.3	0.950
10	0.298	0.014	0.978	0.377	0.060	0.989	0.787	1.4	0.945
25	0.248	0.012	0.968	0.365	0.079	0.997	0.835	1.3	0.983
40	0.176	0.007	0.828	0.355	0.118	0.991	0.060	16.9	0.948
50	0.195	0.013	0.947	0.367	0.140	0.999	0.103	17.9	0.979

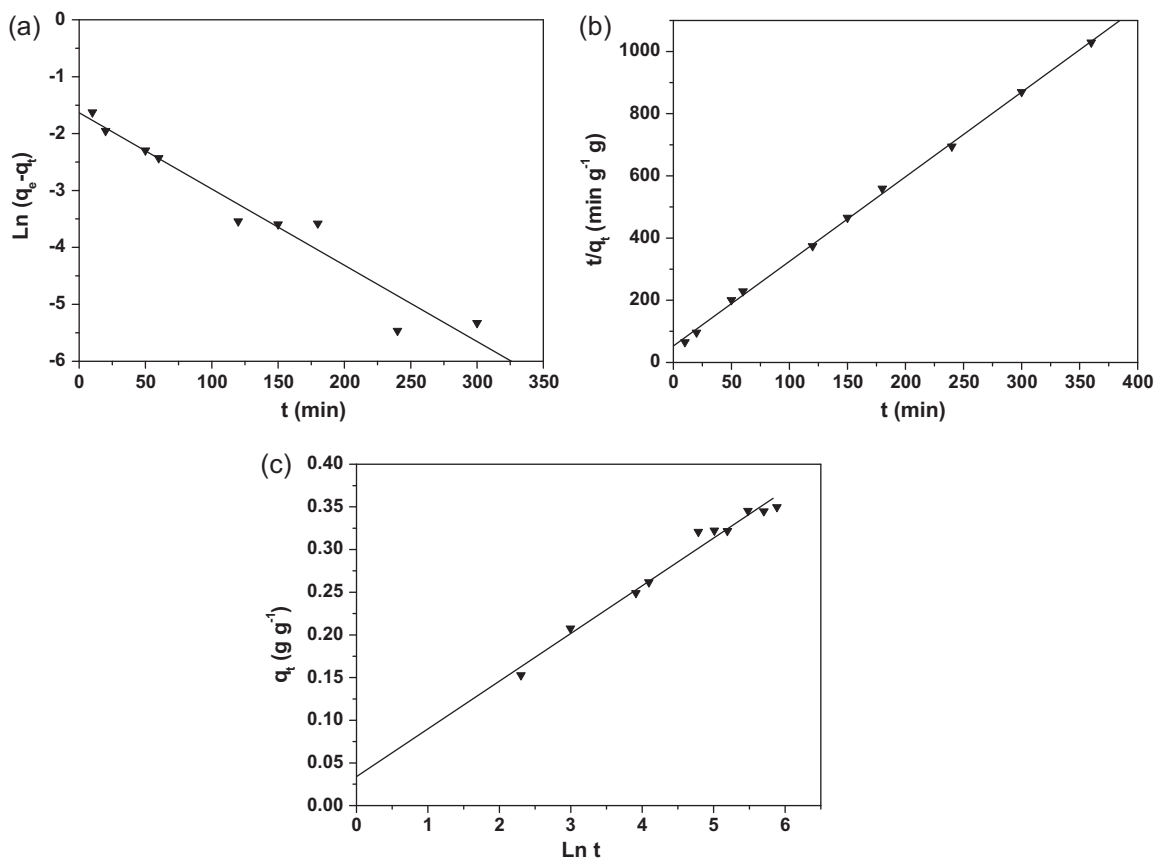


Fig. 3. Linearized plots of the different adsorption kinetic models used on P150-4 at 50 °C: pseudo-first order (a), pseudo-second order (b) and Elovich model (c).

The intraparticle diffusion model was applied to data obtained at 25 °C (Table 3). For both ACs, modelling exhibited multilinearity, meaning the existence of several steps in the adsorption process (Fig. 4). The low values of C indicate that the external diffusion step was not rate controlling. Thus, the first stage corresponds to an intraparticle diffusion rate control [29]. The second step, marked by the lack of evolution of q_t , corresponds to the equilibrium step due to the decrease in gallic acid concentration in the aqueous solution. It is important to note that the K_i rate constant decreased with the ozone exposure time of AC: $K_i = 0.036 \text{ g/g min}^{-0.5}$ for P150-0, $K_i = 0.027 \text{ g/g min}^{-0.5}$ for P150-4 (a reduction of 25%) and $K_i = 0.023 \text{ g/g min}^{-0.5}$ for P150-8 (a reduction of 36%). As for the results obtained with the pseudo-second order model, the ozonation of the AC led to a progressive decrease in the gallic acid adsorption kinetics. This could explain why the duration of the first stage (a phenomenon limited by intraparticle diffusion) increased with the ozone exposure time (approximately 90 min for P150-0 and 130 min for P150-4): the decrease in gallic acid concentration was slower. These results confirm that the formation of oxygen groups on the surface of AC slows down the adsorption of this molecule.

Table 3
Intraparticle diffusion model parameters for gallic acid adsorption on the activated carbons used at 25 °C.

AC	$K_i \text{ (g/g min}^{-0.5}\text{)}$	$C \text{ (g/g)}$	r^2
P150-0	0.036	0	0.986
P150-4	0.027	0.01	0.994
P150-8	0.023	0.02	0.986

4.3. Adsorption isotherms

The experiments were carried out at different temperatures (5 °C, 10 °C, 25 °C, 40 °C and 50 °C) in order to study the influence of temperature on gallic acid adsorption. Fig. 5 shows the gallic acid adsorption isotherms of P150-0 and P150-4 at 5 °C, 25 °C and 50 °C (the isotherms at 10 and 40 °C are not represented in this figure). A contact time of 7 h was chosen whatever the experimental temperature to be sure to reach equilibrium. According to Giles's classification, isotherms of both activated carbons are of type L

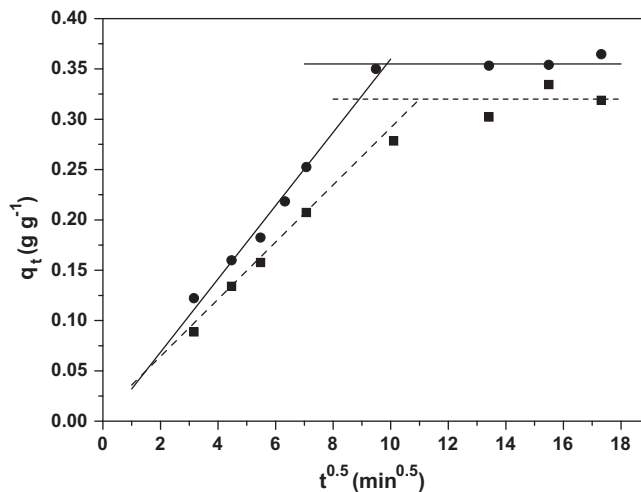


Fig. 4. Influence of ozone exposure time on adsorption kinetics at 25 °C – intraparticle diffusion model (P150-0 (●) and P150-4 (■)).

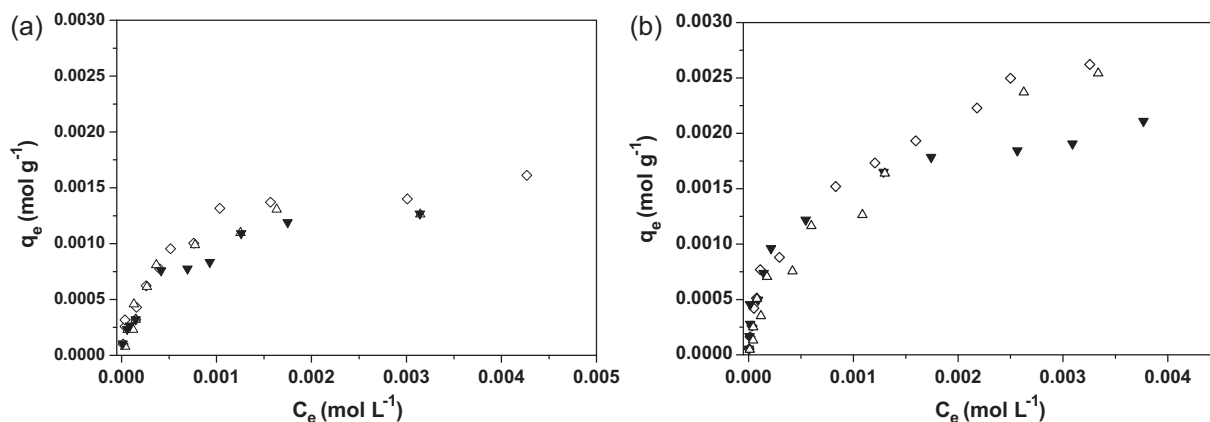


Fig. 5. Gallic acid experimental isotherms of P150-0 (a) and P150-4 (b) ACs at 5 °C (◇), 25 °C (Δ) and 50 °C (▼).

(Langmuir class) in the subgroup 3 which do not present a strict plateau. This figure also shows that an increase in temperature induces a decrease in the adsorption capacity of gallic acid on the ACs used, confirming the fact that gallic acid adsorption is an exothermic process. Besides, the adsorption capacity of the AC submitted to ozone are always higher than those of the initial material under all the experimental conditions used: there was an increase of 37.4% at 5 °C, 28.6% at 10 °C, 51.4% at 25 °C, 32.3% at 40 °C and 32.5% at 50 °C.

The oxidation of AC in liquid phase by ozone was proved to favour considerably gallic acid adsorption whatever the adsorption temperature. This could be explained by the fact that the ozonation of the material increased the oxygen surface groups which could favour interaction between AC and water.

In order to establish the adsorption mechanism and to determine the isotherm parameters, two equilibrium adsorption isotherm models (Langmuir and Dubinin–Radushkevich (D–R) equations) were compared. The results are shown in Table 4 for P150-0 and P150-4 at the different temperatures studied. Fig. 6 also shows the comparison of the two models with experimental results for P150-0 and P150-4 ACs at 5 °C (the models for the other temperatures show the same tendency and are not represented in this figure). The Langmuir model was successfully applied for the two activated carbons used (initial and oxidized) under all the experimental temperatures used. The correlation coefficient is always above 0.97 (Table 4) except for P150-4 at 25 °C, demonstrating that the Langmuir isotherm model provides good fits for gallic acid adsorption on these ACs (Figs. 6 and 7). These results show that gallic acid adsorption is carried out mainly in a molecular monolayer and are in agreement with the shapes of the isotherms represented in Fig. 5.

As shown previously, an increase in temperature induced a decrease in the maximum amount of adsorption (q_m) correspond-

ing to complete monolayer coverage for the two ACs: q_m decreased from 0.00171 mol/g to 0.00141 mol/g for P150-0 and from 0.00273 mol/g to 0.00209 mol/g for P150-4 when temperature increased from 5 °C to 50 °C. These results show that ozonation of the activated carbon favours the adsorption of gallic acid. However, the effect of temperature (between 5 °C and 50 °C) is slightly more important on the P150-4, leading to a 25.6% decrease in their adsorption capacity against 17.5% for the P150-0. According to this model, it is possible to calculate the surface occupied by the gallic acid with the following equation:

$$S_{occ.} (\text{m}^2 \text{ g}^{-1}) = q_m \times S_{Gal.} \times N_A$$

with N_A the Avogadro number (mol^{-1}) and $S_{Gal.}$ the gallic acid surface (m^2). The gallic acid surface was calculated with the *Chemsketch software* ($S_{Gal.} = 4.54 \times 10^{-19} \text{ m}^2$).

The results, presented in Table 4, show that the surface occupied (with regard to the total surface) is higher for ozonated AC and depends on the temperature. The surface occupied of the P150-0 varies from 30.8% (50 °C) to 41.0% (10 °C) against 44.3% (50 °C) to 57.9% (5 °C) for the P150-4. The surface occupied (with regard to the microporous surface) was also calculated to understand the adsorption mechanism. For the P150-0, the microporous surface occupied varies from 62.2% (50 °C) to 82.8% (10 °C). On the other hand, for the P150-4, the microporous surface occupied varies from 92.8% (50 °C) to 121.3% (5 °C). The adsorption of gallic acid under these experimental conditions follows a process with the coating of the micropore walls and of the external surface rather than only the filling of micropores [23]. Thus, the water seems to be adsorbed preferentially by the oxygen surface groups, making it easier for the solute to fill the specific microporous volume not occupied by water. The filling of the

Table 4
Langmuir isotherm parameters for gallic acid adsorption on the activated carbons used at different temperatures.

Activated carbons	T (°C)	Langmuir				
		q_m (mol/g)	b (L/mol)	Covered S_{TOT} (%)	Covered S_{micro} (%)	r^2
P 150-0	5	0.00171	2362	37.5	75.7	0.99
	10	0.00187	2605	41.0	82.8	0.99
	25	0.00147	2443	32.3	65.2	0.98
	40	0.00151	2479	33.1	66.9	0.99
	50	0.00141	2755	30.8	62.2	0.99
P 150-4	5	0.00273	2522	57.9	121.3	0.97
	10	0.00262	3271	55.4	116.2	0.99
	25	0.00229	1740	48.6	101.8	0.90
	40	0.00223	4043	47.2	99.0	0.99
	50	0.00209	4577	44.3	92.8	0.99

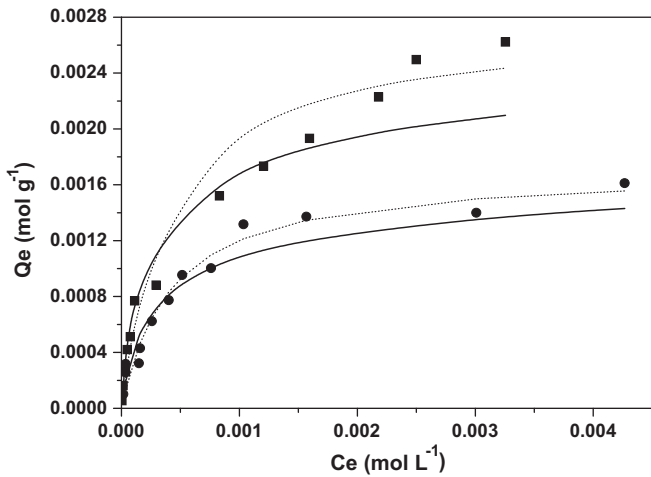


Fig. 6. Gallic acid experimental isotherms of P150-0 (●) and P150-4 (■) and predictive isotherms by Langmuir (dot) and D-R models (lines) at 5 °C.

micropores was favoured by low temperatures and was more sensitive to temperature. There is an increase of the adsorption capacity for the P150-8 at 25 °C.

The D-R model (with $n = 4$) can be applied for gallic acid adsorption on both activated carbons (Figs. 6 and 7) with correlation coefficients higher than 0.93 (Table 4). The adsorption energy can be associated with the transfer of the gallic acid from the aqueous solution onto the surface of the carbon [23]. The calculated adsorption energies are practically similar for both activated carbons at each temperature, but are slightly higher for the P150-4.

Besides, the microporous volume occupied ($W_{0occ.}$) can be estimated using the molar volume of acid gallic ($V_m = 97.2 \text{ cm}^3/\text{mol}$) and the limiting amount filling the micropores (q_{DR}) [22]: $W_{0occ.} = V_m q_{DR}$. As shown previously, there is no modification in the microporous properties of the oxidized AC. Nevertheless, at each temperature studied, the microporous volume occupied was systematically lower than the W_0 determined by nitrogen adsorption at 77 K and increased when the activated carbon was oxidized (Table 5). These results show that the micropores are not fully filled by gallic acid. But there is an increase of the microporous system filling when the activated carbon is oxidized by ozone: the microporous volume is occupied at 22.1% and at 17.1% for P150-0 and at 33.0% and at 27.9% for P150-4 when temperature increased from 5 °C to 50 °C. These results are in agreement with both Langmuir results: the initial ozonation of the activated carbon favours the adsorption of gallic acid, especially in the microporous

Table 5

D-R isotherm parameters for gallic acid adsorption on the activated carbons used at different temperatures.

Activated carbons	T (°C)	D-R			
		q_{DR} (mol/g)	E (kJ/mol)	$W_{0occ.}$ (%)	r^2
P 150-0	5	0.00170	16.4	22.1	0.94
	10	0.00189	17.0	24.6	0.97
	25	0.00206	16.0	26.7	0.94
	40	0.00174	17.8	22.5	0.99
	50	0.00132	19.7	17.1	0.94
P 150-4	5	0.00254	16.8	33.0	0.98
	10	0.00263	17.4	34.1	0.96
	25	0.00244	16.7	31.7	0.95
	40	0.00216	20.1	28.1	0.97
	50	0.00215	20.7	27.9	0.95

system and these values confirm that the adsorption of gallic acid under these experimental conditions follows a process with the coating of the micropore walls and of the external surface rather than only the filling of micropores [23].

5. Conclusion

O_3/AC coupling for wastewaters treatment involves a progressive modification in adsorbent properties. In the present study, it has been shown that under the operating conditions used, ozonation of AC led to a change in its chemical properties, with an increase of surface oxygen groups, without modification of its porous properties. The pseudo-second order kinetic model was the most suitable model to describe the adsorption kinetics of gallic acid. The evolution of the rate constant k_2 showed that the ozonation of AC led to a decrease in the adsorption kinetics. The formation of acid functional groups at the surface of AC following its ozonation could explain the decrease in affinity between the adsorbent and gallic acid. Moreover, the intraparticle diffusion model showed that ozonation of AC does not seem to change the adsorption mechanism.

The isotherm study shows that an increase in temperature induces a decrease in the adsorption capacity of gallic acid on the ACs used, thus confirming the fact that gallic acid adsorption is an exothermic process. Moreover, the oxidation of AC in liquid phase by ozone proved to favour considerably gallic acid adsorption. The adsorption capacity of the oxidized material was increased by over 28% under all the experiments. The experimental results were then compared by checking with the models of Langmuir and Dubinin-Radushkevich. The Langmuir adsorption model gives the best results to describe the adsorption isotherms and determine the isotherm parameters, while the D-R model enables the

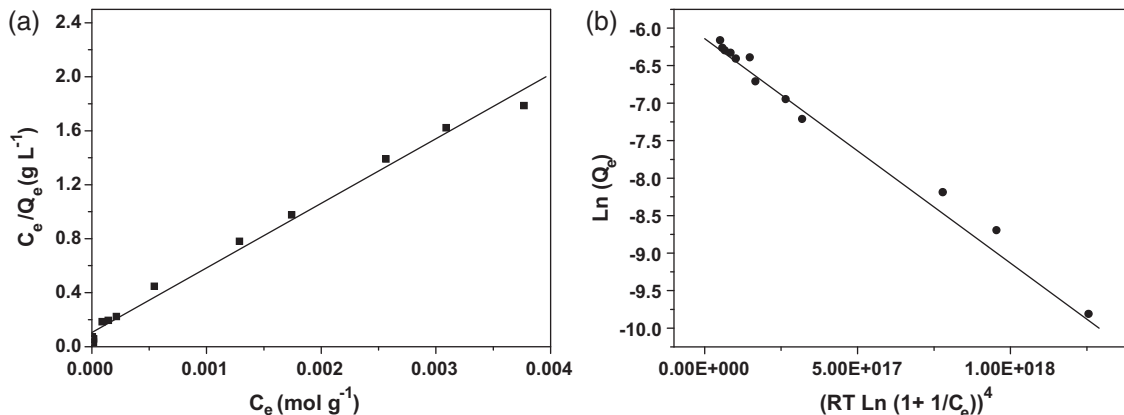


Fig. 7. Linearized plots for both Langmuir and D-R models of P150-4 (■) at 50 °C.

microporous volume occupied to be calculated. These results confirm that the adsorption of gallic acid follows a process with the coating of the micropore walls and of the external surface rather than the filling of micropores.

In an ozone/activated carbon wastewater treatment process, ozone could modify properties of activated carbon. Thus, it is important to follow the evolution of activated carbon properties to guarantee a maximum effectiveness of the material.

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