



Activated carbons prepared from wood particleboard wastes: Characterisation and phenol adsorption capacities

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ABSTRACT

The problems of valorisation of particleboard wastes on one hand, and contamination of aqueous effluents by phenolic compounds on the other hand, are simultaneously considered in this work. Preparation of activated carbons from a two steps thermo-chemical process, formerly designed for generating combustible gases, is suggested. The resultant carbonaceous residue is activated with steam at 800 °C. Depending on the preparation conditions, surface areas within the range 800–1300 m²/g are obtained, close to that of a commercial activated carbon (CAC) specially designed for water treatment and used as a reference material. The present work shows that particleboard waste-derived activated carbons (WAC) are efficient adsorbents for the removal of phenol from aqueous solutions, with maximum measured capacities close to 500 mg/g. However, most of times, the adsorption capacities are slightly lower than that of the commercial material in the same conditions, i.e., at equilibrium phenol concentrations below 300 ppm. Given the extremely low cost of activated carbons prepared from particleboard waste, it should not be a problem to use it in somewhat higher amounts than what is required with a more expensive commercial material. Phenol adsorption isotherms at 298 K were correctly fitted by various equations modelling type I and type II isotherms for CAC and WAC, respectively. Phenol adsorption isotherms of type II were justified by a 3-stages adsorption mechanism.

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1. Introduction

Phenols and phenolic compounds in general are currently produced by industries like petroleum refining, leather and textile manufacturing, olive oil production, etc..., thus significant amounts may be found in the corresponding wastewaters [1,2].

Such wastewaters are an increasing concern and represent a serious potential hazard for human health and aquatic life. Phenolic compounds are indeed very toxic, with a fixed low admissible level of 0.5 mg/L of water [3,4]. A number of derivatives of phenol with their corresponding properties are listed in the review of Dabrowski et al. [5]. Therefore, removal of phenols from industrial effluents is required before sewage disposal. For that purpose, various (more or less) environment-friendly methods have been suggested. Several physicochemical and biological treatment techniques (solvent extraction, ion exchange by resins, chemical oxidation by ozone, aerobic or anaerobic biodegradation, etc...) already exist today, but the most effective and frequently used procedure for phenol removal is adsorption on activated carbons [5–7].

In 2006, the average cost of activated carbon from the major producers was close to \$2500 per ton [4], with a world demand expected to expand 5.2% per year through 2012 to 1.2 millions tons [8]. Activated carbon may thus be considered as a rather expensive product, justifying the big research effort of the scientific community for finding cheaper adsorbents, e.g., bentonites [9,10], zeolites [11], surfactant-treated smectites [12] and montmorillonites [13], chitin [14], fly ash [10], organic beet pulp [14], or wastes of coffee grounds [15].

It has been shown that enhanced adsorption capacity toward phenol occurs on activated carbon having a basic nature, whatever their textural characteristics [16,17]. For example, the adsorptive behaviour of activated carbons possessing oxygenated basic functional groups was described in [18]. However, the basic nature of the activated carbon surface is not only controlled by oxygenated functions. It is indeed well known that nitrogen-containing surface groups confer to activated carbons an increased ability to adsorb acid gases [19,20] and phenolic compounds [21]. For this reason, the first idea of the present work was to prepare nitrogen-enriched activated carbons from wastes of wood particleboards. Indeed, in such materials, wood is the precursor of the carbonaceous adsorbent, while nitrogen is provided by the aminoplastic adhesive: urea–formaldehyde and melamine–formaldehyde resins,

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dispersed all through the board, and impregnating each particle of wood.

Particleboard wastes are zero-cost materials which have already been tested as attractive precursors for producing combustible gases through the two-steps thermo-chemical conversion process presented in Fig. 1 [22,23]. The first step of this process, formerly designed for recovering energy and gases, consists in lowering the nitrogen content of the gases. In the second step of the process, i.e., after the pyrolysis is carried out between 250 and 400 °C, a char containing around 3 wt.% of nitrogen is produced.

The aim of this work is to prepare, characterise, and measure the phenol adsorption properties of activated carbons derived from particleboard wastes. The present paper is organised as follows: the preparation of such cheap adsorbents and the way they were characterised are described in Section 2. The main features of these materials and their corresponding adsorption properties are detailed in Section 3, and compared with those of a commercial activated carbon designed for the adsorption of aromatic compounds in aqueous solution.

2. Materials and methods

2.1. Preparation of the activated carbons

The chars derived from particleboard wastes have been produced in a tubular quartz reactor according to the different steps pictured in Fig. 1 and extensively detailed in refs. [22,23]. The first pyrolysis step was carried out under nitrogen flow, and the following conditions (temperatures and times) were chosen: 250 °C/14.5 min; 300 °C/8 min; 400 °C/2.5 min. These pre-treated samples were then heat-treated (under nitrogen) during 2 min at 800, 900 or 1000 °C. The as-produced chars were finally activated with steam at 800 °C, i.e., partly gasified by an 80/20% gaseous mixture of N₂/H₂O. 30 min of experiment were enough to reach a burn-off typically ranging from 40 to 50%. Before testing the adsorption properties, all the particleboard waste-derived activated carbons (WAC) were thoroughly washed by distilled water in a soxhlet during 24 h.

A commercial activated carbon (CAC): Picahydro sp 23, was supplied by the company Pica (Vierzon, France). This material derives from the physical activation of coconut shells with steam, and was

designed for the adsorption of high concentrations of pesticides and hydrocarbons from water [24]. The average size of the particles is in the range of 8–15 μm, the moisture and the ash contents are both close to 5%, and the specific surface area is around 1000 m²/g (see below).

2.2. Characterisation methods

2.2.1. Composition and surface chemistry

The ultimate analysis of the activated carbons made from particleboard was carried out by the French Central Service of Analysis (CNRS–Vernaison, France). That of the CAC was given by the supplier. Ashes were investigated by semi-quantitative elemental analysis using the energy dispersive X-ray spectrometer (EDX) of a scanning electron microscope (Hitachi S 4800), and identified by XRD of the activated carbons, using a Phillips X'Pert Pro diffractometer equipped with a copper anticathode (Cu Kα: λ = 1.542 Å).

The chemical nature of the activated carbon surface was estimated as follows. Because only low amounts of WAC could be produced by our experimental set-up, the surface functionalities were not investigated by the usual method of Boehm, consisting in pH-metric titration of acidic and basic surface groups by aqueous solutions. Differential thermogravimetric (DTG) analysis was thus preferred for identifying and quantifying their main surface groups. DTG experiments were performed in a Setaram 92-16.18 instrument under argon atmosphere. Each sample was heated from room temperature to 110 °C at 2 °C/min, and was maintained at this temperature for 1 h for removing adsorbed moisture. Then it was heated up to 1100 °C at 2 °C/min, maintained at this final temperature for 30 min, and then cooled at 20 °C/min. The DTG curve was then deconvoluted into a combination of Gaussian peaks using the PeakFit software, each peak being assigned to a specific surface group. At the outlet of the thermobalance, a mass spectrometer was used in order to observe the possible evolution of nitrogenous species, especially NH₃, NO and NO₂. The same instrument was used to quantify the thermo-desorption of CO and CO₂ from the carbon surface as a function of temperature.

The acidic/basic character of the activated carbons was estimated by pH measurement of suspensions, according to the following method. CO₂-free distilled water was first prepared by boiling it during 20 min. 0.4 g of each material and 25 mL of this

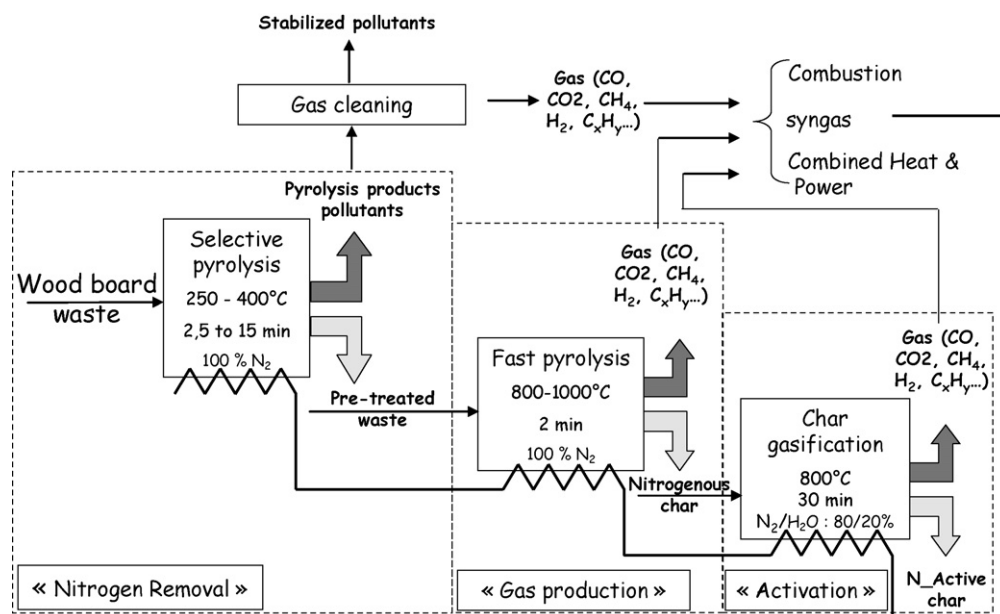


Fig. 1. Scheme of the two-steps process of thermo-chemical conversion of particleboard waste (after [22,23]).

degassed water were then placed in a sealed flask. The measurements of pH were carried out after 24 h of stirring, using a Cyberscan pH1100 (Eutech instruments) pH-meter, equipped with a high chemical-resistance electrode with temperature probe (Bioblock).

2.2.2. Pore texture

The pore texture parameters were determined from the nitrogen adsorption–desorption isotherms obtained at 77 K with an automatic instrument Sorptomatic 1990 (Thermo Finnigan), after the samples were previously outgassed at 523 K for several hours. The surface areas were measured by the BET calculation method [25] applied to the adsorption branch of the isotherms in the range of relative pressures: 0.05–0.2. The micropore volume, V_{DR} , corresponding to pores narrower than 2 nm, was calculated according to the Dubinin–Radushkevitch method [26 and refs. therein]. The total pore volume, sometimes referred to as the so-called Gurvitch volume $V_{0.99}$, was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $p/p_0 = 0.99$ [27]; the Gurvitch volume is assumed to be the sum micro + mesopore volumes. The mesopore volume, V_m , was calculated as the difference between $V_{0.99}$ and V_{DR} . The average pore size, L_0 , was calculated according to the widely accepted following equation [28 and refs. therein]:

$$L_0 = \frac{10.8 (\text{nm kJ mol}^{-1})}{E_0 - 11.4 (\text{kJ mol}^{-1})} \quad (1)$$

in which E_0 is the characteristic adsorption energy of probe molecules, see [29] and refs. therein. E_0 was derived from the nitrogen adsorption isotherms at 77 K, applying the Dubinin–Radushkevich method.

2.2.3. Phenol adsorption experiments

Phenol adsorption isotherms were obtained by introducing different quantities of activated carbon sample (between 15 and 60 mg) in separate flasks (100 mL) containing 10–40 mL of aqueous, unbuffered, phenol solution. The initial concentration of the latter was 400 mg/L, and the pH was always within the range 6–7. The flasks were hermetically closed, not only for avoiding the loss of phenol by volatilisation, but also for preventing the entry of oxygen, which is known to lead to irreversible phenol adsorption through oxidative coupling [30 and refs. therein]. The flasks were then placed in a thermostatic water bath at 25 °C, and stirred during 24 h. Such a time is indeed enough for reaching equilibrium, which is attained after approximately 5 h (see below). The suspension of activated carbon was then filtered, diluted if needed, and the residual phenol concentration was measured by UV absorption in a Shimadzu UV-1700 spectrophotometer. The latter was calibrated

at a wavelength of $\lambda_{\text{max}} = 270 \text{ nm}$ [20], using a number of aqueous solutions of phenol of known concentrations. The amount of phenol adsorbed on the activated carbon was then calculated by difference between the initial (known) and the final (measured) phenol concentrations. Each experiment was done in triplicate, with an average scattering of the results of 5%, never higher than 10%. Only average values are reported in the curves given in the next section.

In order to determine the time required for reaching the equilibrium, phenol solutions were put in contact with each studied activated carbon for different times (ranging from 0.5 to 7 h) at a constant temperature of 25 °C. For that purpose, a number of suspensions were prepared by mixing 15 mg of activated carbon with 40 mL of a solution of phenol at concentration 400 mg/L. The solutions, contained in sealed flasks, were continuously stirred during the experiments.

All the fits of isotherm equations to the experimental sorption data, and the corresponding achievement of the related adjustable parameters, were carried out using the computer program KaleidaGraph™ (Abelbeck Software). The same software also provided correlation coefficient for judging the validity of the fits.

3. Results and discussion

3.1. Characteristics of the as-prepared activated carbons

3.1.1. Proximate and ultimate analyses

The carbon yield after pyrolysis was typically 50% and again 50% after pyrolysis and after activation, respectively, so the activated carbon yield was typically 25%. The composition of the activated carbons produced from particleboard wastes is given in Table 1. These materials were named from their temperatures of first and second pyrolysis step, T_1 (°C) and T_2 (°C), respectively, and thus have the form T_1-T_2 in the following tables and figures. It can be seen that, as usual, the data of carbon content are rather scattered, but are close to 80 wt.%, whatever the heat-treatment temperature. Nitrogen is present, with the exception of one single sample, at levels ranging typically from 1.5 to 2 wt.%. Activation thus decreased the nitrogen content by typically 1 wt.%. Such an amount is lower than what can be found in N-enriched carbons; examples are given in [31,32]. However, the present materials are significantly cheaper. Consequently, even if the resultant performances in phenol adsorption are expected to be lower, such particleboard-derived activated carbons may have a great economic interest.

A few SEM pictures of WAC: 300.800 and 300.1000, are presented in Figs. 2 and 3, respectively; all the other materials derived from particleboard wastes are very similar at this observation scale. The images obtained using secondary electrons (Figs. 2(a) and 3(a)) evidence the typical morphology of biomass-derived carbons, i.e.,

Table 1
Ultimate analysis of the activated carbons investigated in the present work.

Activated carbons prepared from particleboard waste			Elemental analysis				
Temperature of the 1st pyrolysis step (°C)	Temperature of the 2nd pyrolysis step (°C)	Sample name (WAC)	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	Ashes (wt.%)
250	800	250.800	76.0	1.0	1.4	4.0	17.6
	900	250.900	82.3	1.1	1.8	3.6	11.2
	1000	250.1000	78.1	1.0	0.3	3.4	17.2
300	800	300.800	79.3	1.0	1.5	3.9	14.3
	900	300.900	75.8	1.0	1.7	4.1	17.4
	1000	300.1000	82.4	0.9	2.0	4.7	10.1
400	800	400.800	78.2	0.9	1.9	3.6	15.4
	900	400.900	83.9	1.0	1.9	3.9	9.3
	1000	400.1000	84.4	0.9	2.0	4.5	8.4
Commercial activated carbon (CAC)			93	0.8	0.5	2.8	2.9

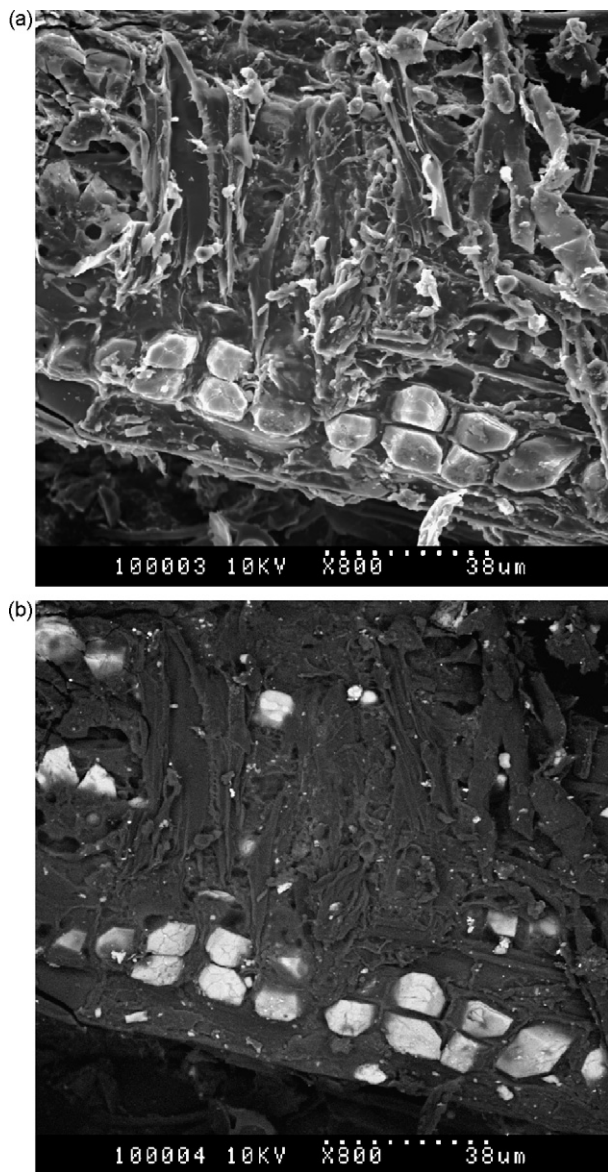


Fig. 2. SEM pictures of one wood particleboard waste activated carbon (WAC): sample 300.800, at a magnification of 800 \times , as seen by (a) secondary and (b) backscattered electrons.

the cellular structure of the original wood is maintained. It can be seen however that, in some grains, a number of pores are totally filled, probably due to the former presence of glue. The same images obtained from backscattered electrons (Figs. 2(b) and 3(b)) reveal the presence of mineral elements heavier than carbon. Thus, ashes are seen as bright zones unevenly distributed on the carbon grains. Such ashes clearly correspond to the aforementioned filled pores, but big blocks are also present all through the material, suggesting that the WAC are highly inhomogeneous materials. EDX spectra of ashes (not shown) evidenced that Ca, C and O are the main elements, followed by K, Na, Si, P and S in decreasing order of abundance. Especially, local EDX analysis revealed that calcium carbonate is the major compound filling the macroscopic pores of the grains. Elemental mapping was carried out using again the EDX instrument of the microscope (not shown); Na, K, Mg and Mn are very homogeneously distributed all over the material, whereas O, P and S are also well dispersed but more concentrated in some smaller areas. By contrast, Ca, Si, Al, Ti and Fe are strongly localised, forming compact clusters. Comparing the position of the latter in each picture

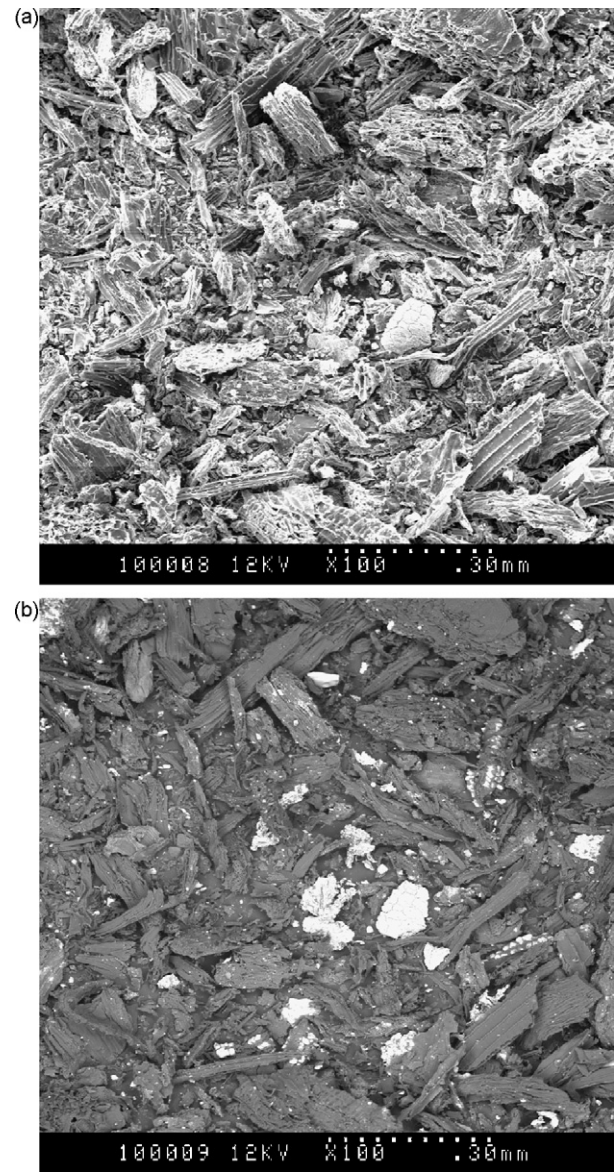


Fig. 3. SEM pictures of one wood particleboard waste activated carbon (WAC): sample 300.1000, at a magnification of 100 \times , as seen by (a) secondary and (b) backscattered electrons.

allows deducing that Ti and Al are associated with each other but also with O (suggesting the presence of titania and alumina and mixed oxides), and that P and Al are found together with O, Si and P (suggesting aluminophosphates, aluminosilicates and mixed salts). Iron is associated with Si and Mn, suggesting metallic impurities. Finally, C and N are found to occur simultaneously all through the material, except where ashes are present.

All the series of activated carbons derived from particleboard wastes present the same qualitative XRD patterns, so only one is presented in Fig. 4 (sample 250.900). The typical diffusion background of disordered carbon can be observed for both WAC and CAC (shown for comparison) materials, whereas narrow, well-marked, diffraction peaks are seen for WAC only. No crystallised compound could be detected by XRD in the commercial activated carbon. As expected, the presence of CaCO_3 was confirmed in the WAC; other compounds like quartz, calcium sulphate, titania, aluminium silicate and potassium carbonate were also clearly evidenced. Only one other diffraction peak could not be ascribed to any simple compound, maybe because complex mixed polymetallic salts of the aforementioned elements are present.

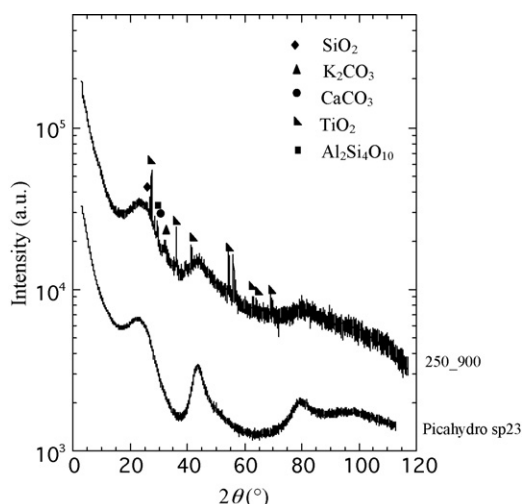


Fig. 4. XRD patterns of CAC (Picahydro sp 23) and one WAC (sample 250_900). The main crystallised compounds detected as impurities in the WAC are given in the figure.

3.1.2. Surface area and porosity

Table 2 presents the textural properties (BET surface area, Gurvitsch, micropore and mesopore volumes, and average pore size) of the materials derived from particleboards pyrolysed at various temperatures and steam-activated at 800 °C. The surface area typically ranges from 700 to 1400 m²/g, i.e., may be compared with that of the commercial activated carbon, close to 1100 m²/g. All the as-prepared activated carbons are mainly microporous, since the micropore fraction (calculated as the ratio $V_{DR}/V_{0.99}$) is most of times higher than 70%. Moreover, the average pore size is clearly below 2 nm, thus corroborating the microporous character of these materials. Near half of the WAC samples have surface area, total and micropore volumes which are lower than those of the CAC, whereas the other half has higher textural parameters. Therefore, the Picahydro sp 23 is a good choice for comparing its properties with those of the WAC presented in this work.

It can also be deduced from Table 2 that, whatever the materials, a higher final temperature of pyrolysis always leads to lower micropore volume and surface area. Indeed, when the temperature is increased, two antagonistic effects are expected: fast and efficient pore formation due to pyrolysis-induced gas evolution, and pore closure and pore collapse due to the structural reorganization of the carbonaceous matter at higher temperature (see [33], for example). 800–900 °C thus seem to be a good optimum for subsequent steam activation of particleboard waste chars at 800 °C. An influence of the first pyrolysis temperature may finally be seen in Table 2. A maximum of pore texture parameters (sample 300.800) may be seen for the same reasons discussed above: competition between pore opening due to thermal decomposition and thermally induced densification.

Table 2

Pore texture of activated carbons prepared from particleboard waste, and comparison with commercial AC.

Activated carbon	S_{BET} (m ² g ⁻¹)	$V_{0.99}$ (cm ³ g ⁻¹)	V_{DR} (cm ³ g ⁻¹)	V_m (cm ³ g ⁻¹)	L_0 (nm)	
WAC	250.800	832	0.462	0.314	0.148	0.664
	250.900	780	0.421	0.295	0.126	0.679
	250.1000	713	0.375	0.265	0.110	0.682
	300.800	1367	0.735	0.530	0.205	0.768
	300.900	1090	0.553	0.421	0.132	0.768
	300.1000	930	0.474	0.357	0.117	0.764
	400.800	1248	0.522	0.486	0.036	0.762
	400.900	1242	0.630	0.475	0.155	0.706
	400.1000	1083	0.530	0.416	0.114	0.764
	CAC	1114	0.482	0.415	0.067	0.774

3.1.3. Surface chemistry

As far as liquid adsorption on solids is concerned, surface chemistry is known to be at least as important as the pore texture; the role of surface functionalities indeed increases significantly relative to the pore size distribution or BET surface area, and in many cases dominates [5]. The acid–base properties may have two separate origins: chemical composition of ashes and surface functions (moieties). The former effect was partly studied in Section 3.1.1, however oxides and salts having an acidic (e.g., silica and silicates, titania) or a basic character (e.g., alkaline and alkaline-earth compounds) are mixed together in proportions that are not accurately known. Additionally, ashes are mainly in the form of compact clusters, i.e., present a rather low surface area. Finally, their solubility in water is expected to influence the acid–base properties of the activated carbon. Generally, since the basic oxides and salts are the most soluble (with comparison to titania or silica), activated carbons soaked into water give it a basic pH. Given the amount of ashes present in WAC, as high as 17 wt.% in some cases (see Table 1), a basic nature would be a priori expected.

Table 3 presents the pH of suspensions of some activated carbons after 24 h of stirring in very pure water. Surprisingly, WAC are the most acidic materials, whereas the CAC, containing the lowest amount of mineral matter, is the most basic one. Such a result suggests that acid–base properties are not controlled by ashes but by surface functions. The latter were quantified by thermodesorption at high temperatures, and the corresponding TG and DTG analyses are presented in Fig. 5. WAC possess much more moieties than CAC, since typical weight losses of 10 and 3 wt.%, respectively, are measured at 1100 °C. Since most surface functions of carbonaceous solids are oxygenated, acid ones, their relative amounts fully justify the values of the pH of suspensions.

When heated under inert atmosphere, such surface functions evolve mainly as CO and CO₂ gases, in agreement with the results given in Fig. 6 obtained from the mass spectrometer; none nitrogenous species could be detected. The DTG data of Fig. 5(b) are indeed the sum of the two MS spectra for CO and CO₂. From the latter spectra, the surface concentrations of CO and CO₂ groups formerly bound to the carbon surface could be calculated, and are given in Table 3; these values are close to those reported elsewhere for various activated carbons [34]. It can be seen that the total amount of moieties is correlated to the pH of the suspensions, thus corroborating the above finding according to which the acid–base character of the active carbons is mainly controlled by their surface functions.

The surface groups can be identified from the occurrence of CO and CO₂ during heat-treatment. The main moieties present on activated carbon surface and their corresponding range of decomposition temperature were discussed in [35]. Although these data are generally widely accepted, they are still discussed in the literature and can be strongly affected by the carbon texture and the heating rate [36]. They are, however, useful for identifying the main oxygenated functional groups. The first two CO₂ evolutions seen in Fig. 6(a), centred on ca 200–300 and 550 °C, and to which

Table 3
Surface chemistry of CAC and selected WAC: pH of 0.4 g of activated carbon let in 25 mL of degassed water during 24 h, and proportion and nature of functional groups derived from DTG–MS analysis.

Activated carbon	pH of suspensions in pure water	Surface concentration of CO and CO ₂ groups		
		CO (molecules/nm ²)	CO ₂ (molecules/nm ²)	Total (molecules/nm ²)
WAC	250_900	0.858	0.631	1.49
	300_900	0.708	0.559	1.27
	400_800	0.464	0.466	0.93
	400_900	0.475	0.530	1.01
CAC	9.40	0.092	0.225	0.32

no simultaneous CO evolution is observed in Fig. 6(b), correspond to carboxyls and lactones, respectively. The final CO₂ loss, around 700–750 °C, should correspond to lactones. No anhydride is present, since no simultaneous evolution of CO and CO₂ is observed near 600 °C. Similarly, neither phenol nor ether is present. The losses of CO only occur at higher temperatures, corresponding to carbonyls followed by quinones. Consequently, all the thermally desorbed surface functions are acid, and were certainly produced by steam activation of WAC. The latter were supposed *a priori* to present good phenol adsorption properties, due to the expected basicity of the nitrogenous moieties. The latter are thus probably ineffective for trapping dissolved phenols, as suggested by the next section, given the high amounts of acidic species at the carbon surface.

3.2. Phenol adsorption

3.2.1. Adsorption isotherms

The adsorption isotherms measured at 25 °C in the conditions detailed in Section 2.2.3, are presented in Figs. 7 and 8 for the commercial (CAC) and the particleboard WAC, respectively. In these

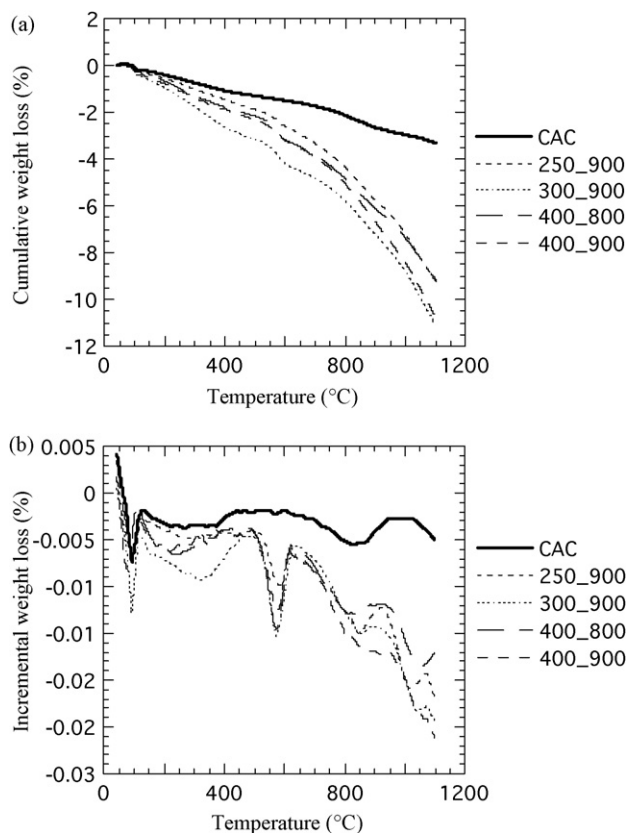


Fig. 5. (a) TG and (b) corresponding DTG analysis of some wood particleboard waste activated carbon (WAC) samples and commercial one (CAC) for comparison.

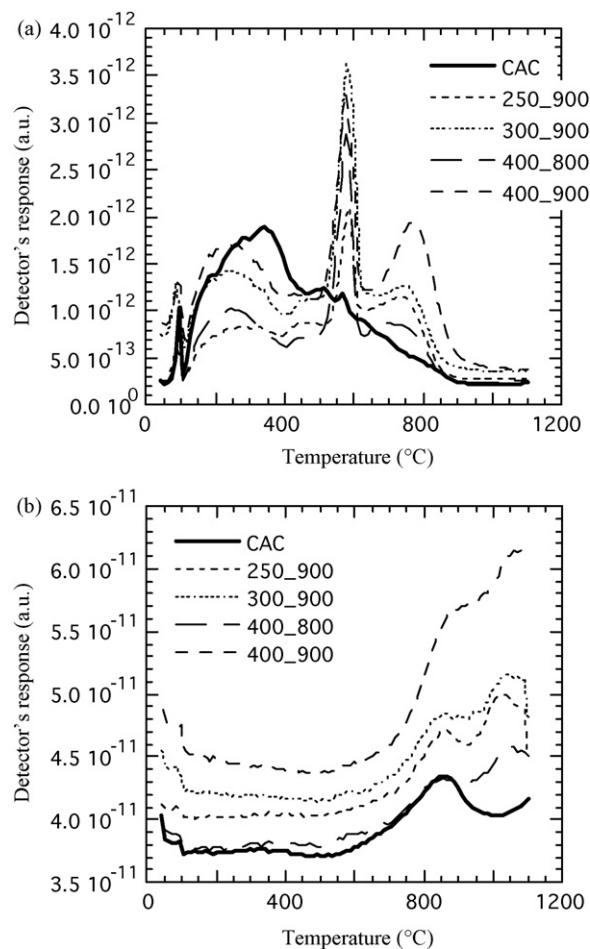


Fig. 6. Thermodesorption of (a) CO₂ and (b) CO from the activated carbon surfaces, as measured by the mass spectrometer during the TG analyses given in Fig. 5.

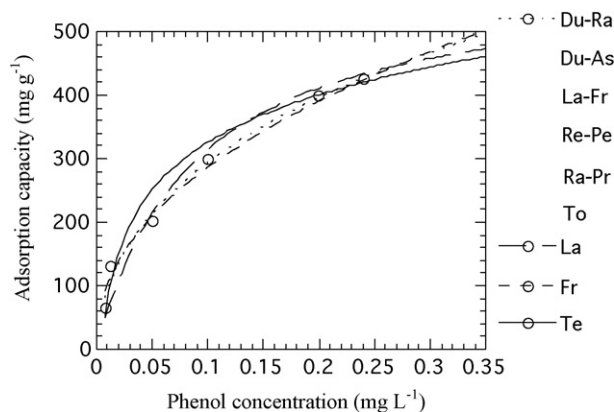


Fig. 7. Phenol uptakes at 298 K of the commercial activated carbon (CAC). The curves were calculated by application of the various models listed in Table 4.

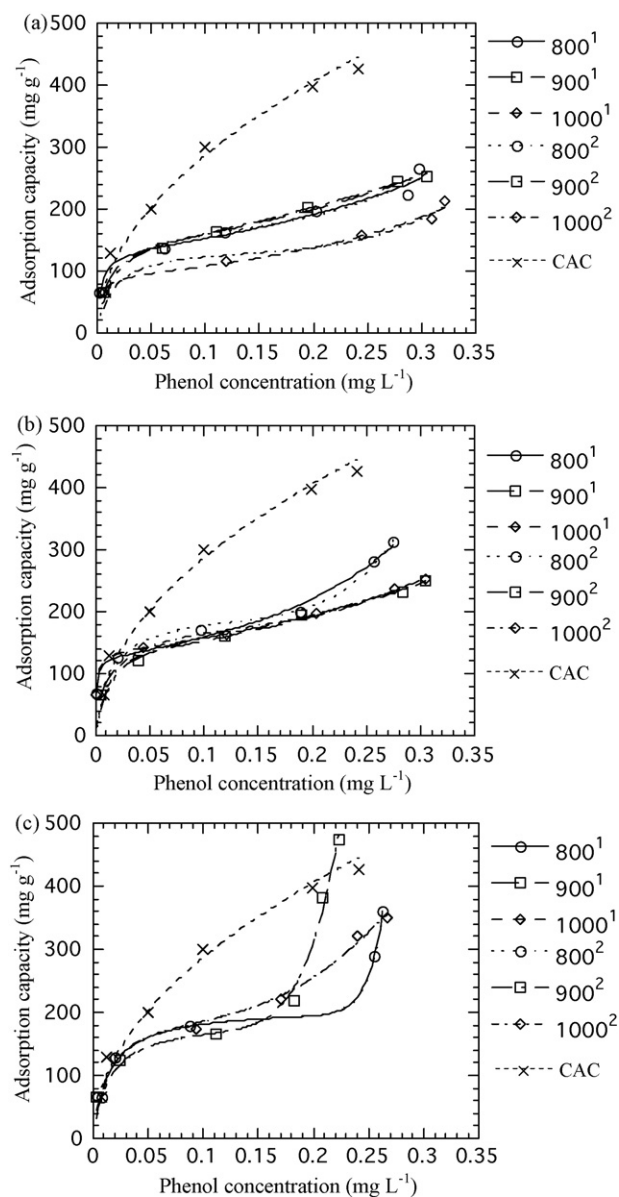


Fig. 8. Phenol uptakes at 298 K for the 3 series of prepared activated carbons, classified according to their temperature of first pyrolysis: (a) 250 °C, (b) 300 °C, and (c) 400 °C. The temperature of the second pyrolysis is given on the plots, and all the isotherms are compared with that of the commercial activated carbon (CAC). The curves of WAC were calculated by application of two of the three models listed in Table 5; the superscripts 1 and 2 mean BET and Zhu–Gu equation, respectively.

figures, the adsorbed phenol amounts per gram of sorbent at equilibrium, q_e (mg/g), are plotted as a function of the equilibrium phenol concentration in the liquid phase, C_e (mg/L). For the sake of clarity, the three series of WAC presented in Tables 2 and 3 are plotted separately in Fig. 8, and the adsorption isotherm of CAC is always given for comparison.

3.2.1.1. Commercial activated carbon. Looking at Fig. 7 first, no asymptotic evolution of the phenol uptake as a function of equilibrium concentration can be seen for CAC. Consequently Langmuir's equation, while widely used for describing phenol adsorption on activated carbons, is not expected to be the best model in the present case. Moreover, it is valid for adsorption on homogeneous surfaces only. For activated carbons presenting a high surface heterogeneity, both geometrical (e.g., different pore sizes and shapes) and chemical (e.g., functional groups, impu-

rities), the most popular Freundlich isotherm should better fit the experimental data. However, any equation presents limitations, so it was decided to test and compare a number of models, including the two aforementioned ones. The additional examined models are Dubinin–Radushkevitch, Dubinin–Astakov, combined Langmuir–Freundlich, Temkin, Redlich–Peterson, Radke–Prausnitz, and Toth equations. Their expression and resultant parameters after application to the experimental adsorption data of Fig. 7 are given in Table 4. The meaning of these different equations, often used for modelling adsorption in the liquid phase, as well as their original bibliographic references, may be found in [37].

Table 4 shows that most of the isotherm equations fit the experimental points very well, since all the correlation coefficients (R^2) are above 0.98. Furthermore, most of the calculated curves given in Fig. 7 cannot be separated from each other. Only Temkin, Langmuir, and to a lesser extent Freundlich, equations do not match the data so satisfactorily.

Dubinin–Radushkevitch and Dubinin–Astakov equations were fitted to the experimental sorption data, always taking fixed the saturation concentration of phenol in water at $C_S = 83$ g/L, which is the maximum solubility of phenol at 298 K. Doing so, energies of phenol adsorption on the surface of CAC of 19 and 30 kJ/mol were obtained, respectively, in agreement with the results published in [38,39]. Langmuir and Langmuir–Freundlich equation give monolayer capacities of 593 and 771 mg/g; taking 41.2 \AA^2 for the molecular area of phenol [40], surface areas of 1565 and 2035 m^2/g , respectively, may be estimated. The first value is closer than what was measured by nitrogen adsorption: 1115 m^2/g , despite the fact that Langmuir–Freundlich equation leads to a better correlation coefficient. However, the latter model has 3 parameters instead of 2 for pure Langmuir, so getting a better fit is also obvious. An alternative calculation suggested in [41] consists in deriving the adsorbed amount at monolayer coverage from the following relationship:

$$q_m (\mu\text{mol}/\text{m}^2) = \frac{10^{26}}{\sigma N_A} \quad (2)$$

where q_m and σ (\AA^2) have the same meaning as above, and N_A is the Avogadro number. Taking again $\sigma = 41.2 \text{ \AA}^2$, one obtains $4.03 \mu\text{mol}/\text{m}^2$, i.e., 422 mg/g since the specific surface area of CAC is 1114 m^2/g . Such calculated value of q_m indeed has the same order of magnitude as the values derived from the fits, especially from that to Langmuir's equation.

Langmuir constant K_L is in good agreement with other reported values close to 8 L/mmol [37,42]. K_F is the so-called Freundlich coefficient ($(\text{mg/g})/(\text{mg/L})^n$), related to the degree of adsorption; the higher its value, the higher adsorbate–adsorbent affinity. A value close to 805 is higher than what was obtained with phenol adsorbing on other commercial materials of rather similar surface area [17] and on activated carbons derived from vetiver roots [43]. However, it compares very well with values found for adsorption of several dyes on activated charcoal [44]. n is an empirical (dimensionless) parameter representing the energetic heterogeneity of the adsorption sites. Adsorption is usually considered as satisfactory when the Freundlich constant n takes values within the range 1–10 [17], which is the case here. The parameter n is found to be close to 2, i.e., is in the range of what was reported for phenol adsorption on commercial carbons and carbons derived from carbonised bark [37,45]. In Langmuir–Freundlich equation, K_{LF} is the equilibrium constant for a heterogeneous solid, and m is the heterogeneity parameter ($0 < m < 1$). In the case of CAC, the value of m was found to be 0.73. Usually, the higher is the surface area, the lower is m , corresponding to a higher surface heterogeneity; the present value of m is close to the one obtained with bituminous coals of much lower surface area [46]. The other tested equations: Redlich–Peterson, Radke–Prausnitz and Toth, all model very well

Table 4
Isotherm parameters obtained from the fit of various equations to the adsorption data of CAC presented in Fig. 7.

CAC				
Isotherm equation		Parameters		R ²
Dubinin–Radushkevich	$q_e = q_{max} \exp \left\{ - \left[\frac{RT \ln(C_s/C_e)}{E} \right]^2 \right\}$	q_{max} (mg/g) 6113.1	E (kJ/mol) 19.36	0.9968
Dubinin–Astakov	$q_e = q_{max} \exp \left\{ - \left[\frac{RT \ln(C_s/C_e)}{E} \right]^4 \right\}$	q_{max} (mg/g) 1332.1	E (kJ/mol) 30.61	0.9958
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_m (mg/g) 592.97	K_L (L/mg) 11.32	0.9861
Freundlich	$q_e = K_F C_e^{1/n}$	$K_F [(mg/g)/(mg/L)^{1/n}]$ 805.86	$1/n$ 0.45	0.9958
Langmuir–Freundlich	$q_e = q_m \frac{(K_{LF} C_e)^m}{1 + (K_{LF} C_e)^m}$	q_m (mg/g) 771.31	K_{LF} (L/mg) 5.65	m 0.73 0.9948
Temkin	$q_e = B_1 + K_T \ln C_e$	K_T (mg/g) 108.07	B_1 (mg/g) 574.74	0.9833
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	K_R (L/g) 26.53	a_R (L/mg) 34.48	β 0.63 0.9969
Radke–Prausnitz	$q_e = \frac{1}{(1/K_{RP} C_e) + (1/k_{RP} C_e^{1/p})}$	K_{RP} (L/g) 26.53	$k_{RP} [(mg/g)/(mg/L)^{1/p}]$ 769.56	p 2.73 0.9969
Toth	$q_e = \frac{q_e^\infty C_e}{[K_{Th} + C_e^{Th}]^{1/Th}}$	q_e^∞ (mg/g) 5770.24	$K_{Th} [(mg/L)^{Th}]$ 0.51	Th 0.20 0.9969

the phenol adsorption behaviour of CAC, and the corresponding parameters are typical of what is usually found with ordinary activated carbons (see [40] for details).

3.2.1.2. Waste particleboard activated carbon (WAC). It can be seen from Fig. 8 that the adsorption behaviour of WAC on one hand and CAC on the other hand, is very different. Adsorption isotherms of the former are clearly of type II, according to Brunauer’s classification [47], whereas that of the latter is of type I. Another popular classification is that of Gilles et al. [48,49], according to which the isotherms presented in Fig. 8 all belong to the Langmuir class (L), that of CAC corresponding to type L1, whereas those of WAC are of type L3. Since the parameters describing the porosity of all the materials are rather similar (see again Table 3), such differences in the isotherm shape can thus be ascribed to surface chemistry, depending both on the chemical composition and on the surface functional groups.

Adsorption isotherms of WAC samples all show an upward curvature in the range of higher equilibrium phenol concentration. Such a shape was already observed in phenol adsorption on some activated carbons [39] and macroreticular resins [50], however at different ranges of concentrations. Type II isotherms in solution were justified by multilayer or aggregate formation at the inter-

face at higher coverage [51]. Physical, multilayer, adsorption may be described by application of BET equation [25], which was found already to be suitable for phenol adsorption [52,53]. Surface aggregate formation was modelled by Zhu and Gu [54] on the basis of two coincident processes, the first one involving the adsorption of molecules on the surface, the second one involving interaction between adsorbed molecules. Finally, a modified form of the BET equation describing the adsorption of a finite number of layers (whereas the original BET deals with an infinite number of layers), has been suggested (see [50] and refs. therein); it reduces to BET and Langmuir equations when the number of adsorbed layers tends to infinity and to 1, respectively. The 3 aforementioned equations are given in Table 5, as well as their corresponding parameters; all fit the experimental data very well, as it can be observed in Fig. 8. It can be seen from the values of R² listed in Table 5 that the best fits are never obtained by application of one particular equation among the 3 ones, but are all statistically equivalent.

In these formulas, the parameters have the following meaning. q_m is again the amount adsorbed in a complete monolayer, K_{BET} and K_{MBET} are the equilibrium (adimensional) constants related to adsorption energy, C_0 is the saturation concentration of the solute in water, q_∞ is the limiting amount adsorbed at high concentration, r is the aggregation number, and K_1 and K_2 are equilibrium con-

Table 5
Isotherm parameters obtained from the fit of various equations to the adsorption data of WAC presented in Fig. 8.

Isotherm equation		WAC								
Name	Parameters	250.800	250.900	250.1000	300.800	300.900	300.1000	400.800	400.900	400.1000
BET	q_m (mg/g)	131.8	145.1	91.5	125.8	136.9	134.6	162.0	87.9	143.1
	C_0 (mg/L)	0.629	0.681	0.583	0.464	0.665	0.645	0.506	0.273	0.443
	K_{BET}	205.4	87.7	241.3	527.5	108.7	618.2	48.9	350.4	99.2
	R ²	0.9869	0.9976	0.9922	0.9958	0.9968	0.9996	0.9803	0.9861	0.9976
Zhu–Gu	q_∞ (mg/g)	446.1	421.5	388.8	752.7	675.6	681.8	713.3	707.7	681.4
	K_1 (g/mg)	52,587	36,790	57,738	94,570	39,076	54,045	283,940	119,490	65,977
	K_2 (g/mg)	9.03	4.32	37.21	250.24	4.40	7.56	7.24×10^9	8.07×10^4	37.03
	r	4.37	3.17	6.11	6.94	3.38	4.32	20.33	9.45	4.73
	R ²	0.9581	0.9935	0.9633	0.9634	0.9334	0.9880	0.9979	0.9913	0.9927
Modified BET	q_m (mg/g)	131.7	127.1	99.2	129.2	119.4	133.1	150.4	99.7	148.5
	C_0 (mg/L)	0.632	0.424	0.703	0.435	0.411	0.618	0.487	0.269	0.459
	K_{MBET}	206.9	72.8	225.1	486.1	94.2	607.2	58.7	170.0	61.8
	s	93480	3.74	224.3	3711	3.81	6.60	99736	2.7×10^{11}	1.83×10^6
	R ²	0.9869	0.9997	0.9611	0.9556	0.9988	0.9998	0.9780	0.9071	0.9943

BET equation: $q_e = \frac{q_m K_{BET} C_e / C_0}{(1 - C_e / C_0) [1 + (K_{BET} - 1) C_e / C_0]}$

[–10pt] Zhu–Gu equation: $q_e = q_\infty \frac{K_1 C_e (1/r + K_2 C_e^{r-1})}{1 + K_1 C_e (1 + K_2 C_e^{r-1})}$

[–10pt] Modified BET equation: $q_e = \frac{q_m K_{MBET} C_e / C_0 [1 - (s+1)(C_e / C_0)^s + s(C_e / C_0)^{s+1}]}{(1 - C_e / C_0) [1 + (K_{MBET} - 1) C_e / C_0 - K_{MBET} (C_e / C_0)^{s+1}]}$

stants for the adsorption and lateral interactions between adsorbed molecules, respectively, and finally s is the number of layers. Both BET and modified BET equations lead to very similar parameters: monolayer capacity, BET constants and saturation concentration. Obviously, the materials presenting the highest phenol adsorption performances, 400.800 and 400.900, is the one having the highest values of both aggregation (r) and layer (s) numbers. While r typically ranges from 3 to 7 for most of samples, in agreement with what was obtained for surfactants on steel surfaces [51], aggregation numbers as high as 20 and 9 were found for 400.800 and 400.900, respectively. Extremely high values of s are seen for some materials, justifying the fact that modified (finite s) and original ($s \rightarrow \infty$) BET equations are nearly the same, whereas r and s values are somewhat similar to each other for other activated carbons (250.900, 300.900, 300.1000). It is not clear why the latter materials lead to nearly identical aggregation and layer numbers, but it should be noted that BET and Zhu–Gu models were built on very different hypotheses. The series 250. T_2 and 300. T_2 , and the sample 400.1000, give values of K_1 which are systematically much higher than those of K_2 . This finding is in agreement with the low curvature at higher coverage observed in the corresponding isotherms: the adsorbate is strongly attached to the surface, and weak lateral interactions lead to only slightly higher adsorbed amounts at higher concentrations. The samples 400.800 and 400.900, being the most efficient adsorbents, present much higher values of K_2 , indicating much stronger lateral interaction, and correspondingly have higher aggregation number r at the highest coverage.

As seen in Table 5, the monolayer adsorption capacities q_m derived from application of the BET model (modified or not) were found to range from 90 to 160 mg/g, i.e., from 0.9 to 1.7 mmol/g. These values compare very well with what was found for macroreticular resins [50] and for activated carbons made from polymers [42]. Additional calculations can be drawn: if the molecular area of phenol is $\sigma = 41.2 \text{ \AA}^2$ [40], the surface area can be deduced from the monolayer capacity. Given the aforementioned values of q_m for the WAC, surface areas ranging from 223 to 421 m²/g are calculated. These values are well below what was measured from nitrogen adsorption at 77 K, suggesting the unavailability of phenol to narrow pores. Maybe in this case the high number of oxygenated functions induces a high affinity for water (the so-called solvent effect), so adsorbed solvent molecules can effectively block some micropores [55], see below.

3.2.2. Discussion of adsorption performances

The highest adsorption capacity achieved by the WAC within the investigated experimental conditions is close to 0.5 g of adsorbed phenol per g of activated carbon. Such a value is very satisfactory in comparison with the results given in [4], for example, for which adsorption capacities within the range of 0.1–0.3 g/g were obtained with nitrogen-doped activated carbons. WAC thus seem to be rel-

evant to the treatment of industrial aqueous effluents, even if a slightly lower efficiency than that of CAC for phenol removal was observed in the range of lower concentration. Higher capacities for phenol were indeed suggested to occur because of larger mean pore size [56]. The latter, calculated by Eq. (1) and given in Table 2, is indeed slightly higher for the CAC, possibly explaining its higher performances at low and medium concentration ranges. However, given the extremely low cost of WAC, it should not be a problem to use it in somewhat higher amounts than what is required with a more expensive CAC. Fig. 8 clearly shows that, even if CAC is a better adsorbent for phenol in the diluted solution, WAC become increasingly more efficient at higher concentration. In addition, the carbon regeneration should be easier than for the commercial materials because the amount adsorbed at low concentration is smaller.

Extrapolating the adsorption isotherms of WAC through the use of the KaleidaGraphTM software, it is easy to calculate the critical equilibrium concentration at which the phenol uptake of WAC becomes higher than that of CAC. The results are given in Table 6. The series 400. T_2 is that for which the phenol adsorption performances are systematically higher than those of CAC as soon as the equilibrium concentration exceeds 0.35 mg/L, and even 0.23 mg/L for the 400.900 sample. Consequently, activated carbons derived from particleboard wastes are not only cheap adsorbents, but may be in some case better than commercial materials designed for the same applications, and especially for phenol removal from high phenol concentration streams.

If the phenol uptakes at an equilibrium concentration of 0.3 mg/L are now considered, see again Table 6, it can be seen that WAC adsorbents have higher performances in the order 400. T_2 > 300. T_2 > 250. T_2 . No clear correlation can be drawn between the phenol uptakes and the temperature of second pyrolysis. And indeed the maximum measured phenol uptakes do not correlate neither with the surface area, nor with the pore texture, whatever the kind of porosity (micro, meso, or total, average pore width) considered. Such a result, already observed elsewhere [39,43], suggests that chemical interactions are involved in the phenol adsorption mechanism. In particular, it is known that the most basic carbon surfaces present higher affinity for phenol [57,58].

According to Jankowska et al. [59], “phenol adsorption is limited by the micropore volume of the carbons, and the actual position beneath this limit is determined by their acid–basic characteristics”. It was stated from Table 2 that the various pore volumes are indeed different, but cannot explain the different adsorption behaviour since no correlation is found between pore texture and phenol uptake. Moreover, the pore-size distributions, calculated either by Horvath–Kawazoe (for micropores) or BJH (for mesopores) method (not shown), are rather similar and hence are not able to explain the different phenol adsorption performances. Additionally, the adsorbed amounts do not show any dependence neither on the total ash content, nor on the elementary composition. Acid/base

Table 6

Adsorption performances of activated carbons at an equilibrium phenol concentration of 0.3 mg/L, and critical phenol concentration at which the adsorption performances of WAC become higher than those of CAC.

Activated carbon sample	Phenol uptake (mg/g) at an equilibrium phenol concentration of 0.3 mg/L	Concentration at which adsorption of WAC exceeds that of CAC (mg/L)
WAC	250.800	0.468 ^a
	250.900	0.496 ^a
	250.1000	0.481 ^a
	300.800	0.348 ^a
	300.900	0.492 ^a
	300.1000	0.472 ^a
	400.800	0.359 ^a
	400.900	0.227
	400.1000	0.323 ^a
	CAC	463.6

^a Extrapolated values.

properties should thus be considered now. According to Terzyk, “the composition of the carbon surface determines the mechanism of phenol adsorption. Carboxyls, i.e., the most acidic, and some of the most basic groups, play the most important role in phenol adsorption at small concentrations, decreasing the phenol adsorption” [39]. The acidic/basic character of an activated carbon depends on delocalized electrons and on surface functionalities, the latter being based on surface-bound hetero atoms, especially oxygen but also nitrogen, sulphur, etc. Acidic properties originate from oxygen moieties such as carboxyls, lactones, carbonyls and phenols. Basic properties are due to other oxygenated groups, especially pyrones, chromenes and ethers, nitrogen-containing moieties, and graphene layers behaving as Lewis base due to their available π electrons for forming donor–acceptor complexes with protonated molecules [32,58].

The following possible interactions between phenol and carbon surface have been proposed [42,60 and refs. therein]:

- Formation of surface complexes through electron donor–acceptor interaction. Thus, carbonyls were suggested to enhance phenol adsorption through a mechanism involving donor–acceptor complexes (carbonyl groups as electron donors and aromatic rings of phenol as acceptors) [5].
- Dispersion interaction between π electrons of the phenolic ring of the adsorbate and π electrons of the graphitic structure.
- Electrostatic interaction in the presence of ions. Phenol being a very weak acid ($pK_a = 9.95$), it is not expected to be dissociated at neutral pH, so this kind of interaction should not exist in the present case.
- Solvent effect. It occurs when some of the most active sites adsorbing phenols are blocked by water adsorption [39]. In other words, some pores may be inaccessible to phenol–water aggregates. For example, carboxyl and hydroxyl groups inhibit the adsorption of phenol and increase the affinity of carbon towards water, and therefore, solvent molecules can block some pores [5].

The change of isotherm shape from CAC to WAC is symptomatic of a change of phenol adsorption mechanism. While ordinary adsorption of a heterogeneous surface is seen for CAC, three distinct stages can be seen on the WAC isotherms. Following what Terzyk suggested in [39], phenol adsorption is low in the range of infinite dilution, due to the influence of carboxylic groups (very acid) and bases (here in the form of already protonated nitrogenous moieties) which hinder phenol adsorption. Since such moieties are more numerous in WAC than in CAC, the corresponding phenol uptake is lower at very low concentration. Because of the adsorbed protons, the carbon surface is positively charged, and the micropores are highly hydrophilic; water adsorption is thus favoured. Such a solvent effect limits the phenol uptake all along the pseudo-plateau of the isotherm, at which micropore filling occurs through π – π interaction and complexation by carbonyls and bases. Micropore filling depends on the pore texture, so the latter electron donor–acceptor interaction only occurs in larger micropores. Finally, at higher concentration, adsorption occurs in the widest pores bearing active sites, i.e., surface functions interacting with phenol in solution. The amount of moieties being much higher in WAC, the adsorption isotherms exhibit an upward curvature at concentrations above ca 0.2 mg/L; WAC thus become more efficient phenol adsorbents than CAC in concentrated solution.

4. Conclusion

In the present work, really encouraging results for the production and application of activated carbons derived from wood particleboard waste were obtained. Indeed, carbonaceous adsor-

bents having specific surface areas within the range 800–1300 m²/g were prepared by pyrolysis and steam activation, which showed adsorption capacities of phenol as high as 0.5 g/g. Such characteristics and features are, though slightly lower in the range of low concentration, close to those presented by a commercial material specially designed for the treatment of water. Taking into account that the investigated CAC is sold at €2000/t, whereas the wood particleboard waste could have a negative cost (typically –€70/t), the potential high economic interest of producing activated carbons from a two-steps thermo-chemical conversion process of particleboard wastes was clearly demonstrated here. Furthermore, high phenol adsorption capacities are obtained above typically 300–500 ppm, making WAC be more efficient phenol adsorbents than CAC in the range of high concentrations.

This work needs to be pursued in order to determine the influence of the parameters of the thermal process on the specific surface area, the pore texture and the adsorption properties of the resultant activated carbons. Especially, the role of the nitrogen content still requires to be investigated in detail. Moreover, activation conditions were not optimized here. Another interesting prospect deals with ammoxidation, which is a classical way of enriching a material with nitrogen. During the first step of our thermal process, high amounts of ammonia and steam are both produced, so a direct use of such a mixture of gases is indeed attractive. Activated carbons with a higher content of nitrogen-based surface functions, and hence possibly higher phenol adsorption properties, than the ones prepared in the present work, could be easily obtained. The corresponding experiments will be carried out in the near future.

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References

- F. Cermola, M. Dellagrecia, R. Iesce, S. Montella, A. Pollio, F. Temussi, A mild photochemical approach to the degradation of phenols from olive oil mill wastewater, *Chemosphere* 55 (2004) 1035–1041.
- S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabinidoo, V. Murugesan, Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon, *Waste Management* 22 (2002) 543–548.
- Décret n° 89-3 du 3 janvier 1989 relatif aux eaux destinées à la consommation humaine à l'exclusion des eaux minérales naturelles Annexe I-1, JO du 4 janvier 1989, <http://aida.ineris.fr/textes/decrets/text2006.htm>.
- H. Polat, M. Molva, M. Polat, Capacity and mechanism of phenol adsorption on lignite, *International Journal of Mineral Processing* 79 (2006) 264–273.
- A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, *Chemosphere* 58 (2005) 1049–1070.
- Z. Tong, Z. Qingxiang, H. Hui, L. Qin, Z. Yi, Q. Min, Kinetic study on the removal of toxic phenol and chlorophenol from waste water by horseradish peroxidase, *Chemosphere* 37 (1998) 1571–1577.
- B. Özkaya, Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models, *Journal of Hazardous Materials* B129 (2006) 158–163.
- Freedonia Group Inc. Reports, World Activated Carbon, May 2008.
- F.A. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, Adsorption of phenol by bentonite, *Environmental Pollution* 107 (2000) 391–398.
- T. Viraraghavan, F. Maria Alfaro, Adsorption of phenol from wastewater by peat, fly ash and bentonite, *Journal of Hazardous Materials* 57 (1998) 59–70.
- N. Roostaei, F.H. Tezel, Removal of phenol from aqueous solutions by adsorption, *Journal of Environmental Management* 70 (2004) 157–164.
- Y.H. Shen, Phenol sorption by organoclays having different charge characteristics, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 232 (2004) 143–149.
- J.Q. Jiang, C. Cooper, S. Ouki, Comparison of modified montmorillonite adsorbents. Part I. Preparation, characterization and phenol adsorption, *Chemosphere* 47 (2002) 711–716.

- [14] A.Y. Dursun, C.S. Kalayci, Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin, *Journal of Hazardous Materials* 123 (2005) 151–157.
- [15] K. Benrachedi, Study of phenol adsorption on waste coffee-drink transformed on activated carbon., *L'eau, l'industrie, les nuisances* 219 (1999) 54–56.
- [16] C.O. Ania, J.B. Parra, J.J. Pis, Effect of texture and surface chemistry on adsorptive capacities of activated carbons for phenolic compounds removal, *Fuel Processing Technology* 77–78 (2002) 337–343.
- [17] V. Fierro, V. Torné-Fernández, D. Montané, A. Celzard, Adsorption of phenol onto activated carbons having different textural and surface properties, *Microporous and Mesoporous Materials* 111 (2008) 276–284.
- [18] M. Franz, H.A. Arafat, N.G. Pinto, Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon, *Carbon* 38 (2000) 1807–1819.
- [19] K. Li, L. Ling, C. Lu, W. Qiao, Z. Liu, L. Liu, I. Mochida, Catalytic removal SO₂ over ammonia-activated carbon fibers, *Carbon* 39 (2001) 1803–1808.
- [20] J. Bimer, P.D. Salbut, S. Berlozecki, J.P. Boudou, E. Broniek, T. Siemieniwska, Modified active carbons from precursors enriched with nitrogen functions: sulphur removal capabilities, *Fuel* 77 (1998) 519–525.
- [21] J. Przepiórski, Enhanced adsorption of phenol from water by ammonia-treated activated carbon, *Journal of Hazardous Materials B135* (2006) 453–456.
- [22] P. Girods, A. Dufour, Y. Rogaume, C. Rogaume, A. Zoualalian, Pyrolysis of wood waste containing urea–formaldehyde and melamine–formaldehyde resins, *Journal of Analytical and Applied Pyrolysis* 81 (2008) 113–120.
- [23] P. Girods, A. Dufour, Y. Rogaume, C. Rogaume, A. Zoualalian, Thermal removal of nitrogen species from wood waste containing urea formaldehyde and melamine formaldehyde resins, *Journal of Hazardous Materials* 159 (2008) 210–221.
- [24] Pica France, Technical Paper, 2008.
- [25] S. Brunauer, P.H. Emmet, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [26] M.M. Dubinin, Fundamentals of the theory of adsorption in micropores of carbon adsorbents—characteristics of their adsorption properties and microporous structures, *Carbon* 27 (1989) 457–467.
- [27] S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, 2nd edition, Academic Press, London, 1982.
- [28] F. Stoeckli, A. Guillot, D. Hugli-Cleary, A.M. Slasli, Pore-size distributions assessed by different techniques, *Carbon* 38 (2000) 929–941.
- [29] F. Stoeckli, A. Slasli, D. Hugli-Cleary, A. Guillot, The characterization of microporosity in carbons with molecular sieve effects, *Microporous and Mesoporous Materials* 51 (2002) 197–202.
- [30] A. Terzyk, The impact of carbon surface chemical composition on the adsorption of phenol determined at the real oxic and anoxic conditions, *Applied Surface Science* 253 (2007) 5752–5755.
- [31] W. Li, D. Chen, Z. Li, Y. Shi, Y. Wan, J. Huang, J. Yang, D. Zhao, Z. Jiang, Nitrogen enriched mesoporous carbon spheres obtained by a facile method and its application for electrochemical capacitor, *Electrochemistry Communications* 9 (2007) 569–573.
- [32] K. Laszlo, E. Tombacz, K. Josepovits, Effect of activation on the surface chemistry of carbons from polymer precursors, *Carbon* 39 (2001) 1217–1228.
- [33] A. Celzard, J.F. Maréché, F. Payot, D. Bégin, G. Furdin, Electrical conductivity of anthracites as a function of heat treatment temperature, *Carbon* 38 (2000) 1207–1215.
- [34] I.I. Salame, T. Badosz, Surface chemistry of activated carbons: combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations, *Journal of Colloid Interface Science* 240 (2001) 252–258.
- [35] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Modification of the surface chemistry of activated carbon, *Carbon* 37 (1999) 1379–1389.
- [36] P. Burg, C. Vix-Guterl, Importance de la chimie de surface des matériaux carbonés, *Actualité Chimique N°* 295–296 (2005) 91–94.
- [37] V.C. Srivastava, M.S. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 272 (2006) 89–104.
- [38] S.S. Barton, M.J.B. Evans, J.A.F. MacDonald, Chemical heterogeneity on the carbon surface and adsorption from binary aqueous solutions, *Polish Journal of Chemistry* 71 (1997) 651–656.
- [39] A.P. Terzyk, Further insights into the role of carbon surface functionalities in the mechanism of phenol adsorption, *Journal of Colloid Interface Science* 268 (2003) 301–329.
- [40] G. Vazquez, J. Gonzalez-Alvarez, A.I. Garcia, M.S. Freire, G. Antorrena, Adsorption of phenol on formaldehyde-pretreated *Pinus pinaster* bark: equilibrium and kinetics, *Bioresource Technology* 98 (2007) 1535–1540.
- [41] D.M. Nevskaia, A. Sepulveda-Escribano, A. Guerrero-Ruiz, Surface properties of activated carbons in relation to their ability to adsorb nonylphenol aqueous contaminant, *Physical Chemistry Chemical Physics* 3 (2001) 463–468.
- [42] K. Laszlo, P. Podkoscielny, A. Dabrowski, Heterogeneity of polymer-based active carbons in adsorption of aqueous solutions of phenol and 2,3,4-trichlorophenol, *Langmuir* 19 (2003) 5287–5294.
- [43] S. Gaspard, S. Altendor, E.A. Dawson, P.A. Barnes, A. Ouensanga, Activated carbons from vetiver roots: gas and liquid adsorption studies, *Journal of Hazardous Materials* 144 (2007) 73–81.
- [44] M.J. Iqbal, M.N. Ashiq, Adsorption of dyes from aqueous solutions on activated charcoal, *Journal of Hazardous Materials B139* (2007) 57–66.
- [45] R.U. Edgehill, G.Q. Lu, Adsorption characteristics of carbonized bark for phenol and pentachlorophenol, *Journal of Chemical Technology and Biotechnology* 71 (1998) 27–37.
- [46] P. Podkoscielny, A. Dabrowski, O.V. Marijuk, Heterogeneity of active carbons in adsorption of phenol aqueous solutions, *Applied Surface Science* 205 (2003) 297–303.
- [47] S. Brunauer, *The Adsorption of Gases and Vapours*, vol. 1, Princeton, Univ. Press, Princeton, NJ, 1945.
- [48] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theory, *Journal of Colloid Interface Science* 47 (1974) 755–765.
- [49] C.H. Giles, A.P. D'Silva, I.A. Eston, A general treatment and classification of the solute adsorption isotherm. II. Experimental interpretation, *Journal of Colloid Interface Science* 47 (1974) 766–778.
- [50] R.S. Juang, J.Y. Shiau, Adsorption isotherms of phenols from water onto macroreticular resins, *Journal of Hazardous Materials B70* (1999) 171–183.
- [51] S.D. Gurumayum Sharma, D. Moreton, B. Vincent, Adsorption isotherm and atomic force microscopic studies of the interactions between polymers and surfactants on steel surfaces in hydrocarbon media, *Journal of Colloid and Interface Science* 263 (2003) 343–349.
- [52] J.E. Garcia, M.M. Gonzalez, J.S. Notario, Phenol adsorption on natural phillipsite, *Reactive Polymers* 21 (1993) 171–176.
- [53] T. Bialopiotrowicz, P. Blanpain-Avet, M. Lalande, Characterization of inorganic carbon-supported microfiltration and ultrafiltration membranes by aqueous phenol adsorption, *Separation Science and Technology* 34 (1999) 1803–1818.
- [54] B.Y. Zhu, T. Gu, General isotherm equation for adsorption of surfactants at solid/liquid interfaces, *Journal of the Chemical Society, Faraday Transactions* 185 (1989) 3813–3817.
- [55] R.W. Coughlin, F.S. Ezra, Role of surface acidity in the adsorption of organic pollutants on the surface of carbon, *Environmental Science and Technology* 2 (1968) 291–297.
- [56] H. Teng, C.T. Hsieh, Liquid phase adsorption of phenol by activated carbons prepared from bituminous coals with different oxygen contents, *Journal of Chemical Technology and Biotechnology* 74 (1999) 123–130.
- [57] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon adsorbent in aqueous solution, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*, vol. 27, Marcel Dekker, New York, 2001, pp. 1–66.
- [58] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, *Carbon* 42 (2004) 83–94.
- [59] H. Jankowska, A. Swiatkowski, D. Gelbin, K.H. Radeke, A. Seidel, Ext. Abstr. Int. Carbon Conf. *Carbon* 86 (1986) 397–398.
- [60] K. Laszlo, E. Tombacz, P. Kerepesi, Surface chemistry of nanoporous carbon and effect of pH on adsorption from aqueous phenol and 2,3,4-trichlorophenol solutions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 230 (2004) 13–22.