**Influence of activated carbon characteristics on toluene and hexane adsorption:
application of surface response methodology.**

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Abstract

The objective of this study was to evaluate the adsorption capacity of toluene and hexane over activated carbons prepared according an experimental design, considering as variables the activation temperature, the impregnation ratio and the activation time. The response surface methodology was applied to optimize the adsorption capacity of the carbons regarding the preparation conditions that determine the physicochemical characteristics of the activated carbons.

The methodology of preparation produced activated carbons with surface areas and micropore volumes as high as 1128 m²/g and 0.52 cm³/g, respectively. Moreover, the activated carbons exhibit mesoporosity, ranging from 64.6% to 89.1% the percentage of microporosity. The surface chemistry was characterized by TPD, FTIR and acid-base titration obtaining different values of surface groups from the different techniques because the limitation of each technique, but obtaining similar trends for the activated carbons studied. The exhaustive characterization of the activated carbons allows to state that the measured surface area does not explain the adsorption capacity for either toluene or n-hexane. On the other hand, the surface chemistry does not explain the adsorption results either. A compromise between physical and chemical characteristics can be obtained from the appropriate activation conditions, and the response surface methodology gives the optimal activated carbon to maximize adsorption capacity. Low activation temperature, intermediate impregnation ratio lead to high toluene and n-hexane adsorption capacities depending on the activation time, which a determining factor to maximize toluene adsorption.

Keywords: toluene adsorption; hexane adsorption; activated carbon; surface response

1. Introduction

Non-methane volatile organic compounds (NMVOCs) are atmospheric pollutants coming from the use of solvents in the industry and the storage, distribution and use of fossil fuels. NMVOCs have direct effect on human health. Moreover, they participate in reactions in the atmosphere with other pollutants contributing to the formation of tropospheric ozone calling them ozone precursors [1].

According to the European Environmental Agency (EEA) 34% of NMVOCs come from energy related sectors with a further 39% from the solvents sector [2].

Toluene and n-hexane are NMVOCs commonly used as solvents in the industry.

Toluene can be considered as representative of aromatic hydrocarbons solvents. It is mainly used to dissolve paints and adhesives. Hexane can be considered as representative of aliphatic hydrocarbons. Hexane is mainly used in the formulation of glues for shoes and leather products as well as for cleansing and degreasing all sorts of items.

The proposed NECD (National Emission Ceilings Directive) target required a 60% reduction of NMVOCs emissions below 1990 emissions by 2010. No new ceiling has been established up to now. According to the NEC Directive Status Report published by the EEA [3], NMVOC projections for the EU-27 are 10 % below the aggregated emission ceiling given in Annex I for 2010, but still 5 % above the Annex II ceiling. Thus, allowable technology is needed to control the NMVOCs emission to the atmosphere to comply with the current NMVOCs emission regulations.

Carbons have recognized adsorption capacity and versatility for different applications [4]. The adsorption of NMVOCs over carbons can operate under a wide range of

conditions. Especially remarkable are the capability of working at low NMVOCs concentration [1]. Moreover, they have the advantage of the recovery of these compounds by desorption to be used again [5].

The efficiency of a given carbon to adsorb a given NMVOC is characterized by the quantity adsorbed at a given adsorbate pressure. The adsorption capacity of a carbon will depend on surface area, pore volume and microporosity [4]. Another important factor for the removal of polar compounds is surface chemistry [4, 6]. In addition to the influence of adsorbent characteristics on adsorption capacity, the composition of gas stream might be specially influencing the NMVOC removal capacity of carbons.

The preparation of activated carbons from biomass and agricultural wastes is widely known [4, 7]. However, some aspects have been developed in lower extent: the production of activated carbons related to their utilization [4], the recovery of solvents and NMVOC removal in low concentration streams.

In this context, the objective of this study was to evaluate the adsorption capacity of toluene and hexane over activated carbons prepared by chemical activation of almond shells with phosphoric acid, according to an experimental design described in [8].

According to the compilation of information carried out in this work, no study has been done on the optimization of the adsorption capacity on activated carbons from almond shells. To achieve this objective, the response surface methodology was applied to predict the physicochemical characteristics of the activated carbons that optimize the adsorption capacity.

2. Experimental Methods

2.1. Preparation of activated carbons

Activated carbons have been obtained from the chemical activation with phosphoric acid of almond shells at different impregnation ratios and temperature and time of carbonization. Almond shell used as starting material is an agricultural residue from Teruel province, Spain. This material was crushed to a particle size of 0.3-0.5 mm. Average ash content of almond shell was 2.5%.

An experimental design was used to obtain the conditions to prepare the activated carbons. The parameters introduced were impregnation ratio (defined as phosphoric acid, wt/precursor, wt), temperature and time of carbonization. A total of 12 activated carbons were prepared according the experimental design. Samples were labelled indicating temperature of carbonization, followed by impregnation ratio and activation time. Example: AT400R05t120 (A: almond shell; T400: activation temperature of 400°C; R05: impregnation ratio of 0.5; t120: activation time of 120 min).

The procedure to prepare the activated carbons is as follows: mixing the almond shell with a determined amount of phosphoric acid of 89 wt % concentration to reach impregnation ratios in the range 0.5-1.5. The suspension was shaken at room temperature during 1 h. The impregnated samples were further thermally treated at different temperatures ranging from 400° to 800°C by passing through a flow of N₂ (which was kept during both heating and cooling), and maintained at the selected temperature during a time ranging from 30 to 120 min.. Solid pyrolysis residues were water washed in Soxhlet until pH>6. The resulting activated carbons were dried at 100°C until constant weight and stored under Ar.

More details of the experimental design and procedure of preparation of the activated carbons can be found elsewhere [8].

2.2. Characterization

Samples were characterized by temperature programmed desorption (TPD), infrared spectroscopy (FTIR), Boehm titration and N₂ adsorption.

The TPD runs were carried out with a custom built set-up, consisting of a tubular quartz reactor placed inside an electrical furnace. In a typical TPD experiment the sample was heated up to 1100°C in Ar flow at a heating rate of 10°C /min. The amounts of CO and CO₂ evolved at each temperature were measured continuously with a quadrupole mass spectrometer from Pfeiffer. The calibrations for CO and CO₂ were carried out by standards diluted in Ar. In a typical run 0.5 g of carbon was placed in a horizontal quartz tube reactor under a stream of 30 ml/min of Ar.

Infrared spectra of the activated carbons were obtained in a Bruker Tensor 27. A small amount of sample finely ground is placed directly on the equipment. The spectra were normalized and the baseline was corrected with the own software of the apparatus.

The selective neutralization method was used to evaluate the acidic character of the surface of the activated carbons according to Boehm's procedure [9]. The amounts of various acidic oxygen functional groups (carboxyls, lactones, phenols and carbonyls) were measured by selective neutralization using bases of different strength.

Approximately 0.5 g of each sample was mixed with 50 ml of a 0.1 N solution of a base (NaOH, Na₂CO₃, NaHCO₃, NaOC₂O₅). The suspension was shaken for 24 h at room temperature. After that time, the solution was filtered and an aliquot was taken. The amount of each base neutralized by the activated carbon was determined by back-titration using HCl 0.1 N solution.

Textural characterization was performed by N₂ adsorption-desorption at 77K. Isotherms were obtained in an apparatus ASAP 2020 from Micromeritics. Prior to the analysis, samples were outgassed at 200°C up to a vacuum of 10⁻⁵ mm Hg. The volume of adsorbed nitrogen was measured from a relative pressure of 10⁻⁷ up to 0.995. Surface area was determined by BET method [10] applied to the adsorption branch of the isotherm. Pore volume corresponding to micropores was calculated using Dubinin-Radushkevich (DR) equation applied to the adsorption branch of the N₂ isotherm [11]. DR equation was also applied to obtain characteristic energy (E₀) and the mean pore width (L₀), estimated taken nitrogen density as 0.808 cm⁻³ and affinity coefficient as 0.33 and the relationship between E₀ and L₀ taken from [12]. Pore volume corresponding to mesopores was calculated with Barret-Joyner-Halenda (BJH) equation applied to the desorption branch of the N₂ isotherm [13]. The total pore volume was taken from the measure of adsorbed nitrogen at a relative pressure of 0.995. The percentage of microporosity can be obtained as the ratio between total micropore volume (calculated by applying Dubinin-Radushkevich equation to the adsorption branch of the N₂ isotherm) and volume adsorbed at relative pressure of 0.995 [14]. Pore size distribution (PSD) was evaluated by density functional theory (DFT) method [15].

2.3. Toluene and n-hexane adsorption

The adsorption-desorption isotherms of toluene or n-hexane vapours in static mode were obtained using a gravimetric analyzer from VTI Corporation (Miami, USA). This apparatus is fully computer controlled and measures adsorption and desorption on a gravimetric microbalance. The sample temperature (298K) is constantly monitored throughout the duration of the experiments and the variation was found to be 0.5K. A

pressure transducer in the range of 0-100 mm Hg (accurate to $\pm 0.12\%$) is used to monitor de vapour pressure in the system. Approximately 100 mg of a sample of activated carbon was placed into a bucket made from stainless steel mesh and was outgassed in situ at 423K under vacuum to a constant weight. Pressure steps in the range of p/p_0 values 0-0.95 were used to obtain the isotherms. After the equilibrium was reached, the organic vapour pressure was increased to the next set pressure value, and the subsequent uptake was measured until equilibrium was re-established.

3. Results and Discussion

In a previous work, the influence of preparation conditions (activation temperature, impregnation ratio and activation time) on surface area, pore volume and surface groups was studied [8]. However, the most interesting study is the prediction of the adsorption capacity through preparations conditions or the physicochemical characteristics of the activated carbon.

As it is well known, the conditions used to prepare an activated carbon change not only the surface area but also porosity and surface chemistry. A methodical study of these properties can help to further apply the response surface methodology in order to fix the most influencing variables among those studied.

Figure 1 depicts the nitrogen adsorption-desorption isotherms of the activated carbons studied in this work. All samples present a type I isotherms, according to BDDT classification [16] with wide knee and in some cases with a continuous adsorption at higher relative pressures, indicating the presence of large micropores and mesoporosity.

Percentages of microporosity given in Table 1 confirm the information provided by the examination of the isotherms. Table 1 summarizes the characterization of porosity of samples. As can be seen, at intermediate impregnation ratios, lower carbonization temperatures are needed to obtain higher surface areas and pore volumes (total, meso and micropore). Figure 2a shows the relationship between temperature of carbonization and impregnation ratio with surface area. As can be deduced an impregnation ratio of 1.0-1.1 at temperatures lower than 600°C is the most appropriate to reach high surface areas, indicating a compromise between the devolatilization process that creates porosity and the intensive dehydration that could collapse the micropores because of weakness of pore walls [7]. On the other hand, the use of impregnation ratios in the extreme of the range studied needs higher carbonization temperatures to obtain high surface areas and pore volumes. The effect of both temperature of carbonization and impregnation ratio on the textural characteristics of the samples obtained follows a trend when the degree of microporosity is investigated, as can be deduced from Figure 2b. At increasing impregnation ratio, the percentage of microporosity decreases, independently of the temperature of carbonization. There is a progressive widening of the micropores that could be explained in terms of intensive dehydration, as is explained above. This can be confirmed following the pore size distributions in Figure 3 obtained by DFT method. Volume of micro and mesopore was obtained from DFT PSD. Both values are represented versus impregnation ratios for each carbonization temperature in Figure 4a and b for micropore and mesopore volume, respectively. As can be seen, the slope of the increase of mesoporosity is higher than that for microporosity. At the impregnation ratio of 1.5, there is a decrease in both micro and mesoporosity, indicating the above

mentioned intensive dehydration, but the trend of percentage of microporosity in maintained as can be confirmed in Figure 2b.

On the basis of the above results one can conclude that at low impregnation ratios, phosphoric acid mainly promotes the development of micropores. At intermediate impregnation ratios pores with a wide range of sizes between ultramicropores and mesopores are developed with a tendency towards wider pores as the impregnation ratio increases. At impregnation ratios higher than 1 wide micropores and mesopores are developed (both V_p 0.995 and volume micropore increase). As mentioned in the literature [17] the porosity is generated with phosphoric acid remaining intercalated in the internal structure of lignocellulosic materials hindering their shrinkage. As the amount of acid used in the impregnation increases, it is reasonable to expect an increase in the volume filled by and the various polyphosphates structures, resulting in larger pore volume and pore size.

In order to establish the influence of textural characteristics of the activated carbons on the adsorption of toluene and n-hexane, the isotherms for both VOCs adsorption at 25°C were obtained. Toluene and n-hexane are molecules with different features, not only their size (n-hexane is 1.03x0.49 nm and toluene is 0.4x0.8 nm) but also their polarity (polarity index of n-hexane is <0.1 and for toluene is 2.4). This fact could explain the differences in adsorption capacity for the same sample.

Figure 5 shows isotherms for the studied carbons. As can be deduced, high adsorption capacities can be obtained with some carbons (high values of mmol/g correspond to near 70 wt%). Toluene and n-hexane isotherms are type I according to BDDT classification. In general carbons obtained at lower temperatures of activation exhibit higher toluene and n-hexane adsorption capacities than those obtained at higher

activation temperatures. Moreover, high adsorption capacities are obtained when isotherms drifts from Langmuir model [18]. This fact is consistent with the adsorption in the mesoporosity of the activated carbons.

Applying Langmuir model [18] to toluene and n-hexane isotherms, limiting value for vapor adsorption (W_m) and constant value K can be obtained. These values are shown in Table 2. W_m values are compared with the experimental ones obtained for toluene and n-hexane adsorption at $p/p_0=0.9$, giving a good correlation, even for isotherms exhibiting some mesoporosity. However, the fit on the low pressure region is limited when there is continuous adsorption at high relative pressures. These results are similar than those found by other authors [19]. Values of K can be related with the widening of the microporosity in a series of carbons, and this development of the microporosity can be related with the degree of burn-off of the activated carbons [20, 21]. However, the textural characteristics cannot explain the toluene and n-hexane adsorption capacities of carbons. Since Table 1 and 2 it can be found that samples AT400R15t30, AT467R067t90 and AT800R0.5t30 exhibit similar surface areas, but their adsorption capacities ranges from the highest values to the lowest values. Other textural parameters (since Tables 1 and 2) cannot explain adsorption capacities either.

It can be found some research works on the adsorption volatile organic compounds in which authors invoke surface chemistry as a negative effect to explain adsorption capacities of carbons [6-8, 22]. So, a detailed study of the oxygen surface groups of the activated carbons was carried out.

The conditions used to prepare the activated carbons change the amount and type of surface oxygen functional groups present on them. The amounts of CO and CO₂ desorbed and the temperatures at which these gases released have been found to be

characteristics of various oxygen complexes. In general it is agreed that each type of oxygen surface group decomposes to a defined product. It has been proposed that CO₂ derives from complexes like carboxylic acids, anhydrides and lactones and CO derives from complexes like phenolic and quinonic groups. The complexes yielding CO₂ have been shown to decompose typically over a range of temperatures 150°-600°C and complexes yielding CO at temperatures in the range of 600°-1000°C [4, 23].

A detailed study of the profiles of CO and CO₂ evolution during a TPD experiment was given in [8]. In order to quantify the oxygen groups evolved, CO and CO₂ peaks were integrated to obtain the total amount evolved for each activated carbon.

The total amount of CO and CO₂ evolved up to 1100°C in a TPD run for each activated carbon is reported in Table 3. The introduction of surface groups that yield CO increase as a general trend at increasing carbonization temperature as can be seen in Table 3. In the case of CO₂ evolution, there is not a relationship between carbonization temperature and the total amount of CO₂ evolved. The impregnation ratio and the time of activation are important parameters influencing the introduction of CO₂-evolving groups.

However, the presence of similar amounts of oxygen groups on the activated carbons cannot explain their adsorption capacities. For example, the amounts of CO and CO₂ evolved for samples AT600R05t75 and AT600R1t30 are similar but their adsorption capacities are quite different (for toluene 2.53 mmol/g and 6.50 mmol/g, respectively).

Considering that TPD is a bulk technique, it can be considered that all the oxygen groups evolving as CO and CO₂ are not on the activated carbon surface, and consequently no conclusive results can be obtained.

The selective base neutralization method gives information only on the oxygen surface functionality of the carbons. Despite that not all the oxygen known to be on a carbon

surface can be measured by titration techniques, Boehm titration [9] was used to obtain the amount of acidic sites on the activated carbon surface. Some oxygen could be bonded within the grapheme layers (in-ring) and hence would be non-reactive, and some carbonyl groups may not be able to react with the alkaline solutions. Table 4 reports the results from Boehm titration. Main contribution to the surface chemistry corresponds to carbonyls type groups, while the low content in phenolic groups has been described previously for activated carbons from lignocellulosic materials activated with phosphoric acid [24]. Assuming that carboxyls and lactones evolve CO_2 in TPD experiments and phenols and carbonyls evolve as CO in TPD experiments, Boehm titration results follow the same trend obtained from TPD experiments.

Figure 6 depicts the IR spectra of the activated carbons. From the point of view to study surface functionalities on carbon the most interesting zone correspond to the range of wavelengths $1700\text{-}800\text{ cm}^{-1}$.

The spectra profiles of the activated carbons are similar but in general the activated carbons obtained at lower temperatures of activation exhibit sharper bands than those activated carbons obtained at higher temperatures of carbonization. The assignment of bands was based on similar stretching frequencies in small molecular organics as well as those obtained in the literature for activated carbons [23, 25, 26]. In order to quantify the surface groups measured by IR, an integration of the region 1100 cm^{-1} and the region 1600 cm^{-1} was carried out, assigning the region around 1100 cm^{-1} to C-O groups and region 1600 cm^{-1} to C=O groups. Table 3 reports the area of the integrated peaks of each IR region. As can be seen, the area measured is higher for region at 1100 cm^{-1} than that for region 1600 cm^{-1} . This fact is consistent with the low presence of carboxyls and lactones and the higher presence of carbonyls obtained from Boehm titration. Thus, IR

results do not explain the differences of the activated carbons adsorption capacities either.

Since the study of functional groups by different techniques it can be deduced that there is not a relationship with adsorption capacity. So, the interrelation between physical and chemical features should be addressed in order to predict the adsorption capacities from the preparation conditions of the activated carbons. As the relationship between preparation conditions and physicochemical characteristics of the activated carbons was established previously [8], adsorption capacity can be related with preparation conditions.

Response surface methodology was used to study and describe the effect of the preparation conditions (temperature of carbonization, impregnation ratio and time of carbonization) on the toluene and n-hexane adsorption capacity of the activated carbons. A second-order polynomial model was used to describe either the toluene or the n-hexane adsorption capacity.

$$Y=A_0+A_1T+A_2R+A_3t+A_{12}TR+A_{13}Tt+A_{23}Rt+A_{11}T^2+A_{22}R^2+A_{33}t^2 \quad (1)$$

being Y the response (either the toluene or the n-hexane adsorption capacity, $V_{m,tol}$ and $V_{m,hex}$, respectively), T, R and t, activation temperature, impregnation ratio and activation time, respectively and A_0 is the constant, A_1 , A_2 , A_3 are the linear coefficients, A_{12} , A_{13} , A_{23} are the interactive coefficients and A_{11} , A_{22} , A_{33} are the quadratic coefficients.

Based on the analysis of variance (ANOVA) of the complete quadratic model, terms of equation (1) with no significant effect on the response can be established. The observation of p -value (significance level) is used to assess the significance of the coefficients on the response. The limits taken were $0.05 < p\text{-value} < 0.2$. If $p\text{-value} < 0.05$

it can be considered that the effect on the response is not due to random variations and it may be concluded that it is a significant effect. On the contrary, p -values greater than 0.2 indicate that the coefficient is not significant, and thus the contribution of the corresponding variable(s) either.

In present case based on the complete model, quadratic effect of the three design variables as well as the interactive effect between time and impregnation ratio exhibit p -values greater than 0.2 for the responses $V_{m,tol}$ and $V_{m,hex}$. These parameters were removed from the model, resulting:

$$Y_1 = B_0 + B_1T + B_2R + B_3t + B_{13}TR + B_{23}Tt \quad (2)$$

being Y_1 responses either $V_{m,tol}$ or $V_{m,hex}$ and B_{ij} the coefficients for each variable or combination of variables.

In order to check the quality of the model, predicted values are plotted versus measured values for the responses in Figure 7. Typical error for each sample is also depicted.

Using that limited quadratic model, isoresponse surface are represented graphically relating each response and two factors, keeping the third factor constant. Because both responses ($V_{m,tol}$ and $V_{m,hex}$) follow the same trend under the same experimental conditions it is possible to determine a common range of each experimental preparation condition to obtain an activated carbon with defined physicochemical characteristics.

As it has been shown above, a combination of surface area and surface chemistry are important factors to obtain high adsorption capacities. As it was stated previously [8] the main design variable influencing surface area is impregnation ratio, so in Figure 8 it can be found response surface for $V_{m,tol}$ and $V_{m,hex}$ as a function of activation temperature and time keeping constant impregnation ratio at 1.1 in the adequate range (0.95-1.20). As can be deduced from Figure 8, the optimal adsorption is in the range of

low temperatures for both responses. However, the range for activation time is wider for $V_{m,hex}$ response, ranging from 30 to 100 min.

The range of temperatures agrees with that corresponding to the optimal surface area as it was obtained in [8]; however, the activation time required for optimal adsorption capacity is lower than that required to optimize surface area.

On the other hand, the optimization of the amount of either CO_2 or CO groups (from TPD experiments) gave a range of activation time (around 95-120 min) that does not fit with the optimal adsorption capacity for both responses, in particular with toluene adsorption.

It has been shown above that the characterization of oxygen functional groups gives similar trends using different techniques, it has no sense to expect different results on the range of activation temperatures optimizing either surface oxygen groups from Boehm titration or IR integrated areas.

Thus, the above results can be understood in terms of a compromise between textural characteristics and surface chemistry to optimize adsorption capacity. Despite higher activation times at low activation temperatures lead to optimize surface area and the amount of CO_2 or CO groups (from TPD experiments), the optimal for toluene adsorption capacity is reached at low activation temperature and time and the optimal for n-hexane adsorption capacity is reached at low activation temperature and high activation time.

Summarizing, the analysis all the responses allows to obtain a compromise among the preparation conditions of the activated carbons, which give a defined and reproducible activated carbons characteristics, to optimize adsorption capacity in the range studied in this paper.

4. Conclusion

High toluene and n-hexane adsorption capacities can be obtained with almond shell based chemically activated carbons. There is not a direct relationship between textural characteristics or surface chemistry and adsorption capacities and a balance between both features should be include to explain high adsorption capacities in some cases.

Response surface methodology has allowed the definition of a range of optimal experimental conditions for the preparation of activated carbon that gives defined and reproducible activated carbon characteristics and optimizes toluene and h-hexane adsorption capacity.

For toluene adsorption, the optimal activated carbon is prepared at low activation temperature, intermediate impregnation ratio and low activation time (in the range 400-430°C, 0.95-1.1 and 30-40 min, respectively). For n-hexane adsorption, the optimal activated carbon is prepared at low activation temperature, intermediate impregnation ratio and wide range of activation time (in the range 400-430°C, 0.95-1.1 and 30-100 min, respectively).

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FIGURE CAPTIONS

Figure 1 : Nitrogen adsorption-desorption isotherms at 77K. Solid symbols adsorption. Open symbols desorption.

Figure 2 : Influence of temperature of carbonization and impregnation ratio on surface area (a) and percentage of microporosity (b).

Figure 3 : Pore size distribution by DFT method.

Figure 4 : Influence of temperature of carbonization and impregnation ratio on porosity.

Figure 5 : Toluene and n-hexane isotherms at 25°C. Experimental: symbols. Langmuir model: lines.

Figure 6 : IR spectra of the activated carbons. 1: AT400R05t120; 2: AT400R1t75; 3: AT400R15t30; 4: AT467R067t90; 5: AT467R117t45; 6: AT533R083t60; 7: AT600R05t75; 8: AT600R1t30; 9: AT667R067t45; 10: AT800R05t30; 11: AT800R15t120.

Figure 7. Predicted values of toluene and n-hexane adsorption capacities versus experimental values.

Figure 8. Response surface at fixed impregnation ratio of 1.1: a) $V_{m,tol}$ and b) $V_{m,hex}$.

Table 1. Textural characterization of the samples.

Sample	S_{BET} m^2/g	$V_{(\text{p}/\text{p}_0=0.995)}$ cm^3/g	V_{meso} cm^3/g	V_{micro} cm^3/g	E_0 kJ/mol	L_0 nm	Microporosity %
AT400R05t120	626	0.376	0.124	0.335	19.3	1,36	89.1
AT400R1t75	1128	0.670	0.385	0.521	16.4	2,17	77.8
AT400R15t30	789	0.482	0.268	0.342	16.3	2,21	71.0
AT467R067t90	785	0.497	0.259	0.392	17.6	1,73	78.9
AT467R117t45	1117	0.724	0.494	0.513	16.0	2,35	70.9
AT533R083t60	891	0.571	0.341	0.426	17.2	1,85	74.6
AT533R083t60(2)	903	0.593	0.378	0.427	17.0	1,91	72.0
AT600R05t75	502	0.301	0.106	0.261	19.9	1,28	86.7
AT600R1t30	926	0.624	0.375	0.435	17.4	1,80	69.7
AT667R067t45	624	0.440	0.176	0.314	19.3	1,37	71.4
AT800R05t30	723	0.425	0.147	0.378	20.4	1,19	88.9
AT800R15t120	990	0.694	0.511	0.448	16.8	2,00	64.6

Table 2. Adsorption capacities W_m and constants K from Langmuir model.

Sample	Toluene		n-hexane	
	$W_{\text{m,tol}}$ mmol/g	K_{tol} cm^3/g	$W_{\text{m,hex}}$ mmol/g	K_{hex} cm^3/g
AT400R05t120	3.65	1.09	2.82	0.69
AT400R1t75	6.54	1.21	5.73	0.31
AT400R15t30	7.44	0.48	5.44	0.29
AT467R067t90	4.02	1.84	3.55	0.40
AT467R117t45	6.89	0.94	5.55	0.28
AT533R083t60	4.95	1.51	4.23	0.37
AT600R05t75	2.53	2.09	2.06	0.64
AT600R1t30	6.50	0.80	4.54	0.32
AT667R067t45	3.37	0.41	2.84	0.57
AT800R05t30	2.68	0.76	2.12	0.76
AT800R15t120	6.10	0.66	5.00	0.19

Table 3. Total amount of CO and CO₂ evolved up to 1100°C in TPD experiments and area of IR regions 1600 cm⁻¹ and 1100 cm⁻¹.

Sample	CO mmol/g	CO ₂ mmol/g	A ₁₆₀₀	A ₁₁₀₀
AT400R05t120	1.985	0.569	0.25	4.35
AT400R1t75	2.170	1.322	0.28	4.51
AT400R15t30	1.798	0.754	0.33	3.90
AT467R067t90	2.587	1.036	0.52	4.75
AT467R117t45	2.181	1.177	0.35	4.60
AT533R083t60	2.232	0.387	0.40	4.94
AT533R083t60(2)	2.180	0.358	0.42	4.79
AT600R05t75	2.833	0.517	0.29	5.10
AT600R1t30	3.045	0.451	0.29	4.70
AT667R067t45	2.865	0.481	0.61	4.41
AT800R05t30	4.135	1.921	0.55	4.60
AT800R15t120	3.722	1.293	0.58	4.85

Table 4. Oxygen surface groups (in mmol/g) from Boehm titration

Sample	Carboxyls	Lactones	Phenols	Carbonyls
AT400R05t120	0.350	0.800	0.800	1.900
AT400R1t75	0.350	0.850	0.988	2.012
AT400R15t30	0.375	1.075	1.750	1.525
AT467R067t90	0.425	1.025	0.900	2.412
AT467R117t45	0.450	0.650	1.100	2.175
AT533R083t60	0.450	0.800	0.875	2.625
AT533R083t60(2)	0.450	0.900	1.025	2.400
AT600R05t75	0.725	0.425	0.725	2.750
AT600R1t30	0.475	0.750	0.975	2.425
AT667R067t45	0.500	1.600	1.200	2.250
AT800R05t30	0.650	0.850	1.225	2.300
AT800T15t120	0.525	1.075	1.000	2.425

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8