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Characterization and phenols sorptive properties of carbons activated by sulphuric acid

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Abstract

In this work, sawdust was used as a source material to prepare activated carbons by chemical activation with sulphuric acid. Texture properties of these carbons were determined by measuring the adsorption of nitrogen at 77 K and of carbon dioxide at 298 K. The nitrogen adsorption isotherms were interpreted by BET equation and α_s-method while carbon dioxide adsorption results were interpreted by applying the D–R equation. The nature of carbon surface functionalities was studied by FTIR spectroscopy and Boehm titration method. The adsorption of phenol, hydroquinone, resorcinol and catechol from aqueous solution at 298 K on to these carbons has been investigated. FTIR shows that the carbon surface acquires an acidic character with carboxylic groups were essentially fixed along with lactonic and phenolic groups. The equilibrium data fit well the Langmuir isotherm. The amounts of phenols adsorbed, without exception decrease with increasing the concentration of acid groups on the carbon surface. Moreover, for each carbon, the amount of phenol adsorbed follows the order phenol > hydroquinone > resorcinol > catechol.

Keywords: Activated carbons; H_2SO_4 activation; Textural properties; Phenols removal

1. Introduction

Phenolic derivatives are widely used as intermediates in the synthesis of plastics, colours, pesticides, insecticides etc. Degradation of these substances means the appearance of phenol and its derivatives in the environment. Most of these compounds are recognized as toxic carcinogens. The presence even in low concentration causes unpleasant taste and odour of drinking water and can exert negative effects on different biological processes.

Different methods designed to remove phenols have been proposed. Adsorption by activated carbons is the best and most frequently used method [1]. Other methods include aerobic and anaerobic biodegradation, oxidation by ozone and uptake by ion exchange resins.

Activated carbons possess excellent adsorption ability for relatively low-molecular weight organic compounds such as phenols [2]. From a general point of view, an activated carbon to be used in such processes must have adequate adsorptive capacity, mechanical strength and chemical purity. Furthermore, all of these specifications should coexist with a low production cost. The most common materials used for preparation of activated carbons are wood, coal, lignin, petroleum coke and polymers [3].

Recently, many investigators have studied the feasibility of using many agricultural byproducts and wastes, which are available at very little or no cost to prepare activated carbon [4–7]. Both texture and surface chemistry of activated carbons determine performance, and the final application of the carbon material will depend on its characteristics. The porous structure of activated carbons is a function of the precursor used in the preparation, the activation method followed and the extent of activation. Activated carbon types produced by applying chemical activation processes contain mainly mesopores, while carbons obtained via gas activation are of the microporous type [8] although even in that case depending on the nature of the parent material and by adjustment of the process conditions, different pore sizes that cover the micro-, meso- and macropore ranges can be obtained [9].

The chemical nature of the surface of activated carbons is the most important factor apart from the porous structure that determines its adsorption properties. The presence of oxygen and hydrogen in the surface groups affects strongly the adsorptive properties of the activated carbons. The origin of these surface groups, may be the original material, the activation pro-

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cess or introduction after preparation via post-treatment [10,11]. Oxygen, for instance, may be present in various forms such as carboxyls, phenols, lactones, aldehydes, ketones, quinines, hydroquinones, anhydrides or ethereal structures [12].

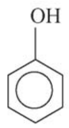
In continuation of our previous work on the preparation of activated carbon from low cost materials [13–16], sulphuric acid was used as an inexpensive nonvolatile dehydrating agent and we examined the influence of its addition on the pyrolysis of sawdust in terms of surface area, porosity and adsorptive properties. The prepared carbons are used as models to study the effect of texture and surface chemistry on the uptake of some selected phenols from their aqueous solutions.

2. Experimental

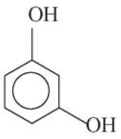
2.1. Adsorbents

The acacia sawdust used in this study was collected from a local lumber mill. Non-activated carbon "CZ" was obtained by carbonizing the original sawdust at 873 K in a nitrogen atmosphere. Sulphuric acid activated carbons CSI–CSIV were prepared by impregnation of the original sawdust with concentrated sulphuric acid, using different acid/sawdust ratios from 3:1 to 6:1 (w/w) respectively. The mixture was left overnight and then boiled until dryness. The mixture was placed in a quartz tube over which nitrogen flowed at a flow rate of 60 ml/min. The sample was moved to the center of a furnace with a reduced nitrogen flow rate of 30 ml/min, heated at 10 °C/min to 575 K and held at this temperature for 4 h. The product was cooled to room temperature, washed with 5% H_2SO_4 and then with bi-distilled water until free from sulphate ions, dried at 393 K for 6 h and stored in stoppered bottles. For all adsorption measurements, a particle size of 0.02–0.1 mm was used.

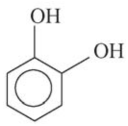
The phenols used in the experiment are listed below:



Phenol



resorcinol



catechol

hydroquinone

The phenols used were analytical grade and were obtained from Aldrich Chemical Company.

2.2. Techniques

The surface areas of carbons investigated were measured by nitrogen adsorption at 77 K and carbon dioxide at 298 K, using a conventional volumetric apparatus. Wafers of KBr containing about 5% of carbon sample were used to obtain the transmission FTIR spectra in the range 400–4000 cm^{-1}. The wafer was dried at 398 K overnight before the spectra were recorded. The titration, in aqueous solution, of the chemical surface groups was carried out following the method proposed by Boehm et al. [17]. According to Boehm et al., the amount of sodium bicarbonate reacted is equivalent to the amount of carboxylic groups, while sodium carbonate reacted with both carboxylic and lactonic groups. The amount of sodium hydroxide reacted minus the sodium carbonate value gives the amount of phenols present on carbons.

Equilibrium adsorption measurements from aqueous solution were obtained by shaking 0.25 g of carbon with 50 ml of the substrate solutions of different concentrations in brown Erlenmeyer flasks thermostated at 298 K. The initial concentration of phenols was determined using a Perkin-Elmer Lambda 3B UV spectrophotometer at λ_{Max} equal 270, 274, 275, 285 for phenol, resorcinol, catechol and hydroquinone, respectively. A time of 48 h was allowed for all the equilibrium measurements.

Breakthrough curves of the carbon samples were obtained using a glass column of 0.6 cm i.d. packed with each sample (bed height 10 cm) on a glass wool support. The column was conditioned with 50 ml of bi-distilled water prior to a 50 mg/l concentration of the phenol being percolated downwards by maintaining constant levels of effluent over the bed. A peristaltic pump was used to control the flow rate at 3 ml/min. Samples of the effluent were collected and their phenol concentration measured.

3. Results and discussion

3.1. Characterization of prepared carbons

The adsorption of nitrogen at 77 K varied according to the carbon adsorbent employed. It was slow for non-activated and slightly activated carbons i.e., for CZ, CSI and CSII samples. More than 10 h were necessary to achieve equilibrium onto these samples. With the other carbons (CSIII and CSIV), the adsorption of nitrogen was found to be relatively rapid with equilibrium being attained in less than 2 h. The slow adsorption of nitrogen on non-activated carbon "CZ" and slightly activated carbons (CSI and CSII) may be attributed to the diffusion of nitrogen in the ultrafine micropores predominating in these carbons [18]. The nitrogen adsorption isotherms of all carbons were of Type I as shown in Fig. 1. The amount of nitrogen gas in (cm^3/g) taken up at the plateau region of the isotherm was converted into the volume of liquid nitrogen (ml/g) contained in the pores per unit mass of carbon. The micropore volume (V_p) calculated on this basis is listed in column 2 of Table 1. Nitrogen surface areas (S_{BET} m^2/g) were calculated by applying the BET equation [19], these areas are listed in column 3 of Table 1.

A further analysis of the nitrogen isotherms using Sing's α_s method [20] was carried out to assist in defining the micro and mesopore volumes of carbon samples. The quantity $\alpha_s = \frac{V_s}{V_x}$, where V_x denotes the volume adsorbed on the reference solid at a fixed relative pressure P_x/P^0. Usually α_s is set equal to unity at $P_x/P^0 = 0.4$. The α_s values reported by Selles-Perez and Martin-Martinez [21] for the adsorption of nitrogen on a non-porous carbon were used for making this analysis. The surface areas (α_s m^2/g) have been calculated from the slope of the linear part of the α_s-plots (taking a line through the origin). The α_s-plots of the carbon samples are shown in Fig. 2 and the S_α surface areas are listed in column (4) of Table 1. It is evident that downward deviations are shown for all carbon samples and continue over a wide range of α_s values. This could be taken as

Table 1
Textural properties of the prepared samples

Sample	V_P (ml/g)	S_{BET} (m^2/g)	S_α (m^2/g)	S_{DR} (m^2/g)	V_0^α (ml/g)	$V_0^{0.1}$ (ml/g)
CZ	0.030	43.00	48.0	70.0	0.022	0.020
CSI	0.058	115.0	118.0	140.0	0.048	0.046
CSII	0.072	152.0	160.0	197.0	0.060	0.058
CSIII	0.086	182.0	184.0	247.0	0.072	0.070
CSIV	0.098	210.0	218.0	358.0	0.079	0.078

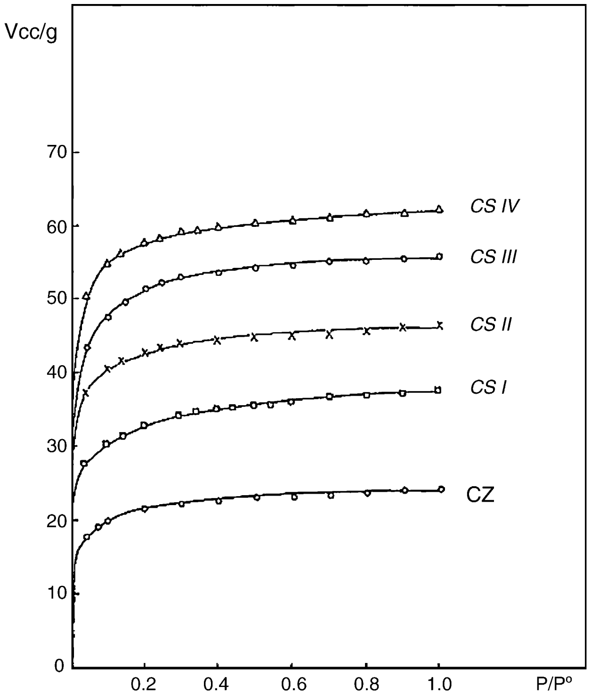


Fig. 1. Adsorption isotherms of nitrogen at 77 K on the carbonized product "CZ" and sulphuric acid-activated carbons.

evidence that most of the existing pores are of the micro-type. Another evaluation of the micropore volume was suggested by Gomez-Serrano et al. [22] as equivalent to the volume adsorbed at $P/P^0 = 0.1(V_0^{0.1})$ is also measured. Table 1 gives the pore volume as obtained from different estimations.

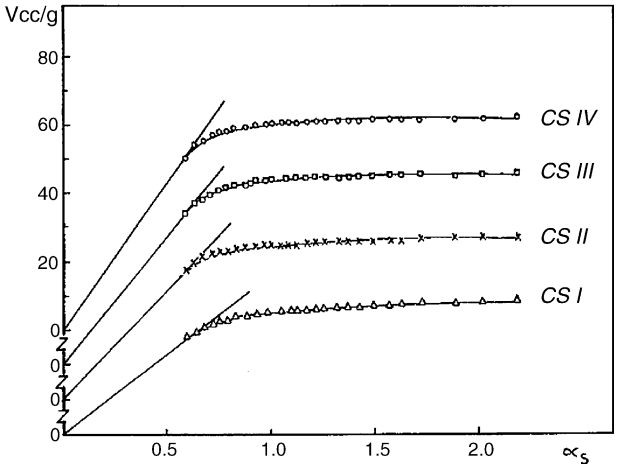


Fig. 2. α_s-plot of nitrogen adsorption on sulphuric acid-activated carbons.

For microporous adsorbents, the surface area may be calculated from the adsorption of carbon dioxide at 298 K. The adsorption of CO_2 by microporous solids can be well explained by Dubinin–Radushkevick (D–R) equation [23] represented below:

$$\log V = \log V_0 - D\{\log(P^0/P)\}^2 \tag{2}$$

The plot of $\log V$ versus $\{\log(P^0/P)\}^2$ is called D–R plot. From the y-intercept of the D–R plot, the micropore volume (V_0) for each sample can be measured and used to calculate the surface area by assuming that the fraction of the surface located in the macropores is negligible. D–R plots for all samples are shown in Fig. 3. The surface areas as calculated from the adsorption of carbon dioxide are given in column 5 of Table 1. The slope of these plots is taken as a measure of the average pore dimension. It appears that the slope of the D–R plot for non-activated sample is very small. Treatment with concentrated sulphuric acid resulted in a slight increase in the slope of the D–R plot, i.e., an increase in the pore dimensions, depending on the amount of sulphuric acid employed.

It is evident from the results in Table 1 that the surface area increases with the increase of the amount of sulphuric acid used. This means that activation with sulphuric acid creates new pores of the micro-type. Table 1 indicates also that comparable areas for each carbon sample are calculated using BET and α_s method. These values are considerable lower than those calculated from V_0, determined from D–R method. Finally, the micropore vol-

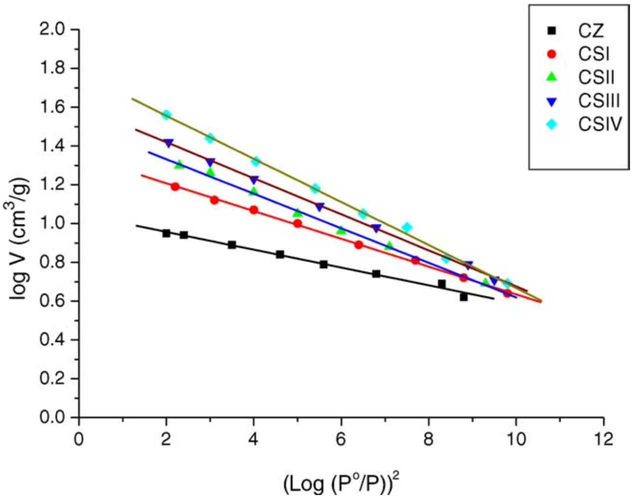


Fig. 3. D–R plots of carbon dioxide adsorbed at 298 K on the studied carbons.

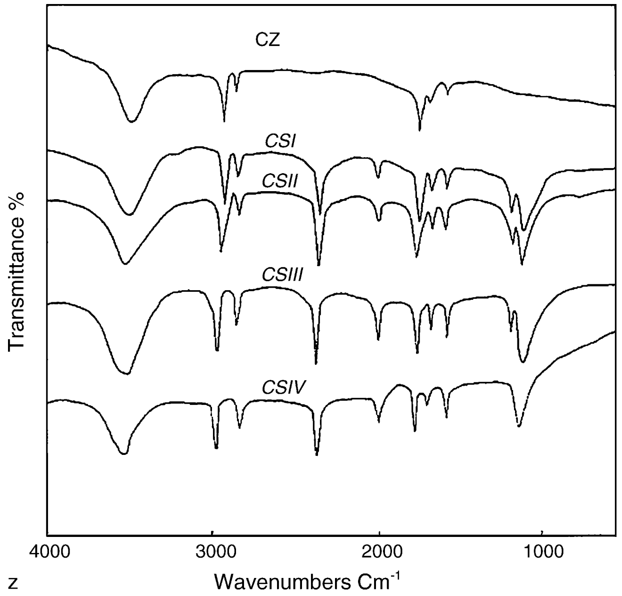


Fig. 4. FTIR spectra of carbonized product “CZ” and sulphuric acid-activated carbons.

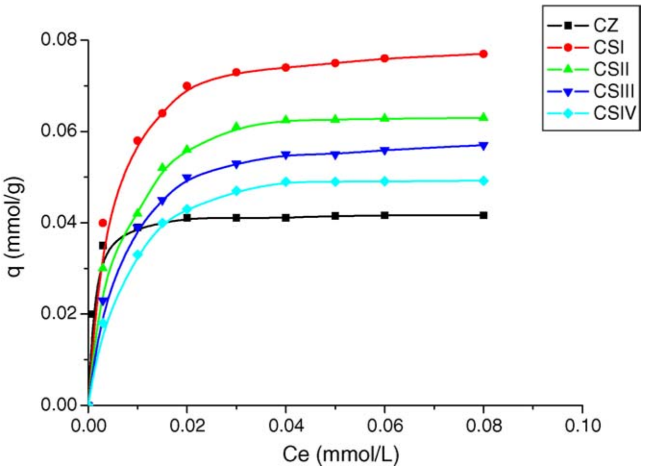


Fig. 5. Adsorption isotherms of phenol on the carbonized product “CZ” and sulphuric acid-activated carbons at 298 K.

umes determined at ($V_0^{0.1}$) are comparable with those obtained from the α_s-method (V_0^{α}). However, the values of $V_0^{0.1}$ and V_0^{α} are always lower than the micro-pore volume (V_p) obtained from nitrogen adsorption isotherms.

The FTIR transmission spectra of the investigated carbons are shown in Fig. 4. The broad bands observed in the spectra of sulphuric acid activated carbons are expected for the surface functional groups, which exist in a wide range of different electronic environments. According to the FTIR spectra presented in Fig. 4 and the literatures [24–26], the studied carbons have surface functionalities with C=O (in carboxylic, anhydride, lactone and ketone) at 1720–1630 cm^{-1}, C=O (lactonic, ether, phenol, etc.) at 1300–1000 cm^{-1}, C–H at 3000–2750 cm^{-1}. The band at about 3500 cm^{-1} can be assigned to the O–H stretching mode of hydroxyl functional groups.

The titration results of the chemical surface groups are presented in Table 2. Inspection of Table 2 reveals that all the carbons possess oxygen functionalities in the form of non-carbonyl, i.e., carboxylic, lactonic and phenolic groups. The concentration of acidic groups in non-activated carbon “CZ” is significantly lower when compared to those obtained from sulphuric acid activation. The total concentration of these groups increased with the increase of the amount of sulphuric acid used in the activation method. However, the total surface acidity of CSIV carbon (4.13 mequiv./g) is slightly higher than the total acidities of CSIII (4.05 mequiv./g) i.e., the total acidities of the two samples are comparable. Table 2 indicated also that phenolic and lactonic groups are more prevalent at low degrees of sulphuric acid treatment (CSI and CSII carbons). Progressive treatment with sulphuric acid decreases the concentration of phenolic groups whereas their lactonic functionality content remains relatively constant. Carboxylic groups were found to increase with increasing severity of acid treatment.

3.2. Adsorption measurements

The equilibrium adsorption isotherms of phenol, resorcinol, hydroquinone and catechol on sulphuric acid activated carbons at 298 K are similar in shape to the Langmuir isotherm. Representative adsorption isotherms are shown in Figs. 5 and 6. Moreover, the application of the linear form of the Langmuir equation was found to be satisfactory over the total range of equilibrium concentrations (not illustrated). The monolayer capacity (mmol/g) for each carbon was calculated from these plots and is listed in Table 3. It is evident from the results in Table 3 that the amounts of phenols adsorbed, without exception decreases with increase of the total acidity of carbon sample as determined using the base neutralization capacity method. Moreover, for each carbon sample, the amount of phenol adsorbed follows the order phenol > hydroquinone > resorcinol > catechol. The fact that more phenol is adsorbed compared with hydroquinone; resorcinol and catechol may refer to the geometry and molecular size of the adsorbate molecule.

Table 2
Concentration and distribution of surface functional groups in tested samples

Sample	Acid:sawdust (w/w)	Phenolic groups (mequiv./g)	Lactones (mequiv./g)	Carboxylic groups (mequiv./g)	Total non-carbonyl (mequiv./g)
CZ	–	0.16	0.26	0.18	0.60
CSI	3:1	0.90	0.70	0.55	2.15
CSII	4:1	1.40	1.25	1.00	3.65
CSIII	5:1	1.10	1.28	1.67	4.05
CSIV	6:1	0.74	1.30	2.09	4.13

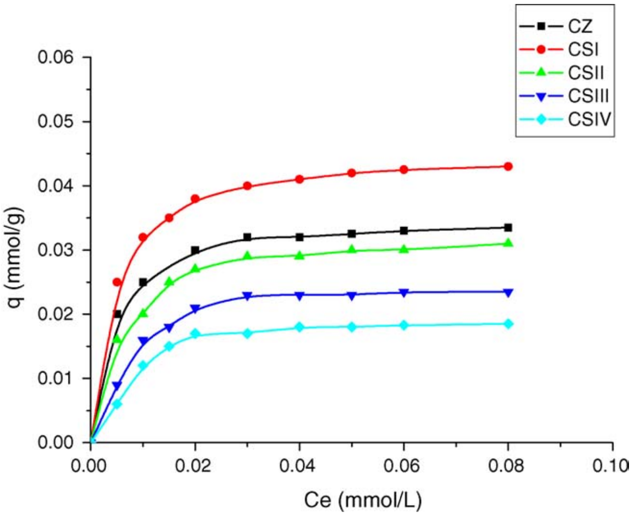


Fig. 6. Adsorption isotherms of hydroquinone on the carbonized product "CZ" and sulphuric acid-activated carbons at 298 K.

As has been previously established [27], phenol adsorption on to activated carbon is achieved by dispersive interactions between the π electrons in the aromatic ring of the adsorbate and π electrons in the carbons. Acidic functional groups on the carbon surface decrease π electron density on the graphene layers of the activated carbons, and, thus, dispersive interactions between π–π electrons are weaker. The fact that, the adsorption of phenols decreases with increasing the surface acidity shows that the chemistry of the carbon surface is an important factor in determining its adsorption capacity. However, the changes induced in the texture of the prepared carbons as a result of sulphuric acid activation do not seem to have a significant role in the adsorption of phenols although activation with sulphuric acid leads to a continuous increase in both micropore volume and surface area. Sulphuric acid activated carbons contain high concentrations of acid functional groups, which may retard the accessibility of micropore structure of the carbons for the adsorption of phenol molecules. These acid functional groups may act as a physical barrier restricting the accessibility of the microporous regions of the carbon samples.

The breakthrough curves of phenol, hydroquinone, resorcinol and catechol using CSI as a selected carbon are shown in Fig. 7. The breakthrough curves are more or less symmetrical around a definite point, which refers to the time at which the effluent concentration equal half of the initial concentration. For phenol this point is located at 123 min, for hydroquinone at 75 min, for resorcinol at 50 min and for catechol at 38 min. The breakthrough capacity $Q_{\text{o.s}}$ expressed in mg substrate per g carbon was obtained for each sample using the following equation [28].

Table 3
Phenol monolayer capacities of investigated carbons

Sample	Acid:sawdust (w/w)	Monolayer capacity (mmol/g)			
		Phenol	Hydroquinone	Resorcinol	Catechol
CZ	–	0.016	0.010	0.008	0.006
CSI	3:1	0.081	0.044	0.033	0.026
CSII	4:1	0.076	0.036	0.022	0.020
CSIII	5:1	0.060	0.028	0.018	0.015
CSIV	6:1	0.048	0.020	0.014	0.013

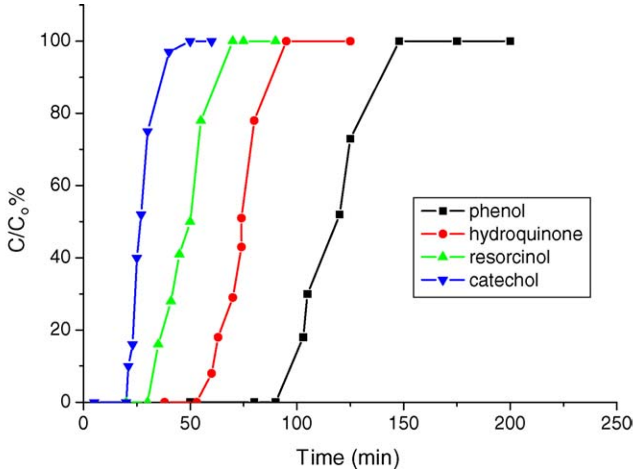


Fig. 7. Breakthrough curves of phenol, hydroquinone, resorcinol and catechol on CSI carbon.

$$Q_{\text{o.s}} = \frac{C_0 V_{\text{mb}}}{W}$$

where C_0 is the initial concentration in mg/ml, V_{mb} the volume (in ml) corresponding to breakthrough $C/C_0 = 0.5$ and W is the weight of carbon sample used. Breakthrough capacity values of 6.12, 3.75, 2.5 and 2 mg/g were measured for phenol, hydroquinone, resorcinol and catechol, respectively. These values follow the order: phenol > hydroquinone > resorcinol > catechol, i.e., the same order found in equilibrium measurements.

4. Conclusions

Non-activated carbon (CZ sample) obtained from heat treatment alone showed lower values of surface area and total pore volume and its surface contained only very small amounts of surface acidity. Treatment of this sample with different amounts of sulphuric acid results in the formation of more surface acidic functional groups and causes slight modifications in the original textural characteristics. FTIR and the selective neutralization method showed that the carbon surface acquires an acidic character with carboxylic groups, which are essentially fixed, along with lactonic and phenolic groups. Hence, treatment with sulphuric acid not only alters the texture properties of the prepared carbons but also their surface chemistry. Phenol adsorption was found to be dependent on the surface acidity of the prepared carbons. The amount of phenols adsorbed, without exception was found to decrease with increasing the concentration of acid groups in the carbon surface.

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