J.Serb.Chem.Soc. 69(5)363-375(2004) JSCS - 3163 UDC 665.587+541.183:541.121 Original scientific paper

An investigation of the functional groups on the surface of activated carbons

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(Received 24 April, revised 16 December 2003)

Abstract: Activated carbons were produced in the laboratory from wood using a 20-run Plackett-Burman experimental design for 19 factors. The obtained batches of activated carbon were analysed by potentiometric titration and FTIR spectroscopy to determine the surface functional groups. The results obtained by potentiometric titration displayed the distribution of individual acidity constants of those groups in the pK range. Considering this parameter, the surface functional groups were divided into carboxyl, lactone and phenol. The linear regression equations reflecting the influence of each operation used for the synthesis on the amount of these functional groups in the obtained activated carbons were generated. The FTIR spectra were used in parallel for the evaluation of the amount and the type of the surface functional groups. Relationships between the two data sets obtained by potentiometric titration and FTIR spectroscopy were evaluated by correlation analysis. It was established that the amount of surface functional groups determined by potentiometric titration positively correlates with the intensity of the peaks of hydrophilic functional groups in the FTIR spectra. At the same time, the negative correlation between potentiometrically determined amount of surface functional groups and the intensity of peaks of hydrophobic functional groups was observed. Most probably, these non-polar formations can take part in the interaction of carbon surface with H⁺/OH⁻ ions and diminish the strength of existent functional groups.

Keywords: activated carbon, functional groups, adsorption, correlation, acid-base equilibrium.

INTRODUCTION

Activated carbons (ACs) are produced with a wide range of properties and physical forms, which leads to their use in numerous applications. They have not been replaced in many industrial processes until now, despite hard competition from the side of polymers, zeolytes and other new-created sorbents. Furthermore, ACs have found usage in a number of new fields and technologies, such as catalysts and catalyst supports, supercapacitors, composite fillers in polymer matrix, gas storage

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and separation, rechargeable batteries, *etc.* The practical use of ACs is, in most cases, based on the fact that the numerous assortments of their modifications are unique in an extremely large surface area, which originates from the porous structure of this material. Due to this large surface area, physical adsorption becomes effective. In many industrial processes physical adsorption plays the most important role. Nevertheless, the surface chemistry of the carbon is also an important factor; this is evident from the constantly increasing number of publications dealing with this topic. The selectivity of ACs for adsorption is dependent on their surface chemistry, as well as on their pore size distribution. The approaches that have been taken to modify the type and distribution of surface functional groups have mostly involved posttreatment of ACs or modification of the precursor composition, although the synthesis route and conditions can also be employed to control the properties of the product.¹ It has been shown that through appropriate chemical reaction, the surface can be rendered more acidic, basic, polar, or completely neutral.² The chemical composition of the precursor also influences the surface chemistry.

It is known that the functional groups are concentrated on the edges of graphene layers.³ Some authors suggest that the distribution of the functional groups on the surface of ACs depends on pore size.⁴ An uneven distribution of functional groups creates surface heterogeneity. Another reason for heterogeneity is the presence of heteroatoms (commonly O, N and S).⁵

Efforts towards a comprehensive understanding of the structure of the surface of ACs are afoot, progressively lining up appropriate information. The basis for this information is a lot of different analytical methods, at the same time these methods are a bare source of ambiguous data. Such a paradox indicates that modern and powerful analytical methods should be applied to the analysis of AC surfaces but the results should be interpreted with definite caution taking into account the extremely complex nature of ACs. Among the elements of complexity are the high surface area resulting from an intricate pore structure, significant differences in the physico-chemical parameters among the heterogeneous surface sites, the occurrance of partial delocalisation of the π -electrons and the ability of certain surface sites to react with water and other solvents. Each analytical method in case of ACs gives only partial information about the surface state. Therefore, a correlation of the obtained results may be useful. The aim of this work was to compare an assortment of surface functional groups of ACs obtained using a set of different operations in the preparation process.

EXPERIMENTAL

The Ac samples in our experiment were synthesized using a set of operations organized in the form of a Plackett–Burman experimental design.⁶ The 20-run design matrix for 19 factors presented in Table I was used to estimate the influence of each operation on the measured parameters. Each position in the column for the rows in Table I represents the batch of ACs prepared using a set of definite preparation conditions (*i.e.*, factors). These conditions (factors) are detailed in Table II. The

given factors were fixed at two levels. The lower level was marked as "-1" the higher one as "+1". Twenty batches of ACs were obtained using this preparation protocol. They were numbered in accordance with the rows in the matrix of the Plackett–Burman experimental design.

TABLE I. A 20-run Plackett–Burman design for 19 factors (operations).

Runs					1	Facto	ors (o	perat	tion 1	numb	ers)	and t	heir	evel	5				
	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12	X13	X14	X15	X16	X17	X18	X19
1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
2	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	$^{-1}$	+1	$^{-1}$	-1	-1	-1	+1	+1	-1
3	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1
4	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	$^{-1}$	+1	-1	-1	-1	-1	+1
5	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1
6	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1
7	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1
8	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1
9	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1
10	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1
11	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1	+1
12	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1	-1
13	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1	+1
14	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1	+1
15	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1	+1
16	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1	+1
17	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1	-1
18	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1	-1
19	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1	+1
20	+1	-1	-1	+1	+1	+1	+1	-1	+1	-1	+1	-1	-1	-1	-1	+1	+1	-1	-1

Pine (*Pinus strobes*) or birch (*Betula papyrifera*) (densities 0.5 and 0.63 g/cm³, respectively) were taken as the raw wood material. Prior to all operations, they were dried at 100 °C for 24 h. The type of wood for each batch was used in accordance with the matrix of the Plackett–Burman experimental design (Table I): pine was used for batches marked with the sign "–1" in column X1; birch was used the batches marked with "+1" in the same column. The next steps in the preparation protocol were chemical activation during pyrolysis by use of CaCl₂ (X2) and NH₄Cl (X3). After treatment with solutions of these reagents, the wood was dried repeatedly and pyrolized at different temperature gradients (operations marked as X4, X5, X6 and X7 in Table II). The produced carbonaceous materials were ground and sieved using an 80-mesh screen. The powder was thoroughly washed, dried and treated with solutions of chemical activators (operations marked as X8, X9, X10, X11, X13 and X14 in Table II) in accordance with the matrix of the Plackett–Burman experimental design (Table I). After executing all these operations, each batch was dried at a certain temperature

,	-		Fixed l	evels	Parameter e	stimators for re-	gr. equations
Jper. No	Operation block	Conditions	(-1)	(+1)	Carboxyl	Lactone	Phenol
X1	Sort of wood	Density/(g/cm ³)	0.50	0.63	0	0	0
X2	Activation during pyrolysis	CaCl ₂ /%	0	10	0	-0.0404	0
X3		$\rm NH_4Cl/\%$	0	10	0.168	0.05409	0
X4	Pyrolysis rate at the temp. interval	$20 - 150 \ ^{o}C$	20	100	0	0	0.08172
X5		$150 - 300 \ ^{\circ}\text{C}$	20	100	0.21493	0.04111	-0.0969
X6		300 – 450 °C	20	100	0	-0.0252	-0.0472
X7		450 – 600 °C	20	100	-0.1592	-0.1217	-0.2752
X8	Activation after pyrolysis	HNO ₃ /%	0	4.5	-0.1212	0.06127	-0.0647
X 9		$\mathrm{H_2C_2O_4}/\%$	0	5	-0.1092	-0.0278	0
X10		$(NH_4)_2S_2O_{8/0/6}$	0	5	0	0.06834	0
X11		$\rm NH_4 NO_3 / \%$	0	5	0	0.03767	0.04814
X12		NaClO ₃ /%	0	5	-0.1733	-0.0654	0
X13		$\rm NH_4Cl/\%$	0	5	0.10174	0.03945	0.12207
X14		${ m H_2SO_4/\%}$	5	25	0.15309	0.07785	0.05323
X15	Saturation	Temperature/°C	20	120	-0.1272	0	-0.0977
X16	Capsulation	Cedar balsam/%	0	3	-0.1489	-0.0959	-0.1228
X17		PVA/%	0	3	0.17707	0	0
X18	Drying	Temperature/°C	40	80	0.12127	0	0
X19	Thermal shock	Temperature/°C	700	1000	0	0.09873	0.05005

Conditions	Carboxyl	Lactone	Phenol
Y intercept (b_0)	1.53146	0.39113	0.74355
Precision estimator $(S(b_i))$	0.0639	0.0065	0.02290
Unbiased deviation $(S(U))$	0.28602	0.02904	0.10239
Calculated F-value	1.08333	1.07143	1.09091
Normal <i>F</i> -distribution	2.6	2.5	2.7

TABLE II. Continued. Statistical evaluation

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(operation marked as saturation, X15, in Table II). The capsulation procedures were executed by treating the carbonaceous powder with an appropriate solution (an ethanolic solution of cedar balsam, X16, or an aqueous solution of poly(vinyl alcohol),X17. The capsulated batches were dried at a certain temperature (X18) and treated under thermal shock conditions (X19). The exposure time in the high temperature zone was 5 s. Finally, each batch of AC was washed with water + dimethylketone mixture (1 : 1), dried and annealed in the tube furnace (nitrogen stream, 2 h, 1100 °C). The synthesized batches of ACs were stored in dark phials filled with nitrogen.

The equipment for the potentiometric titration consisted of a pH meter pH-340 with a glass electrode. The pH changes were measured in solutions of constant ionic strength by adding 0.1 M NaOH or HCl. The pH values were determined after 24 h of contact of the carbon with the solution. The carbon samples were protected by a nitrogen atmosphere during titration and storage.

The FTIR spectra were recorded using a Perkin – Elmer IR – Spectrum BXII spectrometer with a HATR reflectance unit and a ZnSe monocrystal. The powdered samples were placed in a holder on the surface of the monocrystal and evacuated. Before each measurement, the instrument was run to collect the background, which was then automatically subtracted from the sample spectrum.

RESULTS AND DISCUSSION

The functional groups on the surface of ACs are involved in acid – base equilibrium. Due to the complexity and heterogeneity of the carbon surface, inter- and intra-molecular interactions, the strength of these functional groups may be considerably altered. Consequently, as in a case of other complex systems, distinct acidity constants, K_a , for each functional group existing on the surface of an AC cannot be distinguished. In this case, the systems are characterized by a continuous distribution of acidity constants.⁷ Each carbon sample consists of acidic and basic sites with their individual acidity constants K_a .⁸ The fraction of sites with certain K_a in a solution of a definite pH is given by:

$$q = [1 + 10^{(\text{pH}-\text{p}K_a)}]^{-1}.$$
 (1)

In general, an AC sample with a definite set of individual functional groups may be characterized by the Langmuir adsorption isotherm Qvs. pH (with Q being the amount of protons, in mmol/g, either adsorbed or released from the carbon surface). In the case of titration with a base, Q acquires negative values (*i.e.*, protons are released from the carbon surface). The experimentally measured proton-binding isotherm Q(pH) can be represented as an integral equation.:

$$Q(pH) = \int_{pK_1}^{pK_2} q; F(pK_a) dpK_a + Q_0,$$
 (2)

where $F(pK_a)$ is the distribution of acidity sites in terms of pK values, Q_0 is related to an arbitrary reference level and includes the amount of protons reacted with groups outside the integration limits. The function $F(pK_a)$ is a differential quantity, representing the number of sites with pK_a values in the interval $pK_1 - pK_2$. Integration of this function yields the total amount of sites whose pK_a values belong to this interval.

The number of functional groups including even a single heteroatom, *e.g.*, oxygen, is rather significant. This number significantly increases in the case of hete-



Fig. 1. Proton binding isotherms obtained from the batches of AC. The adsorbed/desorbed amount of protons is expressed as *Q*-function. Batch numbers are given next to the corresponding curves.

roatoms, such as sulphur or nitrogen. Therefore, the concept of conventional functional groups is often used to characterize the surfaces of ACs.⁹ These groups are divided into: carboxyl ($pK_a = 2.0 - 4.0$), lactone ($pK_a = 4.0 - 7.0$) and phenol ($pK_a = 7.0 - 10.0$); in the brackets are given the pK_a interval typical for the type of functional groups.⁵

The proton binding isotherms obtained from the potentiometric titration of the 20 synthesized ACs are presented in Fig. 1. These *Q*-functions were differentiated; the amounts of the different types of functional groups in every batch of ACs were determined after integration of the $F(pK_a)$ function over the appropriate pH interval. The obtained results are presented in Fig. 2. The amount of carboxyl functional groups constitutes approximately a half of the total amount of all functional groups for the majority of the AC batches. In several batches, a significant amount of phenol functional groups was found as well. The amount of lactone functional groups in all the synthesized batches is low. Only batch # 8, which is distinguished by an extremely high content of carboxyl, lactone and phenol functional groups, is an exception.



Fig. 2. Amount of conventional surface functional groups found in the batches of AC.

Models reflecting the influence of each operation used in the preparation of ACs on the measured parameters (amount of carboxyl, lactone and phenol functional groups on the surface of ACs) are given in the form of a linear regression:

$$C = b_0 + \sum_{j=1}^{19} b_j x_j,$$
(3)

where *C* is amount of a functional group (mmol/g) on the surface of an AC sample, *b* are parameter estimators (coefficients) in the given equation, x_j are values of the *j*-parameter expressed in terms of dimensionless units. The values of b_j and the statistical evaluation of the corresponding equations are presented in Table II. The adequacy of each regression equation was tested by means of an unbiased variance estimator *S*(U) for experimental error and the *F*-test. On this basis, the absolute values of b_j which were smaller than the precision estimator *S*(b_j) for a certain regression equation were equated to zero. The data in Table II show that all three presented regression equations for carboxyl, lactone and phenol functional groups are adequate.

The values of the b_j coefficients presented in Table II reflect the influence of the operations used for the preparation of ACs on the amount of functional groups. A high positive value of b_j indicates that mainly this *j*-operation acts toward increasing the content of functional groups. A negative value shows that this operation hinders the process of functional group formation. Comparing the obtained b_j values, conclusions about the process of AC synthesis could be made. An increased amount of carboxyl and lactone functional groups is found after chemical activation with NH₄Cl (operation X3 in Table I and Table II). High rates of pyrolysis at low tempera-



Fig. 3. FTIR reflectance spectra obtained from the batches of AC. Batch numbers are given next to corresponding curves.

tures (operations X4 and X5) are favorable for the formation of certain surface functional groups. On the contrary, at high temperatures this process becomes more favorable for low rates of pyrolysis (operations X6 and X7). The reagents used for chemical activation after the first step of pyrolysis may be divided into several groups. Nitric acid is favorable for lactone formation, yet it blocks the formation of carboxyl and phenol functional groups. HN_4Cl and H_2SO_4 are agents which stimulate the formation of all functional groups, while $NaClO_3$ and $H_2C_2O_4$ could be considered as acting in the opposite direction. Capsulation of the granules with cedar balsam (operation X16) prevents the formation of surface functional groups. Thermal shock is favorable for the formation of lactone and phenol functional groups on the surface of ACs. In general, considering the influence of the operations used for the preparation of the ACs, it can be concluded that a definite set of surface functional groups may be synthesized using an appropriate synthesis protocol.

TABLE III. Correlation between the amount of the functional groups and peak heights in the FTIR spectra

		Co	rrelation coef	ficients
Wavenumber/cm ⁻¹	Assignment of peaks*]	Functional gr	oups
		Carboxyl	Lactone	Phenol
610	b	0.699	0.472	0.215
630	b	- 0.066	-0.068	- 0.126
650	b, c	- 0.833	-0.678	-0.304
670	b, c	-0.434	-0.719	-0.552
750	b, c	-0.181	-0.167	0.138
810	с	-0.118	-0.258	-0.024
870	a, c	-0.140	- 0.194	0.077
1050	a, d	- 0.393	-0.179	-0.081
1090	d	-0.271	-0.119	0.049
1150	d, e	- 0.651	-0.354	-0.097
1410	e, g	-0.003	0.020	0.054
1450	e, f, g	0.253	0.563	0.805
1470	f, g	0.566	0.756	0.780
1490	f, g, h	0.389	0.501	0.930
1500	f, g, h, i	0.202	0.302	0.812
1510	f, g, h, i	0.368	0.802	0.469
1530	f, g, h, i	0.555	0.718	0.751
1550	f, g, h, i	-0.036	0.075	0.120
1570	f, g, h, i	-0.128	-0.013	-0.134
1630	f, i, j, k	0.314	0.746	0.326
1650	f, i, j, k	0.170	0.176	0.214
1680	i, j, k	-0.238	-0.126	0.248
1690	i, j, k	0.230	0.456	0.887
1710	i, k	0.788	0.471	0.247
1730	k	- 0.415	-0.709	-0.384

		Correlation coefficients Functional groups				
Wavenumber/cm ⁻¹	Assignment of peaks*					
		Carboxyl	Lactone	Phenol		
1750	k	0.127	0.291	- 0.151		
1770	k	0.208	0.153	0.138		

TABLE III. Continued

*Assignment of peaks: a – aliphatic C–H; b – C–Hal; c – adjacent aromatic C–H; d – stretching C=O; e – bending O–H; f – bending N–H; g – carboxylate ion –COO⁻; h – aromatic compounds (conjugated system); i – double bond region; j – amide C(N)=O; k – keto-group C(R)=O

The FTIR spectra of the synthesized ACs are presented in Fig. 3. The analysed samples are grouped in order to obtain maximum distinctness. The spectra consist of quite a number of small overlapping peaks in the regions of 600 - 700, 1000 -1200, 1400 - 1800 and 3600 - 3800 cm⁻¹. These kind of IR sapectra are typical for ACs.¹⁰ The biggest problem is the assignment of the small peaks to definite functional groups. For this purpose a correlation analysis between the amount of the different functional groups (determined potentiometrically) and the peak height at a certain wavenumber was performed. The correlation coefficients obtained during this analysis are presented in Table III. The assignments of the peaks taken for the correlation analysis are also presented in this Table. The cases of good correlation where the correlation coefficient exceeds 0.4 are clearly seen. The region of positive correlation lies in the range 1470 - 1710 cm⁻¹; significant negative correlations are observed at 650 - 670 and 1050 - 1150 cm⁻¹. Vibrations of keto- aminoand nitro-groups are concentrated in the region comprising positive correlations.¹¹ These functional groups are hydrophilic and can take part in the acid - base equilibrium. Equivalents of these functional groups are detected by means of potentiometric titration and are assumed to be carboxyl, lactone or phenol functional groups. The region of negative correlation lies in the range of aliphatic C-H and adjacent aromatic C-H vibrations. It follows that these non-polar fragments on the surface can diminish the strength of interaction of the carbon surface with H⁺/OH⁻ ions. This fact illustrates the complexity of AC surfaces including their participation in acid - base equilibria as well. The process depends not only on the variety of the functional groups but also on their location on the surface and the affect of neighboring groups on this equilibrium to a significant extent.

CONCLUSIONS

Twenty batches of ACs were prepared from wood using a 20-rum Plackett–Burman experimental design for 19 factors. The synthesis protocol was chosen to obtain the maximum variety of surface functional groups among the AC batches. The amount and type of functional groups were determined by potentiometric titration

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and FTIR spectroscopy. The results of potentiometric titration were used for the evaluation of the influence of synthesis conditions on the amount and type of functional groups formed on the surface of the ACs. Moreover, data from the FTIR spectra were correlated with the results of the potentiometric titrations. The results obtained demonstrate both positive and the negative correlations. The positive correlations are, in most cases, observed in the region of hydrophilic functional groups. The effect of negative correlation is displayed in the range of hydrophobic functional groups and surface formations. The results obtained imply that a set of functional groups on the surface of ACs is affected by mutual interaction to a significant extent.

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PROU^AVAWE FUNKCIONALNIH GRUPA NA POVR[INI AKTIVNIH UGQEVA

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Aktivni ugqevi dobiveni su laboratorijski od drveta kori{}ewem Plackett-Burman-ovog postupka kojim se mo'e u 20 eksperimenata kontrolisati 19 nezavisnih faktora. Dobivene porcije aktivnog ugga analizirane su potenciometrijskom titracijom i FTIR spektroskopijom radi odrelivawa povr{inskih funkcionalnih grupa. Dobiveni rezultati potenciometrijskih titracija pokazali su raspodelu pojedina~nih konstanti kiselosti ovih grupa u odre|noj pK oblasti. Na osnovu ovih parametara povr{inske funkcionalne grupe su podeqene u karboksilne, laktonske i fenolne. Odrejene su jedna~ine na osnovu linearne regresione analize koje pokazuju uticaj svake operacije pri sintezi dobivenih aktivnih ugqeva na broj ovih funkcionalnih grupa. FTIR spektri su kori{} eni, takole, za odrelivawe vrste i broja ovih funkcionalnih grupa. Korelacionom analizom utvrlen je odnos izmeļu podataka dobijenih potenciometrijskom titracijom i FTIR spektroskopijom. Utvrļeno je da postoji dobra korelacija izmelu broja funkcionalnih grupa utvrlenog potenciometrijskom metodom i FTIR spektroskopijom. Meļutim, opa`ena je negativna korelacija izmeļu broja funkcionalnih grupa odre|enog potenciometrijski i intenziteta maksimuma za hidrofobne funkcionalne grupe u FTIR spektrima. Najverovatnije da ove nepolarne strukture uzimaju u~e{}e u interakciji povr{ine aktivnog ugwa sa H⁺/OH⁻ jonima i smawuje ja~inu postoje}ih funkcionalnih grupa.

(Primqeno 24. aprila, revidirano 16. decembra 2003)

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