Distribution of Na, K, Mg and Ca in activated carbons

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The residual content of inorganic ions (sodium, potassium, magnesium and calcium) was determined (by AAS) in activated carbons produced from wood. The effect of preparation conditions on the distribution of inorganic ions was evaluated. It has been established that the high temperature raising rates in the temperature zone above 500 K most probably favors the formation of closed pores inaccessible to the leaching reagents, while both high temperature raising rates below 500 K and the thermal shock are favour the formation of an open-pore structure. Considering the correlation between K and Na residual levels in activated carbons, an assumption was made that potassium, being a biogenic element, opens the ways for sodium to be introduced into the bulk of activated carbon.

Key words: activated carbon, atomic absorption spectroscopy, calcium, magnesium, potassium, sodium

INTRODUCTION

The purity of activated carbon (AC) depends on the source, the manufacturing process and formulation. Ash content of carbon is the residue that remains when the carbonaceous portion is burned off. The ash consists mainly of minerals, such as silica, iron, magnesium, calcium, potassium, etc. Generally, ash in activated carbons is not desirable and considered as impurity. Though, certain sorts of commercial carbons may contain a significant amount of ash; *e.g.*, bone char used as an effective agent for ion exchange contains up to 90% of ash [1]. Mackay and Roberts found that the components of wood (lignin, cellulose) yield chars of similar microporosity, while inorganics (ash) may fill or block some portion of the existing micropore volume [2]. This may partially explain the low surface area observed in carbons with a high ash content. Although all researchers agree as to the role of large amounts of minerals in activated carbons, they are arguing about the microamounts. A fine knowledge of AC structure is necessary in this case. The quality and quantity of ions released into water by activated carbons can modify the adsorption mechanism. Indeed, some ions can co-adsorb when they encounter organic molecules near the surface of the carbon. For example, calcium ions modify adsorption of some organic compounds [3, 4]. Inorganic impurities were found to cause irreversible adsorption. Grant and King [5] studied several possible AC characteristics, including mineral content, that might be responsible for irreversible adsorption of phenolic compounds onto AC surface. Diamadopoulos et al. [6] concluded that an increase of ash content resulted in a linear decrease of phenol adsorption. The presence of mineral impurities in the base material and the method of preparation influence the formation of ringed structures at the edges of the basal planes and yield free valences which are very reactive [7]. Chemical heterogeneity of metal oxides on the carbon surface is related to a specific environment around each hydroxyl group. Coordination of the hydroxyl groups with one or more lattice metal ions yields a variety of sites having different properties. Also, the neighboring sites can be affected by hydrogen bonding between them. Metal oxides of the form $MO_x(OH)_y$ present an assortment of surface hydroxyl groups ranging from Brønsted acids to Brønsted bases [8].

Distribution of inorganic components (calcium, magnesium, potassium and sodium) among the AC samples produced from wood in the laboratory was determined in this research. Three of those elements (Ca, Mg and K) are regarded as biogenic. Ca and Na might be introduced during the process of AC preparation. The objective of this work was to find

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out the influence of preparation conditions on the distribution of these inorganic components.

EXPERIMENTAL

AC samples were synthesized using a set of technological operations presented in Table 1. These operations are described in detail elsewhere [9]. All nineteen operations listed in Table 1 were executed consequently. The matrix used was a 20-run Plackett–Burman experimental design for 19 variables (factors) [10].

The content of inorganic ions in AC samples was determined by ashing ~0.5 g of probe in a SNOL-16 muffle furnace at 900 K for 24 h. The residual ash was dissolved in 25 ml of 10 M hydrochloric acid, filtered and diluted up to 100 ml. The filtrate was analyzed for metals using a Hitachi 170–50 atomic adsorption spectrometer equipped for flame analysis. All AC samples were analyzed for metals (in brackets the adsorption line, in nm, and flame conditions are pointed out): Ca (422.7; acetylene + air), Mg (285.2; acetylene + air), K (766.5; propane + butane + air) and Na (589.0; propane + butane + air).

RESULTS AND DISCUSSION

There is a large number of methods of preparing ACs; they could be divided into physical and chemical processes [11]. These procedures change the physico-chemical structure of AC, i.e. the specific surface area, porosity, surface functional groups (nature and number) and the amount of residual non-carbon components (ash). In the presence of chemical reagents, the process normally takes place at a temperature lower than that used in the physical activation process, and the yields of carbon are usually high. It has been established that oxidative treatment of AC with nitric acid significantly increases the specific surface area of this material [12]. Oxidation increases the surface reactivity and the adsorption of water vapor [13]. The thermal process is essentially marked by a decrease in the number of acidic surface functional groups [14]. Ash may interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions [15]. Almost all activated carbons require some amount of acid leaching to reduce the high ash content. Acetic acid and hydrochloric acid are listed among chemicals most frequently used for this purpose [16].

Table 1. **Technological operations used for preparation of AC samples**

No. of operation	Generalized groups of technological operation (units of variables)	Conditions of technological operations		
		Measured parameters	Levels of variables fixed	
			low(−1)	high (+1)
1	Density of raw material (kg m^{-3})	Wood density	510	630
2	Chemical activation during pyrolysis (wt% of activator)	CaCl$_2$	0	10
3		NH$_4$Cl	0	10
4	Rate of pyrolysis at the interval of temperature (deg/h)	293–423 K	20	100
5		423–573 K	20	100
6		573–723 K	20	100
7		723–873 K	20	100
8	Chemical activation after pyrolysis (wt% of activator)	HNO$_3$	0	4.5
9		H$_2$C$_2$O$_4$	0	5
10		(NH$_4$)$_2$S$_2$O$_8$	0	5
11		NH$_4$NO$_3$	0	5
12		NaClO$_3$	0	5
13		NH$_4$Cl	0	5
14		H$_2$SO$_4$	5	25
15	Saturation (K)	Temperature	293	393
16	Capsulation (wt% of capsulator)	Cedar balsam	0	3
17		PVA	0	3
18	Drying (K)	Temperature	313	353
19	Thermal shock (K)	Temperature	973	1273

Higher ash contents require more vigorous acid leaching. Sometimes the steps of additional burn-off are introduced into the process of AC preparation [17].

Twenty AC samples were produced under the protocol of Plackett and Burman experimental design, varying the methods of activation and purification. These methods were chosen taking into account the conditions mentioned above. The densities of the produced samples differed in a wide range (a bulk density from 134 up to 510 kg m^{-3}, a particle density from 374 up to 579 kg m^{-3}, and a pycnometric density from 1830 up to 2260 kg m^{-3}) [9]. The amounts of inorganic components determined in the AC samples are listed in Table 2. Calcium is prevailing over the other elements; the content of magnesium, potassium and sodium amounts to ~$^1/_{50}$ of calcium levels. This kind of element distribution may be a consequence either of the higher content of Ca in a source material or the technological operations themselves. To answer this question, one should compare the coefficients of technological operations in prediction equations obtained from the Plackett–Burmann experimental design. These data for each element are given in Table 3.

The most significant positive coefficient in the case of sodium is b_{12}. It represents the influence of chemical activation by the use of sodium chlorate. Most probably NaClO$_3$ is a source of contamination itself.

The positive coefficients in the prediction equation of potassium are b_5, b_{12} and b_{16}, characterizing

Table 3. Coefficients of technological operations (b) in prediction equations for the residual content of Na, K, Mg and Ca in AC samples

Coeffi-cients	b values for ions			
	Na	K	Mg	Ca
b_0	0.360	0.270	0.450	8.805
b_1	0	0	0	0
b_2	0	0	0	0.093
b_3	0	0	–0.058	0
b_4	0	–0.046	0	0
b_5	0	0.067	0	0.573
b_6	0	0	0	0
b_7	0	0	0.057	0
b_8	0	0	0	0
b_9	0	0	0.042	0.500
b_{10}	0	0	–0.054	0.140
b_{11}	0	0	0	0
b_{12}	0.283	0.150	0	0
b_{13}	0	0	0	0
b_{14}	0	0	–0.087	0
b_{15}	0	0	0	0
b_{16}	0	0.070	0	4.483
b_{17}	0	0	0	0
b_{18}	0	–0.045	0	–4.169
b_{19}	–0.048	–0.075	–0.161	0

the influence of high pyrolysis rates in the temperature interval 423 K to 573 K, chemical activation with NaClO$_3$ and capsulation with cedar balsam. Cedar balsam, containing up to 0.01% of K [18], should be a possible source of contamination. The role of sodium chlorate is less evident from the data available. The conditions of pyrolysis most probably favor the formation of closed pores. The most significant negative b values in the case of potassium are obtained for the thermal shock at higher temperatures and for the higher temperatures of drying before the thermal shock. These procedures may originate an open-pore structure.

In the case of magnesium, the values of almost all b coefficients are negative. This should suggest that magnesium present in the source material (wood) is lost during the steps of pyrolysis, activation and leaching. Most significant in this process are pre-activation of wood with ammonium chloride, oxidation with ammonium persulfate, activation with sulfuric acid and the thermal shock. These procedures must probably originate an open-pore structure, which favors the loss of magnesium ions in the stages of leaching. The positive values of b in the prediction equation of Mg are obtained for the high carbonization rates at high temperatures. We expect this operation to favor the formation of closed pores inaccessible for leaching.

The prediction equation of Ca contains a significant positive b_2 coefficient, which represents the

Table 2. Na, K, Mg and Ca levels determined in AC samples

No. of sample	Amount of inorganic ions (mg/g of AC)			
	Na	K	Mg	Ca
1	0.75	0.40	0.45	3.25
2	0.07	0.15	0.65	3.20
3	0.05	0.06	0.40	1.50
4	0.06	0.16	0.53	7.00
5	0.06	0.17	0.20	47.50
6	0.75	0.60	0.54	23.00
7	0.56	0.15	0.34	9.75
8	0.06	0.06	0.20	1.48
9	0.06	0.12	0.43	10.30
10	0.74	0.38	0.45	1.28
11	0.13	0.21	0.38	30.00
12	0.14	0.22	0.65	2.30
13	0.76	0.38	0.63	2.00
14	0.76	0.68	0.65	3.50
15	0.68	0.49	0.45	1.80
16	0.76	0.83	0.38	10.30
17	0.07	0.07	0.43	2.88
18	0.63	0.19	0.20	1.53
19	0.08	0.04	0.58	6.00
20	0.07	0.07	0.48	7.53

activation of wood with calcium chloride. It is obvious that the reagent itself is a source of contamination with Ca. Another positive coefficient in this equation is b_{16}, representing the capsulation of AC samples with cedar balsam. The reagent (cedar balsam containing 0.01%) [18] is a source of contamination as well. The technological operations, which raise the most significant negative values to Ca, are activation with oxalic acid and a high drying temperature before the thermal shock. Oxalic acid may extract Ca^{2+} ions, which later are removed by leaching; the higher drying temperature may favor this extraction.

The correlation coefficients among the data elements are presented in Table 4. The coefficients of correlation of inorganic component content are not significant in most cases. The only exception is found for the [K] / [Na] correlation, $r = 0.814$. The graph of [K] / [Na] content distribution is shown in Figure. The higher content of potassium is found in AC samples with a higher content of sodium. The values of Na content are divided into two groups, while K content is distributed gradually. Results of this nature show the possible ways of sodium introduction into the bulk of activated carbon. This is possible during treatment of raw material with sodium chlorate; though, the sodium content is increased only in the case of a higher potassium content. Considering that potassium is a biogenic element, a conc-

lusion about some kind of selective ion-exchange during the preparation of AC samples could be made [19].

CONCLUSIONS

A comparison of the values of parameter estimators in the prediction equations showed that the reagents used for pyrolysis may be a source of contamination. The residual amounts of inorganic ions are hardly removed by leaching. The process of thermal treatment is of high importance for the distribution of inorganic ions in AC samples. High temperature raising rates in the temperature zone above 500 K most probably favors the formation of closed pores, which are inaccessible to the leaching reagents. At the same time, both high temperature raising rates below 500 K and the thermal shock favor the formation of an open-pore structure. Considering the correlations among the amounts of inorganic components in AC samples, a close correlation between K and Na content is established. It is highly probable that potassium, being a biogenic element, opens the ways for sodium to be introduced into the bulk of activated carbon during the process of AC preparation.

Table 4. **Coefficients of correlation among the data elements**

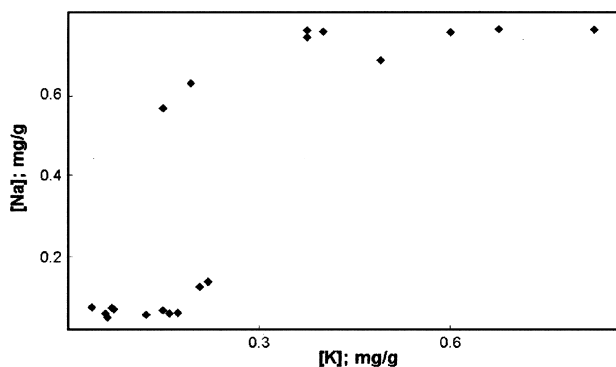| Data elements	Coefficients			
	Ca	Mg	K	Na
Ca	–	–0.352	0.021	–0.187
Mg	–0.352	–	0.229	0.103
K	0.021	0.229	–	0.814
Na	–0.187	0.103	0.814	–

Figure. Plot of residual Na content vs. residual K content in AC samples

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Na, K, Mg IR Ca PASISKIRSTYMAS AKTYVINTOSE ANGLYSE

S a n t r a u k a

Atominės absorbcijos metodu buvo nustatyti liekamieji Na, K, Mg ir Ca kiekiai aktyvintos anglies pavyzdžiuose, paruoštuose iš medienos žaliavos. Tirta aktyvintos anglies paruošimo operacijų įtaka šių neorganinių elementų pasiskirstymui skirtingais būdais paruoštuose pavyzdžiuose. Paruošimui naudota keletas pirolizės, aktyvinimo ir gryninimo operacijų, kurios buvo išdėstytos nuosekliai pagal Placketto–Burmano planavimo matricą, sudarytą iš 20 bandymų 19-ai veiksnių.

Gautieji rezultatai įgalino daryti išvadą, kad dideli pirolizės greičiai, esant aukštesnėms nei 500 K temperatūroms, didina uždarų porų susidarymo tikimybę, todėl gryninimo operacijos būna mažiau efektyvios. Tuo tarpu dideli pirolizės greičiai, esant žemesnėms nei 500 K temperatūroms, bei termosmūgio operacija didina atvirų porų skaičių, o tai leidžia efektyviau išgryninti aktyvintos anglies pavyzdžius. Buvo nustatyta egzistuojanti liekamojo Na ir K kiekio glaudi koreliacija aktyvintose anglyse. Tuo pagrindu padaryta prielaida, kad kalis, esantis medienoje ir būdamas augalų biogeninis elementas, atveria kelius į aktyvintas anglis patekti natriui.