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THE INFLUENCE OF HIGH-TEMPERATURE MODIFICATION OF ACTIVATED CARBON ON THE EFFECTIVENESS OF REMOVING CR(III) AND CR(VI) FROM WATER

Activated carbon was modified by means of air and for 1, 2, 3 hours at the temperature of 300, 400 and 500 °C. The results of this modification were evaluated based on the changes of cation-exchangeable properties of activated carbon (chromium cation adsorption), the changes of anion-exchangeable properties (chromate anion adsorption), the changes in its porous structure (determined on the basis of bulk mass) and adsorption of organic compounds (phenol and methylene blue). Carbons modified by means of air, exhibited better cation-exchangeable properties, but worse anion-exchangeable properties and significantly changed porous structure. Carbons modified by means of nitrogen under conditions of poor air access had also a greater number of cation-exchangeable units, but their porous structure was changed insignificantly.

1. INTRODUCTION

The ion-exchangeable properties of carbon are determined by a number and the structure of functional units on the carbon surface. Simultaneously, the ion-exchangeable properties depend not only on the amount of particular oxides, but also, among others, on the interactions among the constituents of solution, in which adsorption occurs [1]. The complexity of phenomena which happen at the same time make it difficult to evaluate in a fast and simple way the possibility of applying the carbons examined to the specified aims.

The advantage of the carbon is its huge selectivity which allows removal of heavy metals in an effective way at a small interference in such ions as magnesium and calcium. It is possible to use activated carbon to purify water, which is used, among others, for consumption, because there is the possibility of obtaining very tiny final con-

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centrations of contaminants. There is also the possibility of conducting the regeneration of activated carbon which was previously used out during the ion-exchangeable adsorption [2]–[4]. The disadvantage of such a method is, however, low adsorption capacity of technical carbon in relation to ions. That is why a separate problem is, apart from identification and measurement of the amount of functional groups, the enlargement of their number.

The aim of the research was to evaluate the influence of the temperature, oxidation time and oxidizable gas on the carbon surface on the anion- and cation-exchangeable properties of activated carbons. The evaluation of these properties was conducted on the basis of chromate anion and chromium cation adsorption. These contaminants can be found in drinking water and are the subject of research into their adsorptive removal from water [5]–[7].

2. THE METHODOLOGY OF RESEARCH

The granular activated carbon WG-12, produced by GRYFSKAND in Hajnówka, was used in the research. This carbon, in connection with high pH value of water extract, was partially subjected to ash removal by means of 10% hydrochloric acid. The ash in activated carbons consists mainly of SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , MgO , Na_2O , K_2O [8], [9].

The carbon, after drying, was modified in a rotary furnace at the temperature of 300, 400 and 500 °C for 1, 2 and 3 hours at a constant flow of air and nitrogen. Unmodified carbon which had been subjected to ash removal was further called WGO, and other modified carbons were called, e.g., WG300-1p (300 is a modification temperature; 1 stands for modification time (1 h), p is air which is delivered during the modification). The carbon subjected to ash removal and modified carbon were used to the adsorption of chromate anion Cr(VI) and chromium cation Cr(III). The form in which Cr(VI) and Cr(III) appear in the solution is dependent on pH value and the concentration of both ions [10], [11]. That is why the adsorption of chromate anion was conducted in the solution of pH 7, and in the case of chromium cation in the solution of pH 6. The adsorption was conducted under static conditions by adding 1 g of activated carbon to 250 cm³ of Cr(VI) or Cr(III) solution. The time of contact between carbon and solution was established on the basis of the previous research and amounted 24 hours (two hours of shaking and 22 hours of static contact) [3].

On unmodified carbon and on modified carbons there was conducted the static adsorption of phenol at the initial concentration of 600 mg/dm³, methylene number was determined according to the norm: PN-82/c-97555.03 and bulk mass according to the norm: PN-90/C-97554.

3. RESULTS AND DISCUSSION

The results of adsorption of chromium cation on WG-12 technical carbon and modified carbons at the temperatures of 300, 400 and 500 °C are depicted in figures 1–3. All modified preparations have got higher adsorption capacities in relation to chromium cation. There were not observed greater differences within the examined range of temperature and at different times, in the case of modification in the inert gas atmosphere, e.g. nitrogen. In this case, an improvement of adsorption properties (table 2) may be connected with small content of oxygen in the pores of activated carbon being supplemented during the process of putting the carbon again into the rotary furnace and with the lack of air-tightness of the furnace. In such a case, this small amount of oxygen limits the processes of oxidation and causes only the increase in cation-exchangeable capacities of carbons from 10 up to 17%.

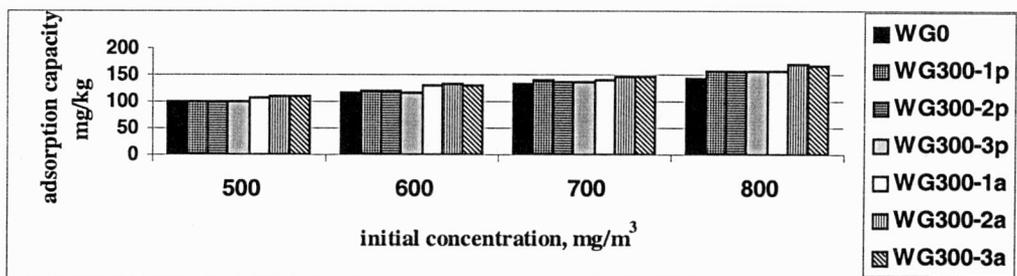


Fig. 1. The adsorption capacities of modified carbons at the temperature of 300 °C in air or nitrogen atmosphere in relation to Cr(III)
p stands for the air delivered during carbon modification, *a* is the nitrogen carried away

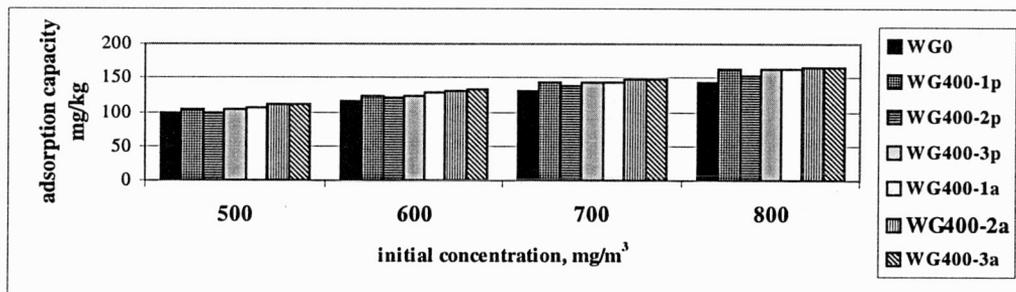


Fig. 2. The adsorption capacities of modified carbons at the temperature of 400 °C in air or nitrogen atmosphere in relation to Cr(III)

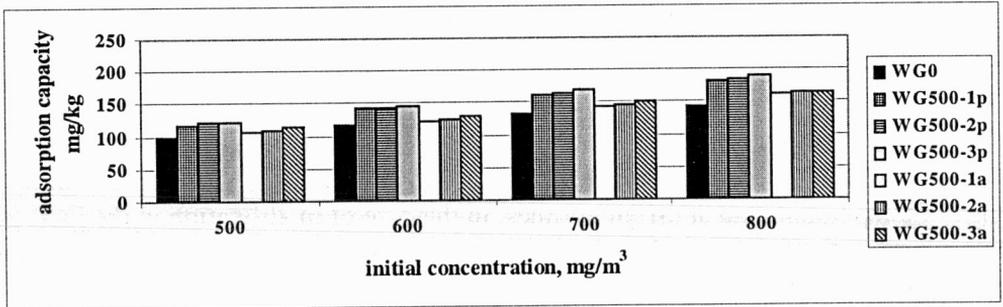


Fig. 3. The adsorption capacities of modified carbons at the temperature of 500 °C in air or nitrogen atmosphere in relation to Cr(III)

In the case of carbon oxidation in air atmosphere, there were also obtained the carbons of higher adsorption capacities in relation to this cation. The differences in the concentrations of Cr(III) removed from the solution due to adsorption by unmodified and modified carbons at the temperatures of 300 and 400 °C were small and ranged from 13 up to 22% (table 1). There were obtained much better results for the carbon modified at 500 °C. At an initial concentration of 800 $\mu\text{g}/\text{dm}^3$ and modification time of 3 hours, the removal of the cation examined was more efficient, i.e. 35%.

Table 1

Removal of trivalent chromium on modified carbons at the initial concentration of 800 $\mu\text{g}/\text{dm}^3$ (%)

Carbon		T = 300 °C		T = 400 °C		T = 500 °C	
		Nitrogen	Air	Nitrogen	Air	Nitrogen	Air
WG0	68						
WG1		79	79	73	82	79	91
WG2		85	79	83	77	83	93
WG3		83	79.5	83	82	84	97

The influence of modification on anion-exchangeable properties, which were analysed on the basis of chromate anion adsorption, was negative in all cases (figures 4–6, table 2). A decrease in adsorption capacities took place both for carbons kept in the nitrogen atmosphere and for carbons kept in the air atmosphere. The results of sorption of chromium ions on carbons modified at 500 °C in the nitrogen atmosphere were found to be most similar to the results of their sorption on unmodified carbons.

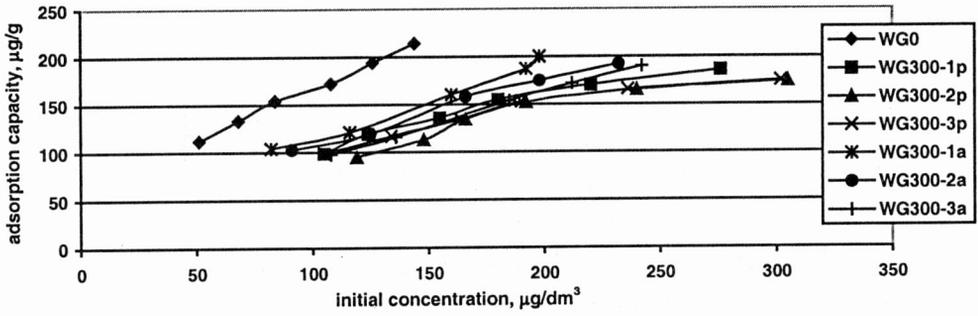


Fig. 4. Isotherms of Cr(VI) adsorption on unmodified carbon and on carbons modified at 300 °C in the air and nitrogen atmosphere

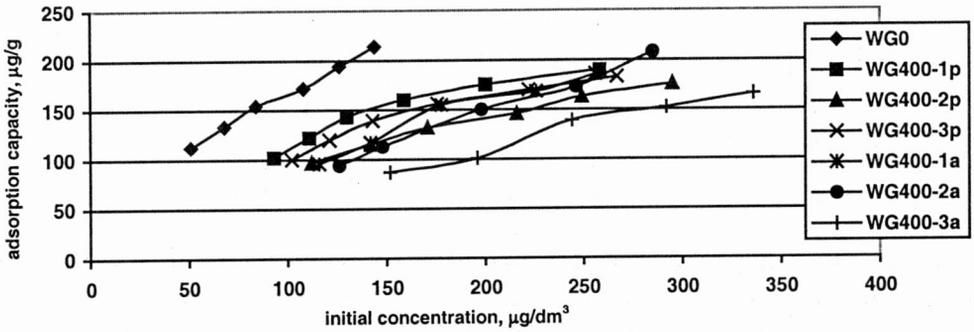


Fig. 5. Isotherms of Cr(VI) adsorption on unmodified carbon and on carbons modified at 400 °C in the air and nitrogen atmosphere

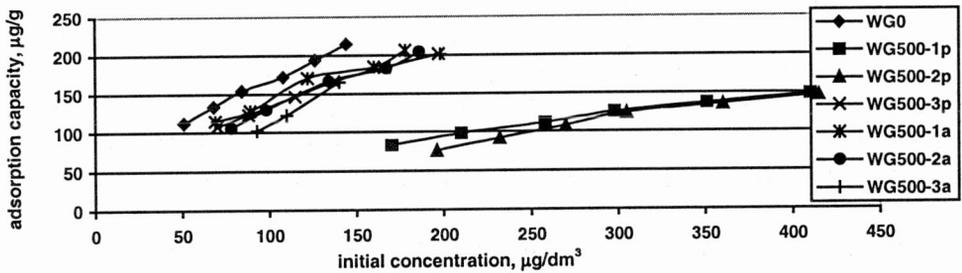


Fig. 6. Isotherms of Cr(VI) adsorption on unmodified carbon and on carbons modified at 500 °C in the air and nitrogen atmosphere

Table 2

The constants of Freundlich and Langmuir isotherms for Cr(VI)

Carbon	Freundlich isotherms			Langmuir isotherms		
	K_F , $\mu\text{g/g}$	$1/n$	R^2	Q_m , $\mu\text{g/g}$	K_L , $\text{dm}^3/\mu\text{g}$	R^2
WG0	10.55	0.603	0.995	384.6	0.0008	0.994
WG300-1p	5.267	0.642	0.970	416.7	0.0031	0.984
WG300-2p	4.331	0.660	0.912	588.2	0.0016	0.856
WG300-3p	7.582	0.560	0.958	344.8	0.0039	0.983
WG300-1a	3.775	0.743	0.975	526.3	0.0029	0.958
WG300-2a	4.299	0.699	0.984	454.5	0.0031	0.972
WG300-3a	1.907	0.84	0.998	769.2	0.0013	0.999
WG400-1p	7.410	0.595	0.944	400.1	0.0039	0.963
WG400-2p	5.522	0.612	0.972	357.2	0.0033	0.998
WG400-3p	6.565	0.603	0.951	385.1	0.0036	0.964
WG400-1a	2.061	0.816	0.961	1000	0.0009	0.993
WG400-2a	1.033	0.934	0.994	2502	0.0003	0.974
WG400-3a	1.110	0.866	0.969	909.1	0.0007	0.971
WG500-1p	10.07	0.441	0.942	322.6	0.0021	0.994
WG500-2p	0.784	0.875	0.973	1666	0.0003	0.982
WG500-3p	7.936	0.614	0.998	357.1	0.0061	0.984
WG500-1a	7.887	0.627	0.971	400.0	0.0056	0.963
WG500-2a	4.48	0.730	0.991	555.6	0.0031	0.994
WG500-3a	1.734	0.731	0.969	1000	0.0001	0.964

In order to evaluate in a complex way the changes which take place in activated carbon during its modification, there were also analysed adsorption properties of these carbons in relation to such organic compounds as methylene blue and phenol and there was determined the bulk mass (table 3). The aim of the research was to analyse the changes occurring in a porous structure during the modification of carbon surface. The values of almost all examined parameters under modification conditions were reduced. This proves that the modification not only has the influence on ion-exchangeable properties of carbons, but also, in this case, on their porous structure. Methylene number, in all cases, decreased during carbon modification by means of both air and nitrogen. In the case of modification in the air atmosphere, we can state that the longer the modification time and the higher temperature, the greater deterioration of adsorption properties in relation to methylene blue. In the case of modification in the nitrogen atmosphere at 500 °C, we also obtained the worst results.

In the case of phenol adsorption during carbon modification by means of air, adsorption of this compound was also lower. The modification of carbon with nitrogen did not have any influence on the results of adsorption of phenol.

The changes in the porous structure are also corroborated by a greater bulk mass of the modified carbons. This is caused by a partial gasification of carbon. In the case

of air usage, carbon is oxidized to carbon dioxide or carbon monoxide. This causes the enlargement of pore volume together with a possible enlargement of their inner surface (in the case of creating new pores) or with the reducing their inner surface (in the case of joining small pores together). The reaction between oxygen and carbon is exothermic and often leads to out-of-control process. This results in a local overheating and in such a case the volume distribution of pores becomes disadvantageous. Such a phenomenon happens because together with a decrease in the bulk mass, the adsorption capacity decreases as well, both in relation to methylene blue and phenol. These are compounds which differ in their particle size.

Table 3

Methylene number, adsorption capacity in relation to phenol,
bulk mass of the carbons examined

Type of carbon	Methylene number, LM			Adsorption capacity in relation to phenol ($C_0 = 600 \text{ mg/dm}^3$), mg/g			Bulk mass, g/dm^3		
WG0	31			123			450		
Modification time									
	1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
WG300p	30	28	28	117	116	118	446	440	431
WG300a	27	26	26	122	122	121	448	448	445
WG400p	29	27	27	115	109	113	431	420	414
WG400a	26	28	27	123	123	124	444	440	439
WG5000	29	26	27	111	107	110	397	355	343
WG500a	24	25	24	123	124	123	439	435	455

4. CONCLUSION

The modification of activated carbon by means of air and nitrogen at the temperature ranging from 300 to 500 °C improves its cation-exchangeable properties, but simultaneously it deteriorates its anion-exchangeable properties.

The change in ion-exchangeable capacities of the carbons examined is the result of the appearance of new oxygen units, the transformation of the existing ones and the changes in porous structure of carbons.

The best results of chromium-cation adsorption were obtained on the carbons modified by means of air at the temperature of 500 °C. At this temperature longer time of modification improved the results of adsorption.

In the case of carbon modification by means of air at the temperature of 300 and 400 °C, the results obtained were similar; however, they were significantly better than

these for the unmodified carbon. In these conditions, the modification time also did not affect significantly the adsorption properties of carbon in relation to Cr(III).

In the case of modification of carbon in the inert gas atmosphere (e.g. nitrogen), there was also observed an improvement of its cation-exchangeable properties. This could be caused by the oxidation of carbon by the oxygen from the air. This oxygen, to a small extent, could be present in the pores of activated carbon subjected to the modification and could enter a furnace which was not airtight. In this case, the obtained better cation-exchangeable properties were not dependent on the temperature, but first of all on the modification time. Longer modification time enabled greater access of air (e.g.: during the process of putting the carbon again into the rotary furnace).

The modification of carbon in all cases decreased the bulk mass, i.e. it increased the pore volume. When carbon was modified by means of air we observed deterioration of its adsorption properties in relation to organic compounds such as phenol and methylene blue. When it was modified by means of nitrogen, both bulk mass and adsorption capacity in relation to phenol and methylene blue decreased, but only to a small extent.

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WPLYW WYSOKOTEMPERATUROWEJ MODYFIKACJI WĘGLA AKTYWNEGO NA SKUTECZNOŚĆ USUWANIA Cr(III) I Cr(VI) Z WODY

Modyfikowano węgiel aktywny za pomocą powietrza i azotu. Modyfikację prowadzono przez 1, 2 i 3 h w temperaturach 300, 400 i 500 °C. Efekty modyfikacji oceniano na podstawie zmian właściwości kationowymiennych węgla aktywnych (sorpcja kationu chromowego), anionowymiennych (sorpcja anionu chromianowego) oraz zmian w strukturze porowatej określonych na podstawie masy nasypowej oraz sorpcji związków organicznych (fenolu i błękitu metylenowego). W efekcie sorpcji na węglach utlenianych powietrzem otrzymano preparaty o lepszych właściwościach kationowymiennych, ale o gorszych anionowymiennych i znacznie zmienionej strukturze porowatej. W wyniku modyfikacji z udziałem azotu i niewielkich ilości powietrza również otrzymano węgle o zwiększonej liczbie ugrupowań kationowymiennych, ale o znacznie mniej zmienionej strukturze porowatej.

