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Effect of the Joule heat-based WG-12 active carbon modification process on the sorption of Cr(III)

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ABSTRACT

The activated carbons used in water technology are most frequently used to remove organic compounds. They can also be used in the adsorption of mineral pollution, among others for heavy metals. The adsorption capacities of activated carbons in relation to these pollutants are slight and their concentrations in water are also low. Heavy metal removal efficiency can be increased by modifying activated carbons. In the article the results of activated carbon modification with the usage of Joule heat are presented. The modification was carried out in the reactor with the height $h = 25$ cm and diameter $d = 5.5$ cm filled with activated carbon. At two sides of the reactor electrodes were placed which were joined with a direct current generator. The flow of the current through the deposit was accompanied by incensement of activated carbon temperature. The modification took place during the flow of carbon dioxide while heating and/or cooling down of this deposit. The effects of modification were evaluated on the basis of Cr(III) adsorption isotherms each time on three parts of activated carbon taken from different heights of the deposit. In the case of deposit modification as the result of heating up to 400°C and cooling down by means of flowing CO_2 with the intensity of 40 dm^3/h much higher adsorption capacities in relation to Cr(III) were obtained if carbon was taken from the bottom and the middle part of the deposit. The carbon from the high part of the deposit decreased its abilities of cation Cr(II) adsorption. Carrying out of the modification process of activated carbon in two cycles of heating up and cooling down is not advisable. The obtained Cr(III) adsorption results are higher than in the case of non-modified carbon, however, they are lower than on carbons modified in one cycle. It is also not advisable to pass carbon dioxide through the deposit during the heating up process. Increasing the speed of carbon dioxide flow during the cooling down of the deposit from 40 to 80 dm^3/h has also been analyzed. The results obtained for Cr(III) adsorption prove that the change of carbon dioxide in the examined range did not have a great influence on the obtained sorbent.

Keywords: Activated carbon; Chromium(III); Sorption

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1. Introduction

For removal of heavy metals from water, it is in many cases purposeful to use active carbons that show potential for the simultaneous removal of organic compounds from water [1–4]. The phenomenon of removal of ions on active carbons is more complex than that of organic compounds. Ions can be effectively removed on carbons that have functional groups of either acidic or basic character on their surface. In the case of the adsorption of cations, the most common mechanism is ion exchange, though ion removal can also take place through the formation of sur-

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face complexes, and is also associated with the possibility of the occurrence of reduction and oxidation processes, as well as the precipitation of insoluble compounds (e.g. hydroxides, carbonates, etc.) in pores [4].

Another issue is the occurrence of different forms of a specific ion (or co-existence of different ions), depending on the pH of solution, in which the process is initiated. So, we observed the occurrence of e.g. Cr(III) in the form of cations of a different valence number and a dynamic radius (due to the formation of aqua-complexes) and, at high water pH values, in the form of an anion.

Active carbons, which are usually manufactured with the aim of removing organic compounds from water, have relatively few oxygen groupings taking part in the sorption of, e.g., heavy metals. Therefore, different works have been conducted aimed at increasing the amount of oxygen on the active carbon surface [5,6]. Oxidation can be done using either oxidizing gases of oxidizing liquids [4,7]. Liquid-phase oxidation (particularly where nitric acid is used) results in the highest increase in the amount of oxygen accumulated. By oxidizing carbons in a gaseous phase, the amount of oxygen can be increased by up to 15%, while in a liquid phase — by up to 25% [8].

One of the metals effectively removed on active carbons is chromium(III) [9–11]. The aim of the work presented in this paper is to assess different conditions of modification of the carbon WG-12 in terms of the removal of chromium (III) from water. Modification was carried out on an innovative testing stand where active carbon was heated up by utilizing its electric conduction (SEOW). As a result of the electric current flowing through it, the carbon bed was heated up (by the released Joule heat). The presented modification was made with the use of carbon dioxide.

2. Testing methodology

Active coal, grade WG-12, manufactured in Poland from hard coal, was used for tests, which was washed with distilled water several times prior to proceeding with measurements. The characteristics of the carbon tested are given in Tables 1 and 2. Then, the carbon was dried at 145°C. So prepared carbon was modified at a temperature of 400°C on the testing stand (SEOW) that utilized the electric conduction of the carbon to heat up the carbon bed (Fig. 1). The modification was conducted in a reactor with a height h = 25 cm and a diameter d = 5.5 cm filled with active coal. On both sides of the reactor, electrodes connected to a direct current source were applied. The flow of the electric current through the bed resulted in an increase in active carbon temperature. The modification took place in the course of carbon dioxide flow during heating and/or cooling of this bed.

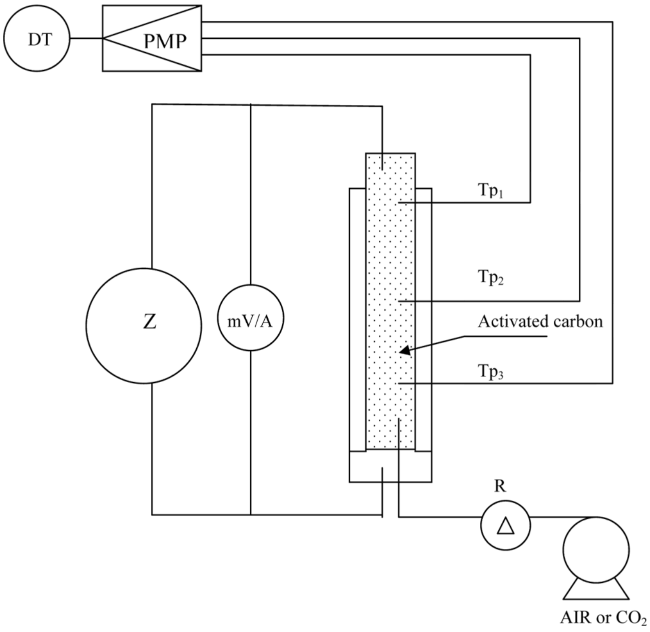

Fig. 1. Testing stand for active carbon modification using the Joule heat (SEOW). PMP – measuring position change-over switch; Z – power supply, DT – detector, Tp_1, Tp_2, Tp_3 – thermocouples, R – rotameter.

The modification on the Joule heat utilizing test stand was carried out in two phases: heating the bed up to a temperature of 400°C either without gas flow (a duration of approx. 6–8 min) or with gas flow and cooling with flowing air or carbon dioxide down to a temperature of

Table 1
Physical and chemical properties of activated carbon WG-12

Parameters	WG-12
Bulk density, g/dm^3	420
pH of water extract	10.1
Methylene blue number, LM	30
Iodine adsorption, mg/g	1050

Table 2
Distribution of capillary volumes in activated carbon WG-12

Carbon symbol	Capillary radius, nm					$\Sigma\Delta V$, cm^3/g	Specific surface, m^2/g
	<1.5	1.5–15	15–150	150–1500	1500–7500		
	Capillary volume ΔV, cm^3/g						
WG-12	0.4213	0.1049	0.0648	0.2731	0.1478	1.0114	1005

100°C (with a gas flow duration during cooling of about 20 min). The measurement of temperatures was taken at three heights along the reactor. The carbon bed during taking up from the reactor was divided into three parts: g – upper part, s – middle part, d – lower part.

Heating of the carbon was done using direct current of a voltage 48 V and 32 V, respectively. Carbons are denoted as follows:

WG0 — unmodified WG-12 carbon

WG/40I — WG-12 carbon modified on the SEOW stand during carbon cooling with CO_2 flowing at a flowing rate of 40 dm^3/h in one heating–cooling cycle

WG/40II — WG-12 carbon modified on the SEOW stand during carbon cooling with CO_2 flowing at a flowing rate of 40 dm^3/h in two heating–cooling cycles

WG/80I — WG-12 carbon modified on the SEOW stand during carbon cooling with CO_2 flowing at a flowing rate of 80 dm^3/h in one heating–cooling cycle

WG/80II — WG-12 carbon modified on the SEOW stand during carbon cooling with CO_2 flowing at a flowing rate of 80 dm^3/h in two heating–cooling cycles

WG/(40+40)I — carbon modified on the SEOW stand during the flow of air in the course of both heating and cooling of the carbon bed in the reactor using CO_2 flowing at a flowing rate of 40 dm^3/h in one heating–cooling cycle.

The following letters added to the coal designation have the meaning as follows: coal taken from: "a" — the lower part of the bed, "b" — the middle part of the bed, "c" — the upper part of the bed.

The initial carbon and the post-modification carbon were used for the measurement of Cr(III) chromium sorption isotherms for initial concentrations from 500 to 1500 mg/m^3. The Cr(III) chromium cation was obtained from chromium chloride, $CrCl_3$. The measurements were carried out from solutions with pH = 6. The pH correction was made with a diluted NaOH solution. At the examined value of solution pH, the chromium occurred as Cr^{3+}, $Cr(OH)^{2+}$ and $Cr(OH)^{+}$, with its predominating forms being $Cr(OH)^{2+}$ (slightly above 60%) and $Cr(OH)_2^{+}$ (more than 38%) [8].

The tests were conducted under static conditions. 1 g of active carbon was added to 250 cm^3 of the solution in appropriate concentration and then the solution was stirred for 2 h, after which it was allowed to stay unstirred for another 22 h. The time of contact of the carbons with the solutions, 24 h, was established based on previous investigations [11].

3. Testing results and their discussion

In the first testing stage, carbon was modified by heating it on the SEOW stand with no flow of gases and then cooling it down with carbon dioxide flowing at a rate of 40 dm^3/h. This modification was carried out in a single heating–cooling cycle. The carbon bed in the reactor was divided into three (lower — WG/40Ia, middle —WG/40Ib and upper — WG/40Ic) parts, and Cr(III) sorption isotherm measurements were made separately on carbon taken from different reactor heights and on the initial carbon WG0 (Fig. 2). The carbons taken from the lower and middle reactor parts are characterized by higher capabilities for the sorption of chromium (III) from the solution, compared with the initial carbon WG-12. The carbon WG/40Ia, that is the one taken from the lower bed part, turned out to be the most effective in absorbing the cation examined. Most of carbon dioxide reached the lower bed part, but, at the same time, this bed part was most intensively cooled, as the inflowing gas was not heated up. The time of carbon dioxide contact with the active carbon, especially at high temperatures, was short (cooling of the bed from 400°C to 300°C for this layer took less than 2 min). The middle bed part was cooled most slowly, because the carbon dioxide was already partially heated up after passing through the lower bed part, and also because it was most strongly isolated from the surroundings with active carbon layers situated above and below. At the same time, however, slightly less carbon dioxide reached this layer, as it was used in reactions with the surface of the lower layer active carbon. The carbon taken from the upper bed part showed much lower sorption capabilities compared to the initial sorbent. Most probably, the processes of thermal decomposition of functional groups during heating up of the carbon predominated in this case over the formation of new ones during cooling. This was most likely due to the shortage of carbon dioxide in the upper layers of the reactor.

At the subsequent stage of testing, measurements of Cr(III) sorption on carbons modified under the same conditions, but in two heating–cooling cycles, were carried out (carbons WG/40IIa, WG/40IIb, WG/40IIc). The sorption isotherms obtained with the use of these carbons showed an unfavourable effect of the double heating–cooling cycle on the sorption capacity compared to the single cycle, if Cr(III) was removed on such sorbents (Fig. 3). Only the carbon taken from the middle bed part

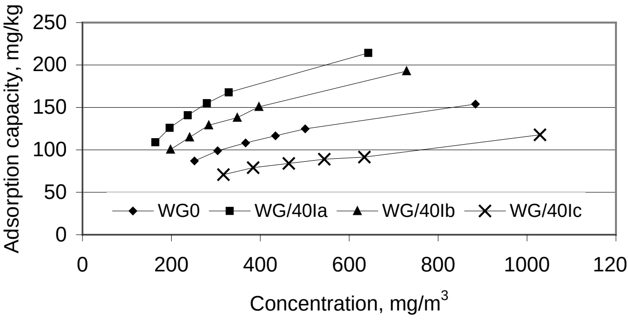

Fig. 2. Isotherms of Cr(III) sorption on carbons modified on the SEOW test stand with cooling CO_2 flow at a rate of 40 dm^3/h in a single heating–cooling cycle

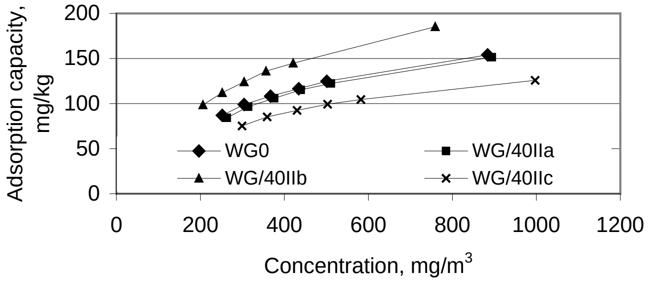

Fig. 3. Isotherms of Cr(III) sorption on carbons modified on the SEOW test stand with cooling CO_2 flow at a rate of 40 dm^3/h in two heating–cooling cycles.

had a sorption capacity higher than that of the initial carbon WG0. Most probably, the functional groups formed in the first heating–cooling cycle were largely decomposed in the subsequent heating phase. The second cooling no longer produced so good results, most likely due to the reduction of the reactivity of the carbon surface.

Measurements were also carried out for carbon modified in one (Fig. 4) or in two (Fig. 5) heating–cooling cycles with a twice as high CO_2 flow (80 dm^3/h) as during cooling. In the case of carbons modified in one cycle (WG/80Ia, WG/80Ib, WG/80Ic), for the coal taken from the lower reactor part (WG/80Ia), sorption capacities by 1.7 times higher than those of carbon WG0 were obtained at the same equilibrium concentration. The sorption of Cr(III) on the carbon taken from the middle part occurred to a slightly greater extent, and on the carbon taken from the upper part to a lesser extent compared to carbon WG0. The CO_2 flow at a higher intensity causes, on the one hand, the inflow of larger amounts of the oxidizing gas, but, on the other hand, faster bed cooling and a shorter time of CO_2 contact with the high temperature-heated carbon.

With the double cycle of modification with CO_2 at a flow rate of 80 dm^3/h (Fig. 5), results of the sorption of the cation under examination were obtained, which were similar to those for carbons modified with a CO_2 flow rate of 40 dm^3/h (Fig. 3). An improvement in Cr(III) sorption capacity was only obtained for the carbon taken from the middle part of the bed.

In the last stage of testing, modification was carried out on the SEOW test stand in such a manner that carbon dioxide was flowing through the reactor at a rate of 40 dm^3/h during the whole process (i.e. during both heating and cooling) (Fig. 6). The carbon WG/(40+40)Ia taken from the lower bed part was characterized by increased Cr(III) cation sorption capacities compared to unmodified carbon. The obtained sorption results were, however, lower than those for carbons modified during cooling only (Fig. 2). This is most likely due to the extension of heating time during CO_2 flow and, as a consequence, a more extensive decomposition of functional groupings at this stage.

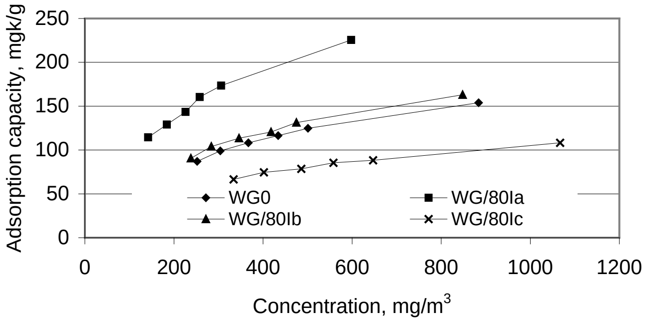

Fig. 4. Isotherms of Cr(III) sorption on carbons modified on the SEOW test stand with cooling CO_2 flow at a rate of 80 dm^3/h in a single heating–cooling cycle.

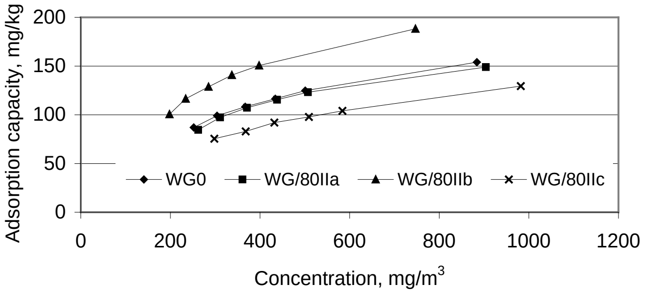

Fig. 5. Isotherms of Cr(III) sorption on carbons modified on the SEOW test stand with cooling CO_2 flow at a rate of 80 dm^3/h in two heating–cooling cycles.

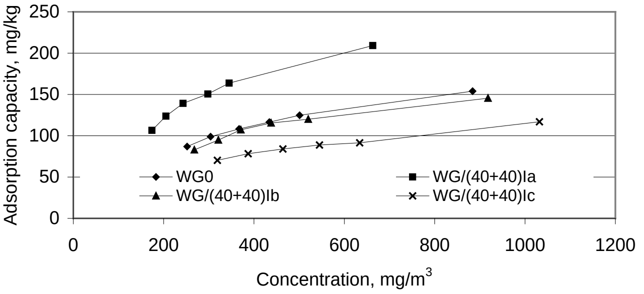

Fig. 6. Isotherms of Cr(III) sorption on carbons modified on the SEOW test stand with cooling CO_2 flow at a rate of 40 dm^3/h in a single heating–cooling cycle.

Table 3 shows maximum (for the initial concentration of 500 mg/m^3), minimum (for C_0 = 1500 mg/m^3) and medium efficiencies of chromium (III) removal from aqueous solutions on the active carbons tested. It can be seen from these results that the highest efficiency of Cr(III) sorption was achieved for carbons modified in a single heating–cooling cycle (without the flow of gases during heating), taken from either the lower or the middle part of the bed (WG/40Ia,WG/40Ib, WG/80Ia,WG/80Ib). If this process was carried out in two cycles, then only the

Table 3
Maximum, minimum and medium degrees of Cr(III) removal on active carbons from aqueous solutions

Carbon	Degres of Cr(III) removal,%		
	Maximum	Minimum	Medium
WG0	58.0	41.1	51.9
WG/40Ia	72.7	57.1	68.0
WG/40Ib	67.0	51.4	61.7
WG/40Ic	47.1	31.4	40.3
WG/40IIa	56.1	40.4	50.8
WG/40IIb	65.7	49.4	59.9
WG/40IIc	50.2	33.5	44.1
WG/80Ia	76.3	60.1	70.4
WG/80Ib	60.3	43.5	54.3
WG/80Ic	44.3	28.0	38.1
WG/80IIa	56.3	39.7	50.9
WG/80IIb	67.0	50.2	61.8
WG/80IIc	50.3	34.5	43.9
WG/(40+40)Ia	71.0	55.8	66.6
WG/(40+40)Ib	55.3	38.8	50.2
WG/(40+40)Ic	46.8	31.2	40.1

sorbent taken from the middle bed part absorbed more of the cation examined compared to WG0. Cooling of the bed at a higher test rate produced a sorbent WG/80Ia that absorbed up to 76.3% of chromium, as against the mere 58.0% for WG0. High sorption efficiency (72.7%) was also achieved using modified coal WG/40Ia.

4. Summary

The methods of modification of the carbon WG-12 for application in Cr(III) cation removal from aqueous solutions enable sorbents of increased sorption capacities towards the ion under examination to be obtained. From among the modification conditions examined, the best one has turned out to be the carbon modification carried out on the SEOW test stand involving heating the carbon up to a temperature of 400°C without the flow of gases and then cooling it down with carbon dioxide flowing at a rate of 40 dm^3/h. In this case, the carbon WG/40Ia taken from the lower reactor part and the carbon WG/40Ib taken from the middle reactor part were both characterized by a considerably increased efficiency of Cr(III) removal compared to unmodified carbon (on average, by 16 and 10%). The carbon modified with the CO_2 flow rate of 80 dm^3/h, as taken from the lower bed part, sorbed on average by 18.3% more chromium than WG0 did, but only by 2.4% more when taken from the middle bed part. So, it is not purposeful to increase the quantity of gas supplied for modification during cooling if the carbon to be obtained will be used for the sorption of Cr(III). Neither it is to carry out modification in more than one cycle, as the obtained sorption results are lower. Modification results are most likely to be influenced by two opposite phenomena: decomposition of oxides during heating and their formation during cooling with carbon dioxide. It is not advisable to pass oxidizing gases during heating when carrying out modification on the SEOW test stand, as they are rather unlikely to be able then to diffuse into the pores due to the thermal expansion of air in the pores. This only increases the heating duration, and so also the duration of decomposition of functional groups. During the cooling of carbon, a suction of oxidizing gases into the pores occurs due to the reduction of the volume of gases in the pores as a result of cooling. The carbon preparation method presented in the paper is a process with low energy consumption compared to the conventional methods of modification, e.g. in rotary furnaces. The obtained results for Cr(III) sorption are comparable to the results obtained on modified carbons during 1 h at 400°C in a rotary furnace [12]. At the same time, as the author's investigation results unpublished yet show, not only heavy metal cations, but also the Cr(VI) anion can be sorbed in a greater quantity on so prepared carbons. Simultaneous increase of the capability to sorb cations and anions as the result of carbon modification at 400°C with CO_2 or air is not possible to be achieved by conventional modification in a rotary furnace.

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