EFFECT OF THE PROCESS OF WG-12 ACTIVATED CARBON MODIFICATION ON THE SORPTION OF CHROMIUM

Abstract: The article presents the results of activated carbon modification with the usage of Joule heat. The modification was carried out in the reactor (h = 25 cm and d = 5,5 cm) filled with activated carbon. The reactor was equipped with two electrodes located on both sides and connected with a direct current generator. The flow of the current through the activated carbon bed was accompanied by gradual increase in activated carbon temperature. The modification took place during the flow of carbon dioxide while heating up and/or cooling down the bed. The effects of modification were evaluated on the basis of Cr(III) and Cr(VI) adsorption isotherms each time on three parts of activated carbon sampled from different heights of the bed. The presented method of modification of the WG-12 carbon for removal of Cr(III) and Cr(VI) cations from aqueous solutions improved sorption capacities of the investigated sorbents towards both ions (WG/400EII/40AIRs, WG/400EI/80AIRs). In the majority of cases, modification increased the efficiency of removing one ion while reducing the other.

Keywords: sorption, activated carbon, modification, chromium

In some cases removal of heavy metals from water can be efficiently performed with activated carbons that also show potential for removing organic compounds from water [1–5]. The phenomenon of removal of ions on activated 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. The most common mechanism behind adsorption of cations is ion exchange, though the ion removal can also take place through the formation of surface complexes, and is also associated with the possibility of occurrence of reduction and oxidation processes as well as the precipitation of insoluble compounds (eg hydroxides, carbonates, etc.) in pores [4].

1 Institute of Environmental Engineering, Technical University of Czestochowa, 42–200 Czestochowa, ul. Brzezicka 60, Poland, phone: +48 34 325 09 17, fax: +48 34 372 13 04, email: jlach@is.pecz.czest.pl
* Corresponding author: jlach@is.pecz.czest.pl
Another issue is the occurrence of different forms of particular ions (or co-existence of different ions), depending on the pH of solution, in which the process is initiated. Thus, we observe 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 aquo-complexes) and, at high water pH values, in the form of an anion. In the case of Cr(VI), the following anions can be present in water solutions depending on their pH: \( \text{Cr}_2\text{O}_7^{2–} \), \( \text{HCrO}_4^- \), \( \text{CrO}_4^{2–} \).

Activated 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 studies are being conducted that aimed at increasing the amount of oxygen on the surface of activated carbon [5–7]. Oxidation can be done using either oxidizing gases or oxidizing liquids [4, 8]. Liquid-phase oxidation (particularly where nitric acid is used) results in the highest increase in the amount of accumulated oxygen. By oxidizing carbons in gaseous phase, the amount of oxygen can be increased up to 15 % while in liquid phase – up to 25 %.

One of the metals that is effectively removed on activated carbons is chromium(III) and (VI) [9–11]. The aim of the work presented in this paper is to assess different conditions of modification of the WG-12 carbon in terms of removal of chromium(III) and (VI) 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 released Joule heat). The presented modification was made with the use of carbon dioxide and air.

### Materials and methods

Activated carbon (grade WG-12, manufactured in Poland from hard coal) was used for tests. Prior to measurements activated carbon was washed with distilled water several times. The characteristics of the investigated carbon are provided in Tables 1 and 2. Then, the carbon was dried at 145 °C. After washing and drying carbon was subjected to modification at temperature of 400 °C on the testing stand (SEOW) that utilized the electric conduction of carbon to heat up the carbon bed [12]. The modification was conducted in a reactor with height of \( h = 25 \text{ cm} \) and diameter of \( d = 5.5 \text{ cm} \) filled with activated carbon. Electrodes placed on both sides of the reactor were connected to a direct current source. The flow of electric current through the bed resulted in an increase in activated carbon temperature. The modification took place as air flowed during cooling of that bed.

### Table 1

<table>
<thead>
<tr>
<th>Index</th>
<th>WG-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density [g/dm³]</td>
<td>420</td>
</tr>
<tr>
<td>pH of water extract</td>
<td>10.1</td>
</tr>
<tr>
<td>Methylene blue number [LM]</td>
<td>30</td>
</tr>
<tr>
<td>Iodine adsorption [mg/g]</td>
<td>1050</td>
</tr>
</tbody>
</table>
The modification on the Joule heat-utilizing test stand was carried out in two phases: heating up the bed to temperature of 400 °C with and without gas flow (duration of approx. 6–8 min), and cooling down with flowing air down to temperature of 100 °C (with gas flow duration during cooling of about 20 min). The measurement of temperatures was taken at three different heights of the reactor. The carbon bed sampled from the reactor was divided into three parts: g – upper part, s – middle part, d – lower part.

The carbons modified on the Joule heat-utilizing test stand were designated with the letter “E”. Heating of the investigated carbon was performed with direct current of voltage of 48 V and 32 V, respectively. The determination of the modification conditions was made in accordance with the principle as shown on the example of the WG/400EI/40AIR g carbon – where WG is the abbreviation denoting active carbon; 400 – temperature up to which the carbon was heated; EI – one cycle of carbon heating and cooling on the SEOW stand; AIR – carbon air flow during cooling, in dm³/h; g – carbon batch originating from the upper part of the reactor (s – from the middle part of the reactor, d – from the lower part of the reactor).

The initial carbon and the modified carbon were used for the measurement of Cr(III) chromium sorption isotherms for initial concentrations ranging from 500 to 1500 mg/m³. The chromium(III) cation was obtained from chromium chloride (CrCl₃). The measurements were carried out from the solutions with pH = 6. The pH correction was made with a diluted NaOH solution. At the examined value of pH solution chromium was present as Cr³⁺, Cr(OH)²⁺ and Cr(OH)⁺, with its predominating forms being Cr(OH)²⁺ (slightly above 60 %) and Cr(OH)₂⁺ (more than 38 %) [9].

Sorption of chromium(VI) occurring in the form of an anion in the solution was also carried out. The isotherms of Cr(VI) were made for initial concentrations ranging from 600 to 2000 mg/m³. The solutions were prepared from potassium dichromate, and the sorption process was conducted from the solution with pH = 6. At this pH, HCrO₄⁻ was predominating form of chromium (13a).

The tests were conducted under static conditions. 1 g of activated carbon was added to 250 cm³ of the solution in selected concentration, and then the solution was stirred for 2 hours and left unstirred for another 22 hours. The contact time for the investigated carbons with the solutions (ie 24 hours) was established based on previous investigations [13].

**Results and discussion**

In the first testing stage, carbon was modified by heating up on the SEOW to 400 °C and then cooling down with air flowing at a rate of 40 dm³/h. This modification was
carried out in a single heating-cooling cycle. The carbon bed in the reactor was divided into three parts (lower, middle and upper). Cr(III) sorption isotherm measurements were made separately on carbon sampled from different reactor heights and on the initial carbon (WG0) (Fig. 1).

![Sorption isotherms of chromium(III) on modified activated carbon WG-12](image)

Fig. 1. Sorption isotherms of chromium(III) on modified activated carbon WG-12

The carbons sampled from the lower and middle reactor parts are characterized by higher capabilities for sorption of chromium (III) from the solution, compared with the initial carbon WG-12. The WG/400EI/40AIRd carbon (sampled from the middle part of the bed) turned out to be the most effective in absorbing the investigated cation. Most of air oxygen reached the lower bed part but at the same time this part of the bed was the 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 minutes). The middle part of the bed was cooled the most slowly, because the air was already partially heated up after passing through the lower part of the bed, and also because it was the most efficiently isolated from the surroundings with activated carbon layers situated above and below. At the same time, however, slightly less oxygen reached this layer, as it was used in reactions with the surface of the lower layer of active carbon. The carbon taken from the upper part of the bed showed slightly lower sorption capabilities compared with 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 is most likely due to the shortage of oxygen 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. 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 with the single cycle for removal of Cr(III) on such sorbents (Fig. 2). Only the carbon sampled from the middle part of the bed showed 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 such promising results. This is most likely due to reduction of the reactivity of the carbon surface.

Measurements were also carried out for carbon modified in one cycle (Fig. 3) with air flow twice as high as during cooling (80dm³/h). In the case of carbons modified using air with a lower flow rate, the carbon sampled from the middle part of the reactor exhibited clearly enhanced Cr(III) sorption capabilities compared with WG0 but also higher compared with the sorbent WG/400EI/40AIR. The carbon sampled from the lower part of the reactor has much higher sorption capacity of chromium cation compared with WG0 while Cr(III) sorption capacity similar to that of the carbon modified at lower air flow intensity. Regardless the modification method applied, sorbents sampled from the upper part of the bed sorbed less Cr(III) in the test conditions compared with unmodified carbon. The air flow at higher intensity causes, on the one hand, the inflow of larger amounts of oxidizing gas, but, on the other hand, faster bed cooling and shorter time of oxygen contact with the high temperature-heated carbon.

Modified carbons were also used for the removal from water of sexivalent chromium occurring in the form of an anion in the water solution. In the case of carbon
modification with air flowing at a rate of 40 dm$^3$/h during cooling, only the carbon sampled from the upper part of the bed sorbed more investigated ions (Fig. 4). The carbons sampled from the lower and middle parts of the bed sorbed more Cr(III) cations compared with the initial WG-12 but less Cr(VI) anions.

If modification was conducted in analogous conditions, except that in two heating-cooling cycles, the obtained sorbents, regardless the sampling height of the reactor, sorbed larger quantities of Cr(VI) than the initial carbon did (Fig. 5). Taking into consideration the sorption of both investigated cation and anion, the carbon modified with this procedure, but sampled from the middle part of the bed (WG/400EII/40AIRs), increased its sorption capacities towards both investigated chromium forms.

As a result of modification on the SEOW stand during air flow at a rate of 80 dm$^3$/g, a sorbent of increased Cr(VI) sorption capacity was obtained for carbon sampled from the middle part of the reactor (Fig. 6). This carbon also absorbed more Cr(III) compared with the initial WG-12. In the remaining cases, the obtained sorbents absorbed less Cr(VI) anions.
When compared the efficiency of Cr(III) and Cr(VI) removal under the test conditions, the Cr(VI) anion was much more effectively removed, both on the initial and the modified activated carbons (Table 3). The efficiency of Cr(III) cation removal on the initial activated carbon WG-12 reached 50%. As the result of modification on the SEOW stand carbons that remove the cations with efficiency above 70% (WG/400EII/40AIRsh, WG/400EI/80AIRsh) can be obtained. Also, in the majority of instances, sorbents of enhanced sorption capacity of the Cr(VI) anions were obtained as the result of modification. The efficiency increased in that case from 96.4% to 98.4%. The differences in efficiencies are not in this case significant, as the equilibrium concentrations, upon which sorption capacities depend, are very small.

Table 3

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Removal degree of Cr(III) [%]</th>
<th>Removal degree of Cr(VI) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr(III)</td>
<td>Cr(VI)</td>
</tr>
<tr>
<td>WG0</td>
<td>49.9</td>
<td>96.4</td>
</tr>
<tr>
<td>WG/400EII/40AIRd</td>
<td>63.6</td>
<td>95.6</td>
</tr>
<tr>
<td>WG/400EII/40AIRsh</td>
<td>69.4</td>
<td>96.1</td>
</tr>
<tr>
<td>WG/400EII/40AIRg</td>
<td>47.9</td>
<td>98.4</td>
</tr>
<tr>
<td>WG/400EII/40AIRd</td>
<td>47.9</td>
<td>97.7</td>
</tr>
<tr>
<td>WG/400EII/40AIRsh</td>
<td>70.7</td>
<td>98.2</td>
</tr>
<tr>
<td>WG/400EII/40AIRg</td>
<td>35.6</td>
<td>98.1</td>
</tr>
<tr>
<td>WG/400EI/80AIRd</td>
<td>63.1</td>
<td>96.5</td>
</tr>
<tr>
<td>WG/400EI/80AIRsh</td>
<td>71.6</td>
<td>98.0</td>
</tr>
<tr>
<td>WG/400EI/80AIRg</td>
<td>38.8</td>
<td>96.0</td>
</tr>
</tbody>
</table>

Only in two cases modification produced sorbents of enhanced sorption capacities for both Cr(III) and Cr(VI) (WG/400EII/40AIRsh, WG/400EI/80AIRsh). For the remaining
modified carbons, increasing sorption capacity for the Cr(III) anion involved reduction of sorption capacity for the Cr(VI) anion, or vice versa. Most probably, a change in the nature of oxygen groupings already present on the surface also took place in this case alongside carbon surface oxidation during modification.

**Conclusion**

The presented method of modification of the carbon WG-12 for removal of Cr(III) and Cr(VI) cations from aqueous solutions allows to improve sorption capacities of sorbents towards both investigated ions (WG/400EII/40AIRₗ, WG/400EI/80AIRₗ). In the majority of cases, modification increased the efficiency of removing one ion while reducing that of the other. Most probably, a change in the nature of oxygen groupings already present on the surface took also place alongside carbon surface oxidation during modification. Among the modification conditions investigated, the SEOW stand modification of carbon with heating it up to 400 °C and then cooling it down with air flowing at a rate of 80 dm³/h turned out to be the best, considering the sorption of Cr(III). In this case, the carbon sampled from the lower part of the reactor and the carbon sampled from the middle part of the reactor are both characterized by significantly increased Cr(III) removal efficiency compared with the unmodified carbon. In the case of sorption of the Cr(VI) anions, these anions were most effectively removed on carbons modified in two cycles of bed heating and cooling with air flowing at a rate of 40 dm³/h.

Modification results are most likely to be influenced by two opposite phenomena: decomposition of oxides during heating and their formation or change in their nature during cooling with air.

**Acknowledgement**

The research was founded from the resources of BS/PB-401/301/12.

**References**

Abstrakt: W artykule przedstawiono wyniki modyfikacji węgla aktywnego z udziałem ciepła Joule’a. Modyfikację prowadzono w reaktorze o wysokości $h = 25$ cm i średnicy $d = 5.5$ cm wypełnionym węglem aktywnym. Z dwóch stron reaktora przyłożono elektrody podłączone do źródła prądu stałego. Przepływ dwa elektrody podłączone do źródła prądu stałego. Przepływ prądu przez złoże towarzyszyło podwyższenie temperatury węgla aktywnego. Modyfikacja następowała podczas przepływu dwutlenku węgla podczas nagrzewania i/lub studzenia tego złoża. Efekty modyfikacji oceniono na podstawie izoterm sorpcji Cr(III) i Cr(VI) każdorazowo na trzech partiach węgla aktywnego pobierano z różnych wysokości złoża. Przedstawione w pracy sposoby modyfikacji węgla WG-12 pod kątem usuwania z roztworów wodnych kationu Cr(III) i Cr(VI) pozwalały na uzyskanie sorbentów o zwiększonych pojemnościach w stosunku do obydwu badanych jonów (WG/400EII/40AIRs, WG/400EII/80AIRs). W większości przypadków modyfikacja zwiększała skuteczność usuwania jednego jonu, ale obniżała drugiego.

Słowa kluczowe: sorpcja, węgiel aktywny, modyfikacja, chrom