

PREPARATION AND CHARACTERIZATION OF COAL - BASED ACTIVATED CARBONS SUPPORTING TiO₂

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Introduction

Preparation of drinking water is often associated with a formation of trihalomethanes (THMs). The compounds are formed in the reactions between humic acids and chlorine, which take place during disinfecting of the water. THMs show a carcinogenic activity and therefore their level in the water must be controlled. One of the methods used for removal of chloroorganics from water is a photolysis in a presence of UV radiation. The possible processes may employ UV light in a combination with H₂O₂, ozone, or TiO₂ [1]. All the mentioned agents can either oxidize the unwanted chloroorganics or act as a catalyst for their photodecomposition. According to some authors [2], using a mixture of TiO₂ together with an activated carbon enhances photocatalytic activity of titania in aqueous pollutant removal. Preparation of TiO₂-containing carbons was performed by several methods: i) by an impregnation with a TiO₂ colloid [3], ii) by the carbonization of a mixture of coal and TiO₂ [4], iii) using ionized cluster beam method [5]. As reported elsewhere [6], titanium promotes development of mesopores during activation of carbons.

In our work we have tried to obtain coal-based activated carbons containing large amount of mesopores, and additionally supporting TiO₂. We have hoped to obtain a material with an ability to adsorb large moleculad humic acids (THMs precursor) and to decompose photochemically (in a presence of UV radiation) THMs already formed.

Experimental

Two Polish (Grodziec and Wirek) and one Czech (Uhli) coals of a different rank were used in this work (see Table 1). In order to impregnate with titanium compound, 10g of

Table 1. Characteristics of coals used.

	Grodziec	Wirek	Uhli
Fixed C, [wt%]	52.5	61.5	69.7
Vol. mat., [wt%]	37.7	33.7	26.0
Moisture, [wt%]	3.2	1.9	1.3
Ash (db), [wt%]	6.6	2.9	3.0

each coal was ground to the form of a fine powder (≤ 100 mesh) and put into a solution of bis(2,4-pentanedionato)-titanium oxide(II), (abbr. TiO(II)-AA) (1.37g) in THF (500cm³). Suspension obtained in this way

was stirred for 2h, followed by the distillation of the solvent under vacuum and at the temperature up to 100°C. The obtained powder was subjected to a rapid heating up to 900°C under N₂ flow and kept at this temperature for 10 minutes to complete carbonization. The temperature-time program for the carbonization process is shown in Fig. 1.

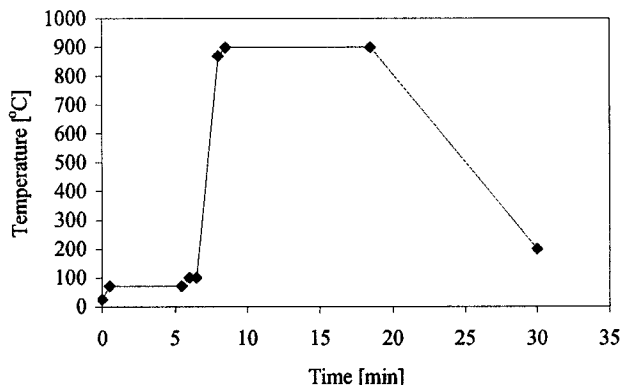


Fig. 1. Temperature-time program for the carbonization process.

The carbonized material was ground again to the particles ≤ 100 mesh and the powders obtained were steam-activated at 900°C for different periods of time (Table 2) according to the pro-gram similar to that applied for the carbonization.

Table 2. Duration of the activation process.

Coal	Activation time, [min]		
Grodziec	60	90	120
Wirek	80	110	140
Uhli	100	130	160

Results

All the raw coals used showed presence of some mineral matter and no special change in their XRD patterns could be observed after the impregnation with Ti(II)O-AA. Only one coal (Uhli) showed rather broad peaks confirming presence of TiO₂ after the carbonization process. However, all the activated carbons showed clearly existence of TiO₂ (rutile form) in their structure. One example is shown in Fig. 2. These changes of the chemical state of Ti seem to be directly related with a decomposition of Ti(II)O-AA introduced to the coals. The pure compound exposed to the same treatments as coals turned to TiO₂ already during the

treatment used for the carbonization process. From the XRD measurements and TEM observations it came out that Ti-loaded activated carbons contained irregularly distributed agglomerates of TiO_2 . Their size varied from ca. 5nm to ca. 500nm in a diameter.

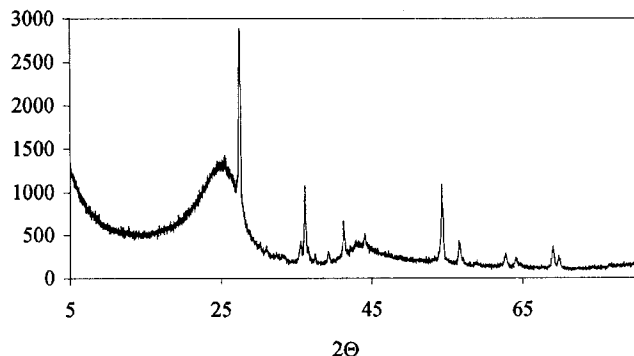


Fig. 2. XRD pattern of Uhli coal after activation.

The Ti content in the obtained activated carbons varied from ca. 5wt% to ca. 11wt% (Fig. 3) and depended on the coal rank and the burn-off. As observed, some amount (few percents) of Ti introduced was lost during the activation, and the loss depended on the activation time.

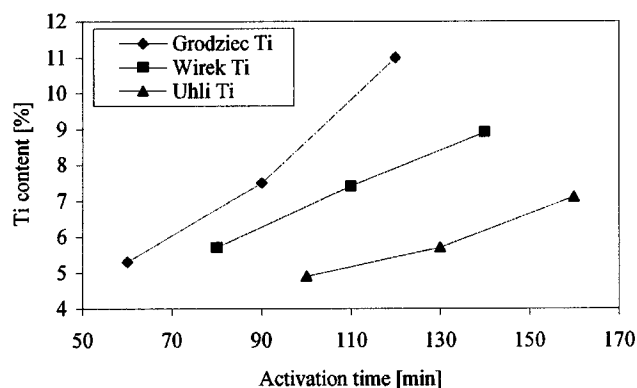


Figure 3. Ti content versus burn off.

All the activated carbons prepared showed N_2 -BET specific surface area of ca. $500\text{-}1000\text{m}^2\text{g}^{-1}$ and D-H specific surface area of mesopores of ca. $100\text{-}500\text{m}^2\text{g}^{-1}$. Both values depended on the rank of coal used and on the sample burn-off achieved during the activation. As illustrated by Fig. 4, low rank coal (Grodziec) showed relatively high amount of mesopores, however, no remarkable influence of Ti on the development of mesoporosity was observed. On the other hand, higher rank coal (Wirek) exhibited rather low mesoporosity, while influence of Ti on the formation of mesopores was found as more pronounced. Seemingly, the higher mesoporosity of active carbons produced from the low rank coal is rather more related with the volatile and mineral matters contents in the coal (Table 1), than with the action of titanium introduced. In

general, coals of a higher rank gave activated carbons containing less mesopores and the mesoporosity was more developed in the Ti-loaded carbons.

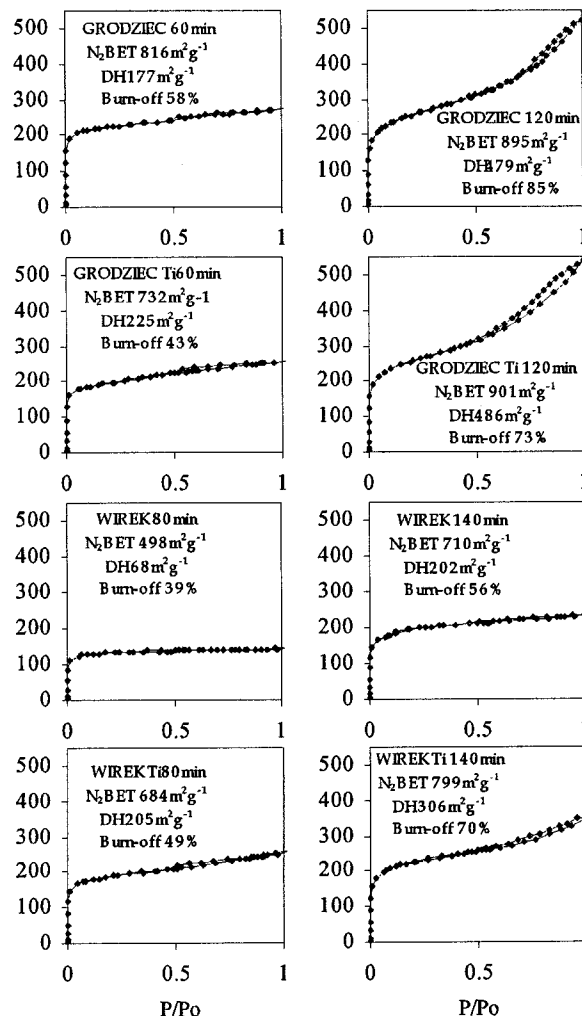


Fig. 4. N_2 adsorption isotherms for selected coals.

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