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## REMOVAL OF ORGANIC MATTER FROM SURFACE WATER BY PAC-ADSORPTION

This paper presents the results of the efficiency of sorption of natural organic matter (NOM) from the Odra River water on powdered activated carbon Norit SA Super. The kinetic curves and adsorption isotherms of dissolved organic compounds, expressed as dissolved organic carbon (DOC) and absorbance at the wavelength of 254 nm ( $UV_{254}$ ), have been included. The paper also describes the character of the porous structure of the powdered activated carbon (PAC) particles.

### 1. INTRODUCTION

Surface water typically contains anthropogenic pollutants which pose a major threat to the environment. These are polycyclic aromatic hydrocarbons, surface-active agents, phenols and their derivatives, pesticides, radionuclides or heavy metals, to name just a few of them. The environmental impact of these substances manifests itself primarily in the adverse effect on living organisms and in the disturbance of biological balance in the aquatic environment.

What is more, the said polluting compounds occur in trace amounts, or their occurrence follows a seasonal pattern, so their removal raises serious technological problems. Another major nuisance linked with surface water treatment is the presence of potential disinfection by-product precursors, i.e., some natural organic pollutants that occur primarily in the form of low-molecular-weight dissolved or colloidal fractions.

Taking into account the variability of surface water composition and the heterogeneous nature of the organic matter to be removed, it is of crucial importance to choose a proper activated carbon and to determine the technological parameters of the process. According to the literature [1], [2] the treatment effect can be enhanced by optimizing the PAC-adsorption process, i.e., allowing sufficiently long contact time, as well as determining the optimal PAC dose, the point of its addition and the mixing

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conditions.

There are many more factors affecting the efficiency of PAC-sorption, e.g., the molecular structure and solubility of a chemical compound, the porous structure of the adsorbent and a chemical character of its surface.

Some researchers [3]–[5] report that an important factor limiting the sorption of dissolved organic matter is the concurrence of pore-blocking water pollutants and their competitive interactions with the activated sites of the PAC. That is why the understanding of the character and the adsorption kinetics of the pollutants to be removed allows the utilization of the adsorptive capacity of the PAC to be maximized under particular conditions.

This paper presents the results of bench-scale research onto the kinetics of PAC-adsorption of dissolved organic compounds (expressed as DOC and  $UV_{254}$ ). The water samples used in the study were collected from the Odra River in the summer of 2005. The kinetic curves and adsorption isotherms for the river water samples tested have been included. Consideration was given to the problem of how the adsorption kinetics of the dissolved compounds was influenced by the porous structure of the PAC particles.

## 2. MATERIALS AND METHODS

### 2.1. RAW WATER

To determine the amount of dissolved organic compounds in the Odra River water, use was made of two conventional parameters,  $UV_{254}$  and DOC.

The concentration of organic fractions in the water examined (expressed as total organic carbon, TOC) averaged  $4.91 \text{ g C/m}^3$ , whereas the proportion of DOC in total organic carbon was high, amounting to 0.88 on average. The major parameters of the river water are summarized in table 1.

Table 1

Major physicochemical parameters of the Odra River water		
Parameter	Unit	Range
TOC	$\text{g C/m}^3$	4.50–5.86
DOC	$\text{g C/m}^3$	4.15–4.70
$UV_{254}$	$\text{m}^{-1}$	11.58–13.04
SUVA	$\text{dm}^3/\text{mg m}^{-1}$	2.61–3.10

### 2.2. POWDERED ACTIVATED CARBON

Use was made of the Norit SA Super powdered activated carbon produced by steam activation of special vegetable raw materials [6].

Assuming a slotted shape of the pores, the PAC structure was analyzed using

a high-vacuum gravimetric apparatus of McBain–Bakr type. On the basis of the benzene adsorption and desorption isotherms obtained the PAC pore volumes and surfaces were calculated.

The Dubinin–Raduszkiewicz theory was used to calculate the volume of micropores. The distributions of mesopore volumes and surfaces were determined on the basis of the benzene desorption branch over the range of relative pressure ( $p/p_0$ ) from 0.12 to 0.97, making use of the Kelvin equation [7].

### 2.3. KINETIC PAC-ADSORPTION TESTS

Kinetic PAC-adsorption tests were carried out in square 2-dm<sup>3</sup> volume reactors. PAC was used in suspension and its doses ( $D_{\text{PAC}}$ ) varied from 10 to 100 g/m<sup>3</sup>.

The tests were carried out for 3 hours. Water samples were collected hourly, but during the first hour of the sorption process additional samples were collected after 15, 30 and 45 minutes. The samples were immediately filtered through a 0.45  $\mu\text{m}$  filter paper and analyzed for DOC and UV<sub>254</sub>. Thereafter the following parameters of the Langmuir adsorption isotherm were determined: equilibrium concentration ( $C_E$ ) and adsorptive capacity ( $x$ ). The data obtained were approximated by the Langmuir isotherm equation [8]:

$$x = \frac{x_m \cdot b \cdot C_E}{1 + b \cdot C_E}, \quad (1)$$

where  $x$  is the amount of organic compounds adsorbed at equilibrium;  $x_m$  stands for monolayer capacity;  $C_E$  denotes the adsorbate equilibrium concentration; and  $b$  is the Langmuir isotherm parameter.

## 3. RESULTS AND DISCUSSION

The isotherms of benzene adsorption and desorption presented in figure 1 substantiate a high proportion of micropores in the porous structure of PAC ( $S_{\text{BET}} = 1016 \text{ m}^2/\text{g}$ ). This finding is also confirmed by the rapid increase in benzene steam adsorption at low relative pressure as well as by the fact that the hysteresis loop begins at the low  $p/p_0$  values. Moreover, according to the classification of the International Union of Pure and Applied Chemistry (IUPAC) [9], both the type of the hysteresis loop and the shape of the adsorption isotherm testify to the presence of narrow fissures formed between two planes and, consequently, the dominance of micropores in the adsorbent examined.

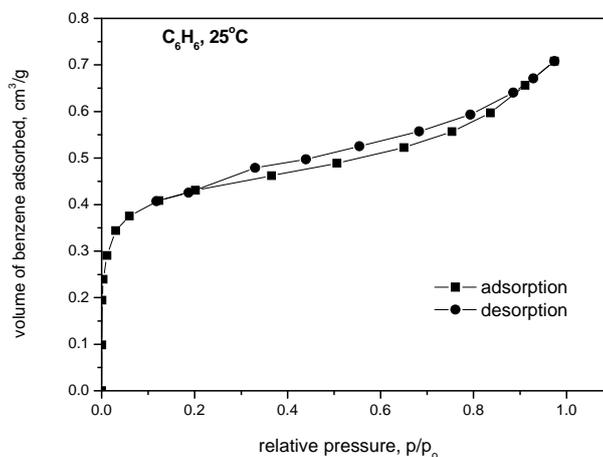


Fig. 1. Benzene adsorption and desorption isotherms

Porosity is one of PAC properties that contribute to the efficiency of sorption of organic pollutants differing in molecular size. The porous structure of PAC is shown in table 2.

Table 2

Characterization of powdered activated carbon Norit SA Super

Micropores		Mesopores			Total 2–50 nm
Total < 2 nm	2–3 nm	3–5 nm	5–10 nm	10–50 nm	
Volume, cm <sup>3</sup> /g					
0.392	0.077	0.052	0.082	0.116	0.327

It is the microporosity of PAC that makes it suitable for the removal of organic pollutants from the Odra River water. In the course of our study, the value of the SUVA index (Specific Ultraviolet Absorbance, which expresses the ratio of  $UV_{254}$ ,  $m^{-1}$ , to the concentration of DOC,  $mg/dm^3$ ) was lower than  $3.10 dm^3/mg m^{-1}$ . This suggests the dominance of primarily nonhumic hydrophilic and low-molecular-weight fractions in the water tested [10], [11]. What is more, PAC has well developed mesopore surfaces, especially in the range from 2 to 3 nm ( $S_{meso2-3} = 64.2 m^2/g$ ), which also allows the removal of higher-molecular-weight water pollutants and a quick transport of low-molecular-weight particles inside the adsorbent.

One of the basic factors affecting the efficiency of organic matter sorption is the time of the contact between PAC and a water sample. The changes in the  $UV_{254}$  value and DOC concentration persisting in the solution (plotted as a function of time in figure 2) were approximated in terms of the following function:

$$C_e = a - b \cdot \ln(t + c), \quad (2)$$

where  $C_e$  is the amount of the adsorbate persisting in the solution, expressed as  $\text{DOC}/\text{DOC}^0$  or  $\text{UV}_{254}/\text{UV}_{254}^0$ ;  $t$  denotes the time of the contact between PAC and a water sample;  $a$ ,  $b$ ,  $c$  are the parameters of the function.

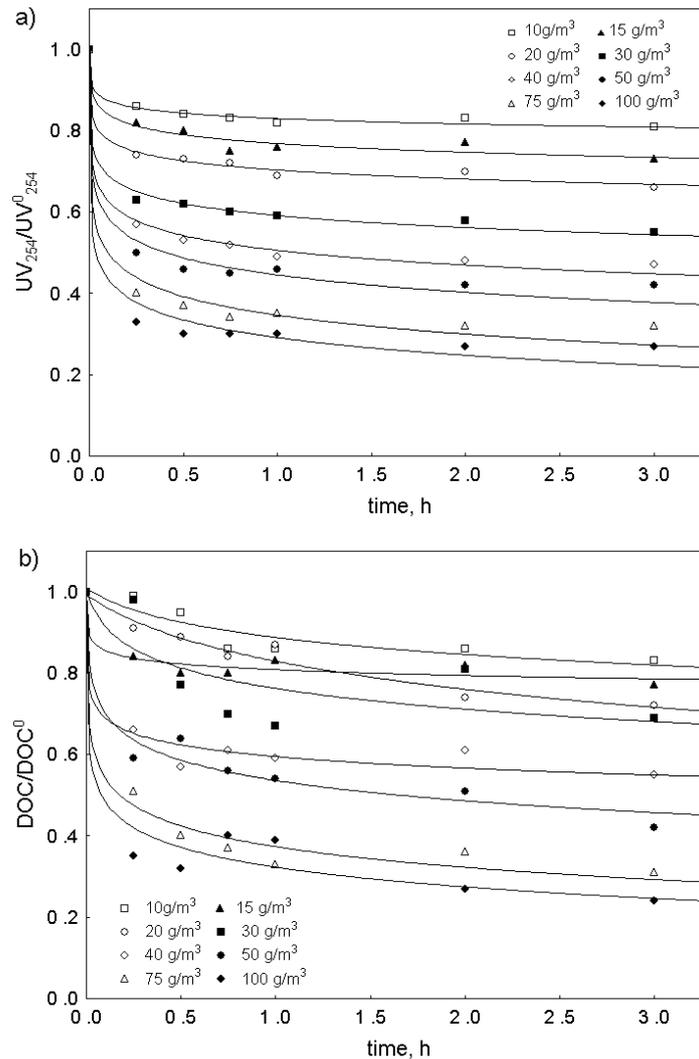


Fig. 2. Kinetic adsorption curves for  $\text{UV}_{254}$  (a) and  $\text{DOC}$  (b)

The experiments have revealed that the higher the dose of the adsorbent, the greater the extent of  $\text{UV}_{254}$  and  $\text{DOC}$  adsorption. Moreover, the notable differences in

dissolved organic matter removal between particular PAC doses imply that the adsorptive capacity of the carbon was effectively utilized. Besides, the efficiency of adsorption was greater when the contact time was longer. The adsorption process was effective over the entire range of PAC doses only to a certain moment.

For example, in the 30th minute of the process, with a PAC dose of  $15 \text{ g/m}^3$  (figure 3), the efficiency of DOC and  $\text{UV}_{254}$  reduction in the water sample was 19.5% and 20.2%, respectively. Between the first and third hours of the process, the removal efficiency increased by 6.7% and 3.0% for DOC and  $\text{UV}_{254}$ , respectively. At PAC doses up to  $50 \text{ g/m}^3$ , during the first hour of the process, the extent of reduction in DOC and  $\text{UV}_{254}$  changed slightly, amounting to several per cent. At PAC dose of  $\geq 50 \text{ g/m}^3$ , however, sorption efficiency was noticeable, and in some instances rose by more than 30% for the same duration of the process. In the first three hours, the extent of adsorption depends (among other things) on the type of the pollutants that are to be removed. In the riverine water under study, low-molecular-weight compounds ( $\text{SUVA} \leq 3.10 \text{ dm}^3/\text{mg m}^{-1}$ ) were dominant; they need a shorter time than high-molecular-weight compounds to reach the active sites on the surface of the adsorbent. A significant fraction of the large organic pollutants may also block the active centres of PAC and thus make them inaccessible to the smaller ones.

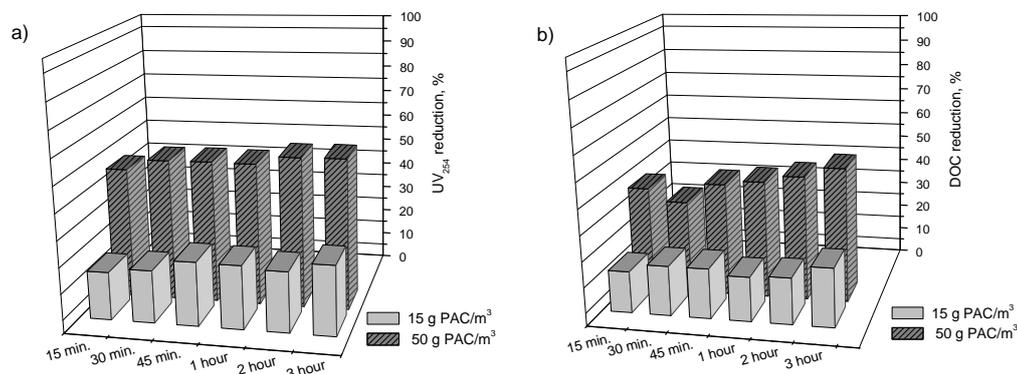


Fig. 3. Removal of  $\text{UV}_{254}$  (a) and DOC (b) with  $D_{\text{PAC}} = 15$  and  $50 \text{ g/m}^3$

Similar observations of the sorption of NOM have been reported by NAJM and co-workers [12]. Their study involved the Colorado River water where low-molecular-weight NOM was dominant and the efficiency of TOC removal was analyzed during a 4 hour kinetic jar test. They have shown that during the first 30 minutes of adsorption the majority of small, low-molecular-weight organic fractions are adsorbed comparatively quickly onto the PAC surface, while the same process in the case of large, high-molecular-weight compounds lasts longer.

Under particular conditions, sorption occurs until the concentration of the dissolved substance persisting in the solution and the concentration of the dissolved substance on the inner surface of the adsorbent reach a dynamic equilibrium. Thus, to describe the division of the adsorbate between the solution phase and the adsorbent phase, the concentration of the dissolved substance adsorbed per unit mass of the adsorbent was related to the concentration of the dissolved substance persisting in the solution at constant temperature.

To describe such a division in our study, we used the Langmuir isotherm, which had been verified many times, especially in sorption systems involving low initial concentrations of the adsorbate, such as those made use of in water treatment trains [8]. The adsorption isotherms for UV<sub>254</sub> and DOC are shown in figure 4. The isotherms obtained indicate that the sorptive properties of the PAC are encouraging with respect to the organic pollutants present in the Odra River water.

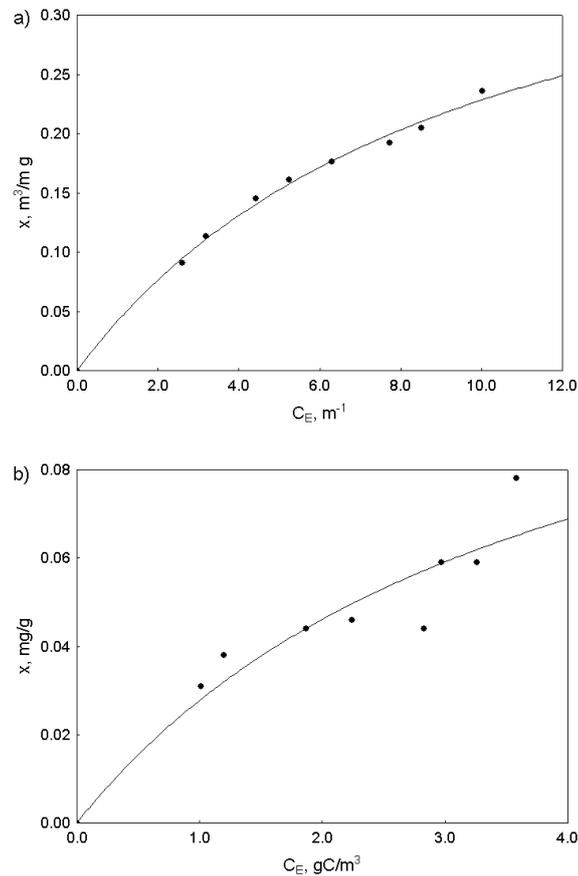


Fig. 4. Adsorption isotherms for UV<sub>254</sub> (a) and DOC (b)

The parameter  $b$  of the Langmuir isotherm is the index of its convexity. The higher the  $b$ -value, the greater the affinity of the adsorbate for PAC. At the sorption of the dissolved fraction expressed as  $UV_{254}$  (figure 4a), the  $b$ -value equalled 0.102 m. The value of monolayer capacity  $x_m$  was  $0.452 \text{ m}^3/\text{m}\cdot\text{g}$ .

However, the Langmuir isotherm parameter values which describe the division of the pollutants expressed as DOC (figure 4b) between the solution phase and the adsorbent varied according to a different pattern compared to the parameter values describing the division of the pollutants expressed as  $UV_{254}$ . The  $b$ -value for DOC equalled  $0.258 \text{ m}^3/\text{g}$  and the monolayer capacity  $x_m = 0.135 \text{ mg/g}$ .

These results suggest that adsorption of dissolved organic matter expressed as  $UV_{254}$  is more efficient than that expressed as DOC. This implies that the riverine water contained large portions of NOM which had their maxima of absorbance at the wavelength of 254 nm; these compounds are mainly classified as aromatic organic substances.

#### 4. CONCLUSIONS

The results of the study allow the following conclusions:

- The amount of the organic matter adsorbed depended greatly on the specific surface and porous structure of the adsorbent. If low-molecular-weight compounds are to be removed, it is advisable to use PAC structures which are rich in micropores.
- The efficiency of dissolved organic matter sorption on Norit SA Super increased with increasing the dose of adsorbent and extending the contact time. But there were also some major factors which limited the process: the character of the pollutants to be removed, the presence of water pollutants which blocked the carbon pores, and the competitiveness of the pollutants with respect to the active sites of the adsorbent.
- The results obtained for DOC and  $UV_{254}$  in the process were approximated by the following function:  $C_e = a - b \cdot \ln(t + c)$ , which is the best fit. The Langmuir isotherm exactly described the adsorption of dissolved organic fractions from the water under test, and the powdered activated carbon used in the study showed a strong affinity for the adsorbates expressed as DOC and  $UV_{254}$ .

#### ACKNOWLEDGEMENT

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#### USUWANIE SUBSTANCJI ORGANICZNYCH Z WODY POWIERZCHNIOWEJ W PROCESIE SORPCJI NA PYLISTYM WĘGLU AKTYWNYM

Podano wyniki badania efektywności sorpcji organicznych domieszek wody z Odry na pylistym węglu aktywnym Norit Super SA. Przedstawiono krzywe kinetyczne oraz izotermy adsorpcji związków organicznych mierzonych jako poziom rozpuszczonego węgla organicznego (DOC) i absorbancja przy długości fali 254 nm ( $UV_{254}$ ). Omówiono również charakterystykę struktury porowatej stosowanego pylistego węgla aktywnego.