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Original scientific paper

## Influence of different carbon monolith preparation parameters on pesticide adsorption

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**Abstract:** The capacity of carbon monolith for pesticide removal from water, and the mechanism of pesticide interaction with the carbon surface were examined. Different carbon monolith samples were obtained by varying the carbonization and activation parameters. In order to examine the role of surface oxygen groups on pesticide adsorption, the carbon monolith surface was functionalized by chemical treatment in HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and KOH. The surface properties of the obtained samples were investigated by determination of the Brunauer, Emmett and Teller (BET) surface area, pore size distribution and temperature-programmed desorption. Adsorption of pesticides from aqueous solution onto the activated carbon monolith samples was studied using five pesticides belonging to different chemical groups (acetamiprid, dimethoate, nicosulfuron, carbofuran and atrazine). The presented results show that higher temperature of carbonization and amount of activating agent enable microporous carbon monolith with higher numbers of surface functional groups to be obtained. The adsorption properties of the activated carbon monolith were more readily affected by the number of surface functional groups than by the specific surface area. Results obtained after carbon monolith functionalization showed that  $\pi$ - $\pi$  interactions were the driving main force for adsorption of pesticides with an aromatic structure, while acidic groups played an important role in adsorption of pesticides with no aromatic ring in their chemical structure.

**Keywords:** carbon monolith; activation; surface properties; adsorption; pesticides.

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## INTRODUCTION

The possibility of producing carbon materials with high specific surface areas, microporous structure, high adsorption capacity and high degree of surface reactivity brings a variety of applications for these materials. Carbon monolith (CM) is a relatively new carbon material. Depending on the application, CM can be produced with the desired shape and morphology, and controlled composition, structure and porosity. CMs are potentially useful in a wide variety of applications, such as residential water filtration, volatile organic compound emission control,<sup>1–4</sup> indoor air purification, chemical separation,<sup>5</sup> catalysis, biocatalysts,<sup>6</sup> adsorption, *etc.* In a previous work, cylindrical CM impregnated with silver was successfully used for the disinfection of drinking water.<sup>7</sup> Due to the fact that finer silver particles had higher resistance to attrition from the surface of the carbon material in comparison to larger ones,<sup>8</sup> the CM surface was efficiently modified and an Ag deposit was obtained in the form of fine crystals with small crystallite sizes.<sup>9</sup> The last few years have been marked with a growing interest in carbon monolith as an alternative for conventional carbon materials. In the present study, an attempt was made to use activated CM as an adsorbent for the removal of pesticides from aqueous solutions.

Pesticides are the group of hazardous compounds that, due to their extensive application in agriculture, may contaminate surface and groundwater with potential risks for wildlife and human health.<sup>10</sup> Environmental contamination occurs when pesticides drift away from the application sites and infiltrate the groundwater by leaching through the soil.<sup>11,12</sup> Several methods are available for removal of pesticides, such as photocatalytic degradation, combined photo-Fenton and biological oxidation, advanced oxidation processes, aerobic degradation, nanofiltration, ozonation and adsorption.<sup>13</sup> Adsorption on activated carbon is the most widespread technology used to deal with the purification of water contaminated by pesticides.<sup>14–17</sup> The adsorption capacity as one of the most important properties is directly determined by the surface structure of the activated carbon material.

As the surface characteristics of a carbon material depend on the nature of the carbon precursor and the processing conditions during production,<sup>18</sup> the main objective of this work was to determine the appropriate carbonization and activation parameters in order to obtain a material with good adsorption properties toward pesticides. Chemical activation, either through carbonization followed by activation, or through a direct activation, as one of the most important steps during the preparation, has attracted extensive attention.<sup>19–21</sup> Basta *et al.*<sup>22</sup> found that a 2-step KOH activation was much more advantageous than a single-step activation for obtaining carbon materials with a high Brunauer, Emmett and Teller (BET) surface area. The factor that influence the final porous texture of activated carbon materials obtained by chemical activation are the activation agent, the activating agent/carbon material ratio, the heating rate and the acti-

vation temperature.<sup>19</sup> In the present work, different carbon monolith samples were obtained by changing the carbonization temperature and the amount of potassium hydroxide used as the activation agent. The adsorption properties of the resulting CM samples were determined by adsorption of five pesticides: acetamiprid, dimethoate, nicosufurone, carbofuran and atrazine. The influence of the carbonization temperature and the activation parameters on the specific surface area, surface functional groups and adsorption properties of the activated CM samples were studied. Additionally, in order to examine the role of surface oxygen groups in pesticide adsorption, the carbon monolith surface was functionalized by different chemical treatments.

## EXPERIMENTAL

### *Material*

CMs precursor in the shape of cylinder (length 3.0 cm, diameter 1.8 cm) with 8600 parallel capillary channels (each with a diameter of 80  $\mu\text{m}$ ) inside the cylinder were purchased from Fractal Carbon (London, UK). The design and structure of the employed CM is shown in Fig. 1. This is a composite material, consisting of a glassy carbon bed and activated carbon on the inner capillary walls.

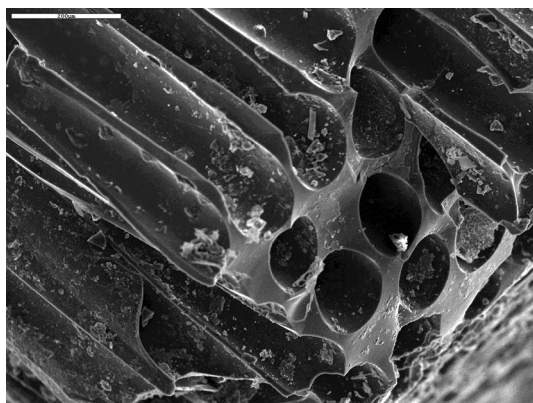


Fig. 1. SEM Photograph of the carbon monolith and cross-section (magnification: 100 $\times$ ).

### *Activation of the carbon monolith*

The carbon precursor was first carbonized at two different temperatures, 700 and 1000  $^{\circ}\text{C}$ , under a constant nitrogen flow rate, at a heating rate of 5  $^{\circ}\text{C min}^{-1}$ , and the samples CM7 and CM1, respectively, were obtained. Only sample CM1 was further tested and compared with samples activated with KOH, as sample CM7 was not fully carbonized due to its lower carbonization end-temperature. The carbonized samples, CM7 and CM1, were mixed with KOH pellets in different weight ratio of KOH:carbonized material (1:1 and 2:1). The samples were placed in a furnace and heated at a rate of 5  $^{\circ}\text{C min}^{-1}$  to 900  $^{\circ}\text{C}$ . The activation process was realized under a constant nitrogen flow rate. The resulting products were thoroughly washed with tap water and finally distilled water to remove the residual KOH until the pH value of the washed solution ranged from 6 to 7. Four samples obtained in this way were used for further examination. The scheme of activated carbon monolith production is shown in Fig. 2. The samples were denoted as CM719, CM729, CM119 and CM129. The first number in the

sample code represents a temperature of carbonization: 7 for 700 °C and 1 for 1000 °C; the second number in the sample code represents the amount of activating agent used: 1 for the KOH:carbon material ratio 1:1, and 2 for the ratio 2:1; the last number specifies the activating temperature: 9 for the 900 °C.

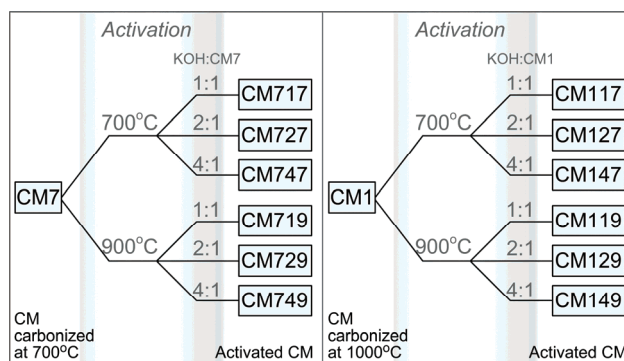


Fig. 2. Scheme for the production of activated carbon monolith.

#### Chemical surface treatment

The chemical treatments involved submerging the sample CM719 in HNO<sub>3</sub>, KOH and H<sub>2</sub>O<sub>2</sub> solution. The chemically treated samples were designated CM/A, CM/B and CM/P, respectively. Samples CM/A and CM/B were obtained by heating CM719 in 4 M HNO<sub>3</sub> and 4 M KOH, respectively, for 2 h, while CM/P was obtained by submerging CM719 in 4 M H<sub>2</sub>O<sub>2</sub> at room temperature until complete decomposition of the H<sub>2</sub>O<sub>2</sub> (when there was no further gas evolution). After chemical treatment, modified samples were thoroughly washed with distilled water to neutral pH and dried at 110 °C for 24 h. All samples were stored in a dessicator until use.

#### *pH<sub>slurry</sub>* of the chemically treated samples

The pH values of aqueous slurries of the CMs samples were measured. The slurries were prepared with boiled distilled water in the ratio of 10 ml g<sup>-1</sup>; these suspensions were stirred and the pH values were measured several times until a constant value was reached.

#### Specific surface area and porosity

Specific surface area of all CM samples was determined by nitrogen adsorption at liquid nitrogen temperature using an automatic surface area analyzer, model 4200 (Leeds & Northrup Instruments, USA). The N<sub>2</sub> adsorption and desorption isotherms of samples CM119, CM129, CM719 and CM729 were measured at -196 °C, using the gravimetric McBain method. The specific surface area,  $S_{\text{BET}}$ , pore size distribution, mesopore including external surface area,  $S_{\text{meso}}$ , and micropore volume,  $V_{\text{mic}}$ , for the samples were calculated from the isotherms. The pore size distribution was estimated by application of the Barret, Joyner and Halenda (BJH) method<sup>23</sup> to the desorption branch of the isotherms. Mesopore surface and micropore volume were estimated using the high resolution  $\alpha_s$  plot method.<sup>24</sup> Micropore surface,  $S_{\text{mic}}$ , was calculated by subtracting  $S_{\text{meso}}$  from  $S_{\text{BET}}$ .

#### Surface oxygen groups

Temperature-programmed desorption (TPD) in combination with mass spectrometry was used to investigate the nature and the thermal stability of the CM surface oxygen groups. The

TPD profiles were obtained using a custom-built set-up, consisting of a quartz tube placed inside an electrical furnace. A CM sample was outgassed in the quartz tube and subjected to TPD at a constant heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  to  $900\text{ }^{\circ}\text{C}$  under high vacuum. The amounts of CO ( $Q_{\text{CO}}$ ) and CO<sub>2</sub> ( $Q_{\text{CO}_2}$ ) released from the carbon monolith sample (0.1 g) were monitored using an Extorr 300 quadrupole mass spectrometer (Extorr Inc., USA).

#### *Pesticide adsorption*

Adsorption of pesticides (acetamiprid, dimethoate, nicosulfuron, carbofuran and atrazine) by the CM samples (0.5 g) was performed from 50 ml of an aqueous solution of pesticide in batch system with constant shaking. The initial concentration of each pesticide was 500 ppb. The concentration of pesticides was determined at the end of 2 h adsorption period using an HPLC–MS/MS method.<sup>25</sup>

#### *HPLC–MS/MS Analysis*

Surveyor HPLC system (Thermo Fisher Scientific, USA) was used for the separation of the analytes on the reverse-phase Zorbax Eclipse XDB-C18 column, 75 mm long, 4.6 mm i.d. and 3.5  $\mu\text{m}$  particle size (Agilent Technologies, USA). The mobile phase consisted of methanol (A), water (B) and acetic acid (C). The composition was linearly changed as follows: 0 min 59 % A, 40 % B, 1 % C; 10 min 99 % A, 1 % C; 15 min 59 % A, 40 % B, 1 % C. The flow rate of the mobile phase was  $0.5\text{ ml min}^{-1}$ . A 10  $\mu\text{l}$  aliquot of the aqueous solution was injected into HPLC system. Quadrupole ion trap mass spectrometer, LCQ Advantage (Thermo Fisher Scientific, USA), was used for detection and quantification of pesticides. The electrospray ionization technique was used and all pesticides were analyzed in the positive ionization mode. External calibration method and the selected reaction monitoring (SRM) mode was used for quantification of all pesticides.

## RESULTS AND DISCUSSION

The values of the specific surface area obtained by the dynamic method (Table I) showed an increase in the specific surface area on activation. It could be noted that specific surface area of activated CM samples depended on both amount of KOH amount and activation temperature. The increase in the KOH amount together with activation at  $700\text{ }^{\circ}\text{C}$  led to the development of a specific surface. During the activation process, the decomposition of KOH was followed by a gasification process under high temperature:



Stronger activation, *i.e.*, increased ratio of KOH, opened up the porous structure and increased  $S_{\text{BET}}$ .<sup>26</sup> The specific surface area of both CM samples increased on activation at  $900\text{ }^{\circ}\text{C}$  using two ratios of hydroxide. However, further increasing the amount of the activating agent decreased the specific surface area, probably due to enhanced gasification process. Therefore, an over-gasification might have occurred with the detrimental effect of reducing the surface area, especially the micropore surface area.<sup>27</sup> This phenomenon was also observed by Laine and Calafat.<sup>28</sup> The highest values of specific surface area were obtained for the samples carbonized at  $700\text{ }^{\circ}\text{C}$  and activated at  $900\text{ }^{\circ}\text{C}$ .

TABLE I. The amount of pesticides adsorbed on the CM samples ( $q / \mu\text{g g}^{-1}$ )

Sample	Spec. surf. area, $\text{m}^2 \text{g}^{-1}$	Acetamiprid	Dimethoate	Nicosulfuron	Carbofuran	Atrazine
CM7	4.17	11.2	0.00	17.8	1.96	12.0
CM1	6.42	14.9	2.90	2.30	9.19	15.0
CM717	1.44	9.60	7.58	11.1	22.8	5.59
CM727	321	51.4	36.2	18.6	52.6	41.6
CM747	324	38.5	18.6	12.4	35.0	24.9
CM719	388	47.8	48.0	47.7	47.9	48.0
CM729	714	44.6	44.9	44.6	44.8	44.8
CM749	609	44.9	44.9	44.9	44.9	44.7
CM117	93.6	39.0	26.3	13.1	43.7	30.1
CM127	110	28.5	46.5	8.05	63.6	21.0
CM147	133	28.5	22.7	5.50	47.6	16.3
CM119	105	44.6	44.4	43.7	44.7	44.3
CM129	616	66.6	62.0	58.2	68.2	64.7
CM149	59.2	41.2	43.7	26.2	75.0	27.3

The concentration of the pesticides remaining in the aqueous solutions after adsorption on the CM samples was determined by the HPLC–MS/MS method. From the obtained MS<sup>2</sup> spectra of the pesticides (Fig. 3), the most abundant fragment ions were selected. The selected reaction monitoring (SRM) mode was used for quantification of all pesticides. The amounts of pesticides adsorbed on CM samples are presented in Table I. The CM samples activated at 900 °C had better adsorption properties toward the examined pesticides. Since the amounts of pesticides adsorbed were not proportional to the values of specific surface area, it could be assumed that the specific surface area is not a key factor in the adsorption of pesticides.

The porous texture of CM samples with best adsorption properties (CM119, CM129, CM719 and CM729) was determined by physical adsorption of N<sub>2</sub> at –196 °C. The nitrogen adsorption isotherms of selected CM samples are presented in Fig. 4. According to the IUPAC classification,<sup>29</sup> the isotherms are of type I, which are associated with microporous materials. The pore size distributions, shown in Fig. 5, confirm that examined samples were microporous, with most of the pore having a radius smaller than 2 nm. Activation with the higher amount of hydroxide slightly increased the amount of mesopores.

The specific surface areas calculated by the BET equation ( $S_{\text{BET}}$ ), micropore and mesopore area, micropore volume and average pore radius are listed in Table II. The  $S_{\text{BET}}$  values cover a wide range 172–1144  $\text{m}^2 \text{g}^{-1}$  and follow the same trend as the values of the specific surface areas obtained by the dynamic method. However, the values of the specific surface area of selected CM samples obtained by dynamic method and the McBain method show some discrepancies. These discrepancies are even more pronounced with increasing  $S_{\text{BET}}$  and in microporo-

sity. The reasons for these discrepancies lie in the employed experimental conditions. In the case of microporous materials, it is essential to estimate the experimental conditions for the achievement of equilibrium  $N_2$  adsorption, due to the slow nitrogen adsorption within the micropores. The experimental conditions used in the McBain method enabled equilibrium adsorption of  $N_2$ , while in the case of the fast dynamic method, equilibrium nitrogen adsorption was not achieved. Consequently, the dynamic method did not give complete surface coverage and results obtained by this method are lower than those obtained by the McBain method.

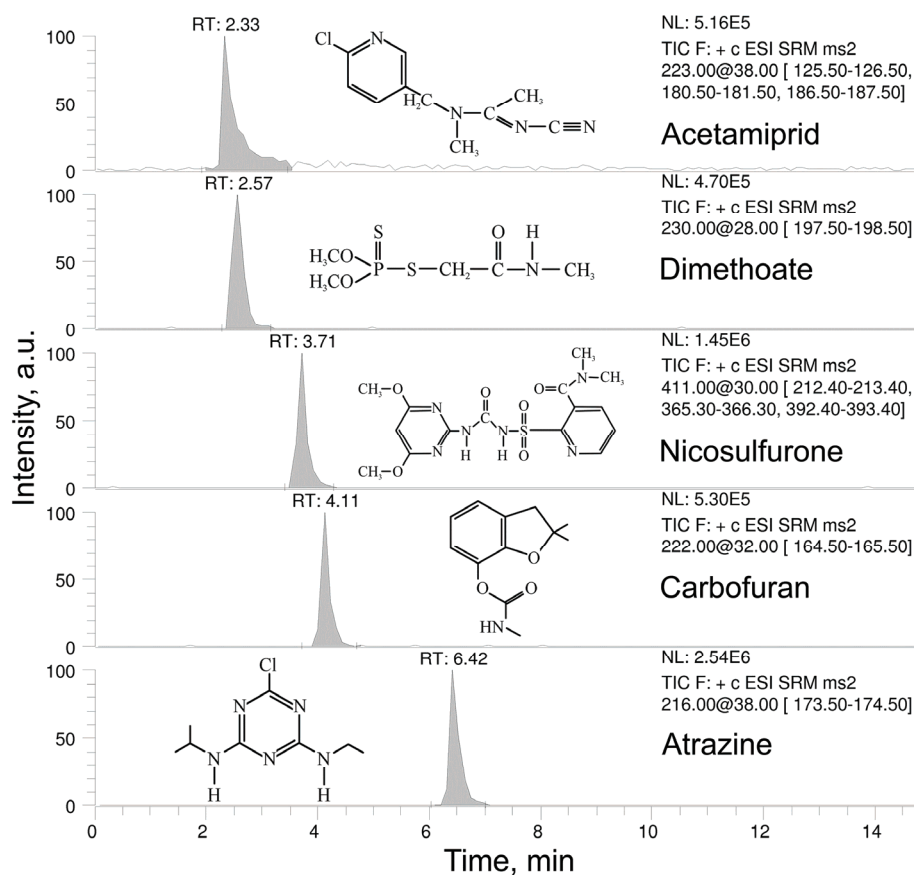


Fig. 3. HPLC Chromatogram of aqueous solutions of the pesticides.

TPD provides quantitative information on the total number of surface oxygen groups. Surface oxygen complexes on carbon materials decompose upon heating by releasing CO and  $CO_2$ . Thus, the TPD peaks of CO and  $CO_2$  at different temperatures correspond to specific oxygen groups. The decomposition temperature is related to the bond strength of specific oxygen-containing groups.



Thus, the position of the peak maximum at a defined temperature corresponds to a specific oxygen complex at the surface. For example, CO<sub>2</sub> is released by decomposition of carboxylic groups at 373–673 K,<sup>30–32</sup> or lactone groups at 463–923 K.<sup>30,33</sup> Both CO and CO<sub>2</sub> peaks originate from the decomposition of carboxylic anhydrides in the temperature range 623–900 K.<sup>30,31</sup> Phenols, ethers, carbonyls and quinones give rise to CO at 973–1253 K.<sup>32,34,35</sup> The quantities of CO and CO<sub>2</sub> released during the TPD experiments correspond to the total amount of surface oxygen groups.

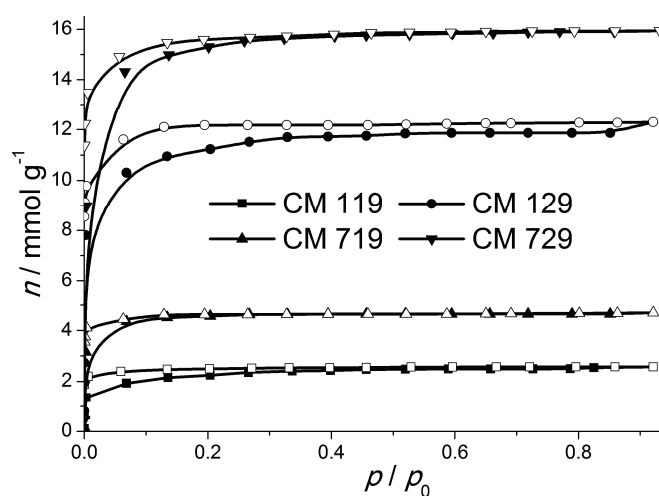


Fig. 4. Nitrogen adsorption isotherms, the amount of N<sub>2</sub> adsorbed as function of the relative pressure for CM samples. Solid symbols, adsorption; open symbols, desorption.

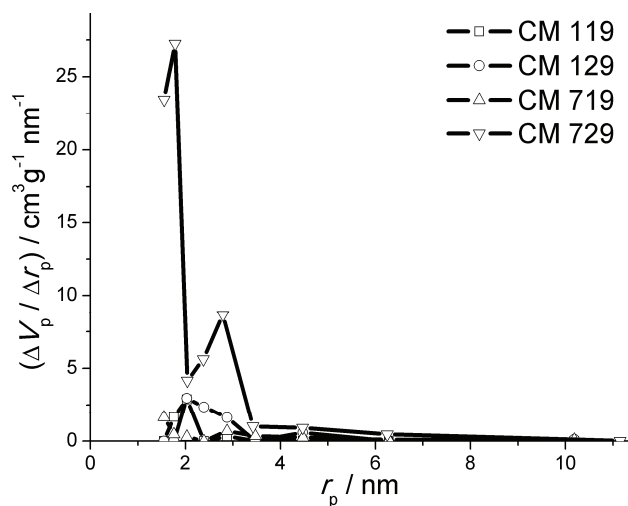


Fig. 5. Pore size distribution for the CM samples.



TABLE II. Porous properties of the CM samples

Sample	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$S_{\text{micro}} / \text{m}^2 \text{g}^{-1}$	$S_{\text{meso}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{micro}} / \text{cm}^3 \text{g}^{-1}$	$r_p / \text{nm}$
CM1	6.42	—	—	—	—
CM119	172	168	4	0.084	1.54
CM129	843	823	20	0.396	1.78
CM719	398	396	2	0.160	2.03
CM729	1144	1133	11	0.540	2.03

TPD profiles of CO and CO<sub>2</sub> evolution for all CM samples are shown in Fig. 6. The TPD profiles of all the tested activated CM samples showed intensive peaks at relatively high temperatures (from 650 to 780 °C). In addition, the CO desorption profiles had a maximum at the temperature which coincides with the maximum in CO<sub>2</sub> desorption profile, which indicates the existence of anhydride groups.<sup>36</sup> The existence of these peaks was not observed in the TPD profiles of

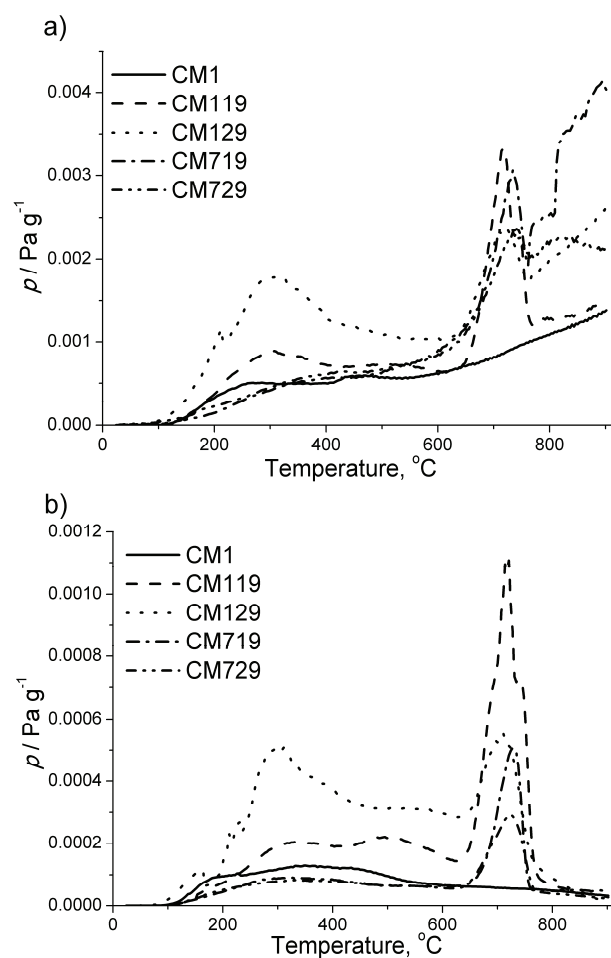


Fig. 6. TPD spectra of the CM samples. a) CO and b) CO<sub>2</sub> desorption profiles.

CM1.<sup>30</sup> Therefore, the presence of a large number of anhydride groups on the surface of the activated CM samples is probably the consequence of the KOH activation process. The appearance of a desorption peak at a low temperature (around 300 °C) in the CO profiles of all samples may be due to thermal decomposition of carbonyl groups in  $\alpha$ -substituted ketones and aldehydes.<sup>37</sup> The CO<sub>2</sub> desorption profile (Fig. 6b) for sample CM129 showed an intensive TPD peak at around 300 °C related to the presence of carboxylic groups. For samples CM1 and CM119, the TPD peak at 300 °C was less intensive but also present, while for the CM samples carbonized at 700 °C (CM719 and CM729), a peak at this temperature was not observed.

The amounts of CO and CO<sub>2</sub> released from the surface of CM samples were obtained by integration of corresponding TPD curves (Table III). For the CM samples carbonized at 1000 °C, the increased amount of activating agent enhanced the number of surface oxygen groups. The highest number of surface oxygen groups was observed for the CM129 sample. On the other hand, for the CM samples carbonized at 700 °C, the increased amount of KOH decreased the number of surface oxygen groups. Comparing the results of the specific surface area and TPD, no proportionality between these results was found. Therefore, it could be concluded that the development of porosity and specific surface area during the activation process was not accompanied with the formation of surface oxygen complexes.

TABLE III. Amounts of CO ( $Q_{CO}$ ) and CO<sub>2</sub> ( $Q_{CO_2}$ ) evolving from the surface oxygen groups of the CM samples

Sample	$Q_{CO} / \text{mmol g}^{-1}$	$Q_{CO_2} / \text{mmol g}^{-1}$	$Q_{CO} + Q_{CO_2} / \text{mmol g}^{-1}$
CM1	1.404	0.297	1.701
CM119	2.068	0.772	2.840
CM129	3.103	1.031	4.134
CM719	2.637	0.335	2.972
CM729	2.173	0.283	2.456

The amount of pesticides adsorbed on the CM samples after a 2-h adsorption period is presented in Fig. 7. The adsorption main force was expected to be the dispersion force between the  $\pi$  electrons in the pesticide structure and the  $\pi$  electrons on the surface of the carbon material.<sup>12</sup> The presence of aromatic rings in pesticide structure increases the possibility of such interactions due to delocalized  $\pi$  electrons over the ring. Moreover, a branched substituent on the aromatic ring increased the level of pesticide adsorption. The obtained results showed that all the activated CM samples had good adsorption properties toward the selected pesticides compared to the CM1 sample. In addition, there was no strong adsorption competition between examined pesticides on the activated CM surfaces. The amounts of pesticides adsorbed on the samples CM119, CM719 and

CM729 were rather similar. According to the TPD results, these samples had similar total amounts of surface oxygen groups and despite of the differences in the specific surface area, they adsorb similar amounts of pesticides. It could be noted that the adsorption capability of these samples follows the same trend as that of the total number of surface oxygen groups. The most pronounced adsorption capability was observed for the sample CM129 with the highest number of surface oxygen groups. According to a suggested mechanism,<sup>12</sup> the specific surface area should have a crucial influence on pesticide adsorption. In the case of pesticide adsorption on activated carbon monolith surface, the specific surface area seems to play a secondary role, which implies that this mechanism cannot be applied for the pesticide adsorption on a carbon monolith surface.

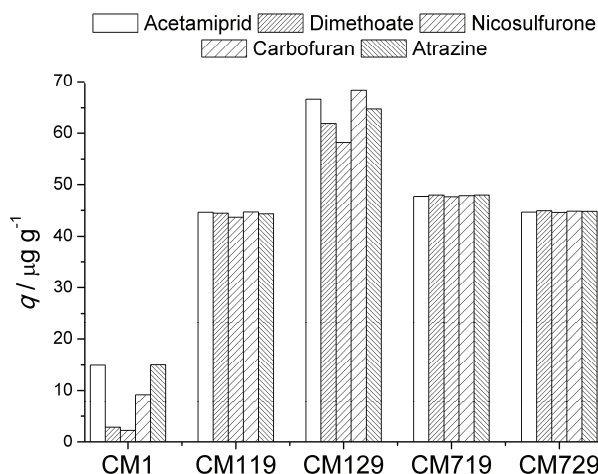


Fig. 7. Amount of pesticides adsorbed on the surface of the CM samples.

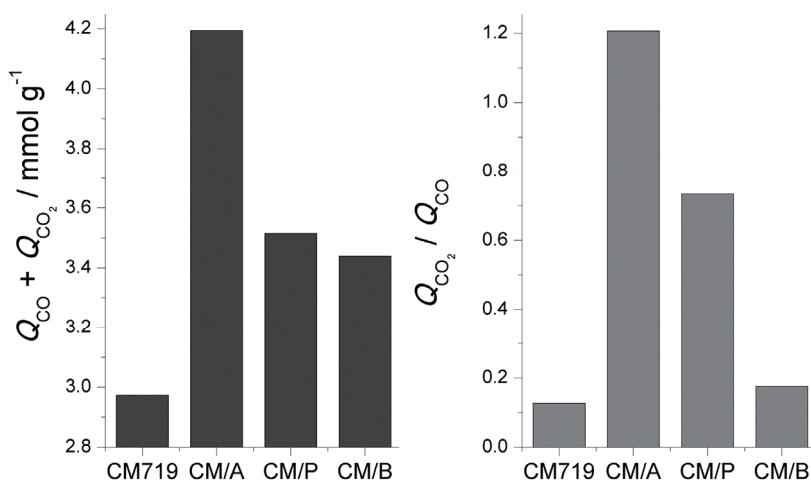
In order to examine the role of surface oxygen groups in pesticide adsorption on carbon monolith surface, sample CM719 was functionalized in a way to change surface chemistry. The nature and number of surface oxygen groups were changed by chemical treatment with different reagents. Specific surface area values for modified CM samples are presented in Table IV. It could be inferred from these results that CM modification results in almost negligible alterations in specific surface area values (less than 10 %). Based on these results, it could be concluded that the porous features of the CM were not greatly altered by chemical treatment.

According to the  $\text{pH}_{\text{slurry}}$  values (Table IV), it can be noted that samples CM719 and CM/B exhibited basic character, while the oxidized samples CM/A and CM/P became more acidic, showing that the majority of the created functionalities were acidic in nature.

TABLE IV. Values of the specific surface area and  $\text{pH}_{\text{slurry}}$  value for the chemically modified CM samples

Sample	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$\text{pH}_{\text{slurry}}$
CM719	398	9.1
CM7-A	380	4.3
CM7-P	362	5.0
CM7-B	385	9.3

The nature of the functionalities created on the carbon surface after the chemical treatment with  $\text{HNO}_3$ ,  $\text{KOH}$  and  $\text{H}_2\text{O}_2$  was studied by TPD method. The influence of chemical treatment on the surface oxygen groups was examined through the total amount of surface oxygen groups ( $Q_{\text{CO}} + Q_{\text{CO}_2}$ ) and the ratio of evolved  $\text{CO}_2$  and  $\text{CO}$  ( $Q_{\text{CO}_2}/Q_{\text{CO}}$ ) (Fig. 8). The TPD results showed that chemical treatment enlarged total number of surface groups, especially for the sample treated with  $\text{HNO}_3$  (sample CM/A). Treatments with  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  increased surface oxidation, which resulted in the evolution of the large amounts of  $\text{CO}_2$ . These results are consistent with the  $\text{pH}_{\text{slurry}}$  results and indicate that acidic groups, such as carboxyl and lactone, which are  $\text{CO}_2$  evolving groups, were additionally formed in the  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  treatments. Although  $\text{KOH}$  treatment increased the total amount of surface groups, the  $Q_{\text{CO}_2}/Q_{\text{CO}}$  ratio stayed almost unchanged, compared to the unmodified sample, which is in agreement with the  $\text{pH}_{\text{slurry}}$  results.

Fig. 8. Total amount of the surface oxygen groups ( $Q_{\text{CO}} + Q_{\text{CO}_2}$ ) and  $Q_{\text{CO}_2}/Q_{\text{CO}}$  ratio for the CM samples.

According to the results obtained for the chemically modified samples, it is possible to modify the surface functionality of an activated carbon monolith without changing considerably the porous texture. In this way, a proper under-

standing of the role of the functionality of an activated carbon surface in the retention of pesticides from aqueous medium at low concentration could be acquired.

As the structure of pesticides plays an important role in adsorption, two pesticides, dimethoate and carbofuran, with different chemical structure characteristics were chosen for an examination of the adsorption properties of the chemically modified CM samples. The amounts of pesticides adsorbed on the modified CM samples are presented in Fig. 9.

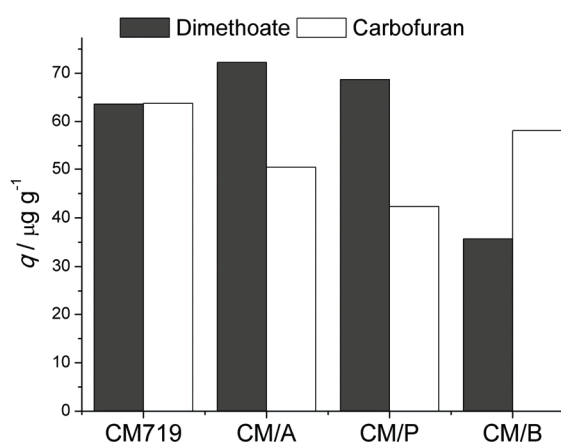


Fig. 9. Amount of dimethoate and carbofuran adsorbed on the surface of the chemically treated CM samples.

It could be seen that chemical treatment affected the adsorption capacity of the examined CM samples. The efficiency of carbofuran adsorption decrease after chemical modification, which was the most pronounced for the oxidized samples. Due to the aromatic structure of carbofuran, dispersion forces between the  $\pi$  electron density of the graphene layers on the CM and the aromatic ring of the adsorbate could be expected. The decrease in the adsorption rate observed after oxidation was most probably due to an alteration of the  $\pi$  electronic density on the carbon surface because of its functionalization. The majority of the surface groups have electron-acceptor character. Functionalization of the carbon monolith withdraws  $\pi$  electrons from the graphene layers, and then the contribution of dispersive interactions to adsorption is reduced. Sample CM/B showed more pronounced adsorption efficiency toward carbofuran, compared to the oxidized samples. Although CM/B had considerable number of surface oxygen groups, it displayed pronounced basic character. One of the reasons for the basic behavior of the carbon surfaces could be the  $\pi$  basicity of the exposed graphene layers.<sup>38</sup> Therefore, the good adsorptive capacity of CM/B toward carbofuran was probably the consequence of the increased  $\pi$  density and dispersive interactions.

On the other hand, the adsorption of dimethoate is not driven by the mentioned  $\pi$ - $\pi$  interactions, due to the absence of an aromatic ring. The obtained results showed that the adsorption capacity increased after oxidation (samples CM/A and CM/P), following the same trend as the  $Q_{CO_2}/Q_{CO}$  ratio. With respect to the  $pH_{slurry}$  values and increased  $Q_{CO_2}/Q_{CO}$  ratios obtained for the oxidized samples, it could be concluded that  $CO_2$  evolving groups play an important role in the adsorption of dimethoate.

#### CONCLUSIONS

In this study, microporous activated carbon monolith samples were produced by changing the parameters of carbonization and activation. Larger specific surface areas were obtained by using higher amounts of the activating agent for samples obtained at carbonization temperatures of 700 and 1000 °C. TPD analysis showed the presence of anhydride groups on all activated CM samples and carboxylic groups on CM samples carbonized at 1000 °C. The possibility of using the produced materials for pesticide removal was also tested. Although, all the tested activated CM samples had good adsorption properties, the most pronounced adsorption capability was observed for the sample CM129, which contained higher numbers of surface oxygen groups. From the obtained results, it could be concluded that the specific surface area is not a crucial factor for pesticide adsorption on the surface of CM. On the other hand, the nature and the number of surface oxygen groups show a dominant effect on pesticide adsorption. Additional functionalization of the CM surface showed that  $\pi$ - $\pi$  interactions were the main force for the adsorption of pesticides with aromatic structure, while acidic groups play an important role in adsorption of pesticides without aromatic ring in their chemical structure.

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#### ИЗВОД

#### УТИЦАЈ ПАРАМЕТАРА ДОБИЈАЊА КАРБОН МОНОЛИТА НА АДОРПЦИЈУ ПЕСТИЦИДА

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У овом раду је испитиван капацитет узорака карбон монолита за адсорпцију пестицида, као и механизам интеракције пестицида са површином угљеничног материјала. Различити узорци карбон монолита добијени су варирањем параметара карбонизације и активације. У циљу испитивања улоге површинских кисеоничних група у адсорпцији пестицида извршена је функционализација површине третирањем са  $HNO_3$ ,  $H_2O_2$  и

КОН. Добијени узорци окарактерисани су одређивањем специфичне површине и расподеле пора, као и методом температурно-програмиране десорпције. За испитивање адсорпције пестицида из водених раствора коришћена је смеша пет пестицида који падају различитим хемијским групама (ацетамиприд, диметоат, никосулфурон, карбофуран и атразин). Приказани резултати указују на то да повећање температуре карбонизације, као и удела активационог агенса, омогућавају добијање микропорозног карбон монолита са већим садржајем површинских кисеоничних група. Утврђено је да површинске кисеоничне групе имају доминантан утицај на адсорпционе карактеристике активираних узорка. Добијени резултати након функционализације површине карбон монолита показују да  $\pi$ - $\pi$  интеракције представљају главну покретачку силу за адсорпцију пестицида са ароматичном структуром, док киселе површинске групе имају водећу улогу у адсорпцији алифатичних пестицида.

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