

Activated Carbons Modified by Ar and CO₂ Plasmas – Acetone and Cyclohexane Adsorption

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Low temperature plasma treatment is currently a scope of many research as interesting tool for enhancing surface properties of many types of materials, e.g. polymers, metals, carbon blacks. Activated carbons (AC) due to their physicochemical properties play a major role as a structural element of gas filters commonly used in respiratory protection for adsorption of many different vapors from contaminated air. It is well known that various surface function groups presented on the AC play a significant role in the hydrophobic/hydrophilic nature of them. This paper refers to the initial study of the effect of low temperature gas plasma treatment on commercially available activated carbon. To treat activated carbon by low temperature plasma, a granulated carbon was placed in a rotating test chamber. The chamber was filled with the relevant reactive gas. The effects of plasma treatment on activated carbon surface and the adsorption properties for two selected organic vapors were studied by analyzing water vapor adsorption isotherm as well as by measurement of adsorption dynamics of those vapors onto gas filter bed made of plasma treated carbons. On the basis of the obtained results it could be concluded that low temperature plasma technology may be used for improving activated carbon properties towards better adsorption of specific low temperature organic vapors.

Keywords: activated carbons, plasma treatment, adsorption.

1. INTRODUCTION

The large surface area, specific structure of pores consisting of micro-, meso- and macropores as well as chemical functional groups on the surface of activated carbons have direct influence on their applications. Activated carbons, because of their unique physicochemical properties play a major role as a structural element of gas filters used in respiratory protection against different hazardous contaminants like organic and inorganic vapors.

The physical and chemical structure of carbon could be changed by various methods, i. e.: activation conditions (different agents, temperature and time of the process), precursor, additives, etc. The chemical functional groups on carbon surface mainly derived from activation process, precursor(s), temperature treatment and post chemical treatment. The surface functional groups on carbons are responsible for the physicochemical properties of the carbons [1–4]. Since the modification of the surface chemistry of carbons is considered as a promising and attractive way toward new applications of carbon, a number of researches focused on how to modify the surface functional groups of carbon materials are reported [5–9]. From the chemical point of view the surface of porous carbon mainly contains the following heteroatoms: oxygen, nitrogen, hydrogen and sulfur, bonded to the edges of the carbon layers and usually collected in functional groups [10]. The number of surface structural groups plays a main role in deciding on the hydrophobic/hydrophilic

nature of activated carbon. The oxygen-containing functional groups have significant influence on carbon performance especially in catalytic reactions [11] and in adsorption process [12].

Introducing the functional groups with oxygen could be achieved mechanically, chemically by treatment in gaseous or liquid agents or electrochemically [13–15].

The plasma treatment process is considered as a promising technique for modification of the carbon adsorbents surface. Plasma could treat the carbon surface physically or chemically. In the case of physical treatment, the porosity of the carbon is changed. In the case of chemical treatment, in turn, the chemically active species on the surface are produced. The use of different gaseous agents during plasma treatment makes it possible to introduce basic or acid functional groups onto the surface. Some experimental works had been reported on activated carbon treatment with oxygen, nitrogen and argon plasmas. The oxygen plasma appeared not to significantly change the structure of pores of the carbon, indicating that the process took place only on the external surface of the carbon. The treatment with argon plasma indicates direct influence on carbon porosity. The modification of the carbon-surface by the nitrogen plasma yielded a significant increase in adsorption of odor and acidic molecules [16–21].

This paper refers preliminary study of the effect of gas plasma treatment of commercially available activated carbon R1Ex taking into account possibilities related to use of plasma treatment for enhancing the adsorption properties of activated carbons. Studies related to the development of activated carbons with dedicated adsorption properties against specific gaseous agents, for

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example highly volatile organic vapors, are very important for occupational safety purposes. Development of the novel carbons with unique physicochemical properties will have direct influence on reducing hazards and risk related to inhalation of hazardous substances by workers in many sectors of industry.

2. METHODS

To treat activated carbon by gas plasma, commercially available granulated carbon R1Ex was placed in a rotary test chamber of a plasma device (Tetra 30, Diener Electronic, Germany) presented on Figure 1. The chamber was evacuated by means of a vacuum pump, and back filled at a small flow rate with selected gases (argon or carbon dioxide). When the radio frequency (13.56 MHz) power was turned on, the gas in the chamber dissociates, and the formed ions, radicals, electrons react with samples of R1Ex carbon surfaces. Duration of each gas plasma treatment for carbon samples was 5, 20 and 40 minutes. Two gases were used for the treatment: argon and carbon dioxide. The power of glow discharge was 120, 200 and 300 W.



Fig. 1. The plasma equipment and method of carbon placement in the test chamber

The effects of plasma treatment was studied by analyzing the water vapor adsorption isotherm obtained for samples of carbons treated with both gases respectively as well as by testing of breakthrough time for carbon bed made of the modified carbon. The breakthrough time is the time taken in test for permeation of a gaseous chemical through a protective equipment (such as a gas filter in case of respiratory protection) [22].

In order to assess changes in dynamic adsorption of modified carbon against selected organic vapors, the breakthrough time were determined for a plastic, cylindrical canister filled with the modified R1Ex carbon. Air with a set humidity of (70 ± 10) RH, at a temperature of 293 K with acetone or cyclohexane vapors were forced through the carbon bed. The complete experimental conditions for testing breakthrough time are presented in

Table 1. The basic properties of organic vapors used for breakthrough tests are presented in Table 2.

Table 1. Experimental conditions for the acetone and cyclohexane breakthrough time determination

Vapor	Concentration
Acetone	1000 ppm
Cyclohexane	1000 ppm
Test conditions:	
Test temperature	293 K
Air humidity	(70 ± 10) %
Volumetric flow rate of air-vapor mixture	5 dm ³ /min
Gas filter bed diameter	15 mm
Gas filter bed depth	60 mm

Table 2. Basic properties of acetone and cyclohexane

Substance	Mass [g/mol]	Boiling temp. [°C]	Dipole moment [Debye]
Acetone CH ₃ COCH ₃	58.08	56.2	2.69
Cyclohexane C ₆ H ₁₂	84.15	80.7	0.00

3. RESULTS AND DISCUSSION

Experimentally obtained adsorption isotherms of water vapor on the carbon treated with Ar and CO₂ plasmas show sigmoidal shape, typical for adsorption isotherms type V, according to IUPAC classification (IUPAC, 1994) [23]. Examples of water vapor isotherms for carbon treated with Ar and CO₂ are presented in Figures 2 and 3 respectively. For low values of relative pressure water vapor adsorption is relatively small but increases from pressure of about 0.3. In order to find differences between samples of activated carbon treated a conclusion from the theory of volume filling in micropores [24] was used.

According to the theory for activated carbons with microporous structure formation of monolayer of water in micro- and mesopores finishing at the pressure equals to 0.6. This give a possibility to calculate a geometrical surface of micropores walls.

$$S_g^{H_2O} = a^{0.6} \cdot \omega, \quad (1)$$

where: $S_g^{H_2O}$ is the geometrical surface of micropores walls; $a^{0.6}$ is the adsorption for relative pressure $p/p_0 = 0.6$; ω is the surface of 1 mmol of water on adsorbents surface (62.27 m²/mmol).

For untreated carbon R1Ex the geometrical surface of micropores are presented in Table 3.

On the basis of obtained water vapor adsorption isotherms for the carbon R1Ex treated with Ar and CO₂ plasmas, the geometrical surfaces of micropores were calculated – the $a^{0.6}$ values are presented in Table 4 and Table 5. The values of water adsorption for relative pressure 0.6 are presented in Figures 4 and 5, respectively.

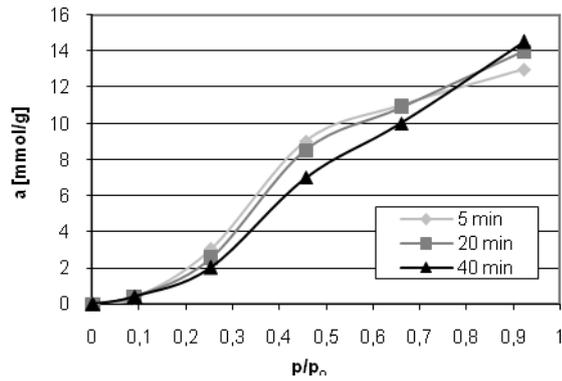


Fig. 2. Isotherms of water sorption for R1Ex carbon treated with argon plasma

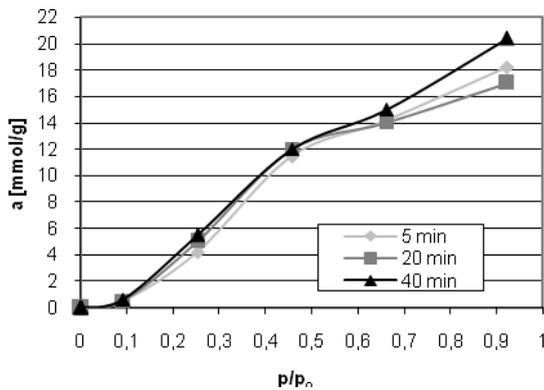


Fig. 3. Isotherms of water sorption for R1Ex carbon treated with carbon dioxide plasma

Table 3. Geometrical surface of micropores for untreated R1Ex carbon

Sample	R1Ex
$a^{0.6}$ [mmol/g]	10.6334
$S_g^{H_2O}$ [m ² /g]	662

Table 4. Calculated values of the geometrical surface of micropores walls for R1Ex carbon treated with argon plasma

Parameter	Treatment time, min	Power [W]		
		120W	200W	300W
$S_g^{H_2O}$ [m ² /g]	5	632	615	552
	20	610	614	532
	40	553	549	526

Table 5. Calculated values of the geometrical surface of micropores walls for R1Ex carbon treated with carbon dioxide plasma

Parameter	Treatment time, min	Power [W]		
		120W	200W	300W
$S_g^{H_2O}$ [m ² /g]	5	775	789	770
	20	789	809	782
	40	801	775	796

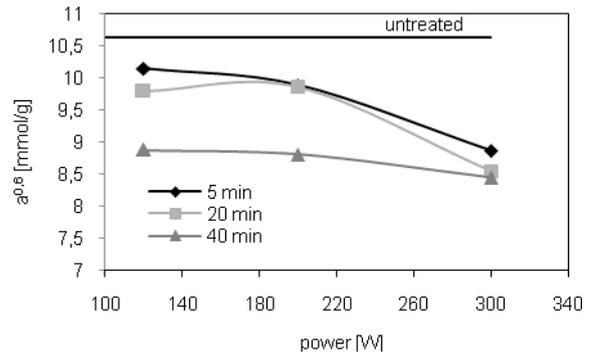


Fig. 4. Plots of calculated values of water adsorption for relative pressure 0.6 for R1Ex carbon treated with argon plasma

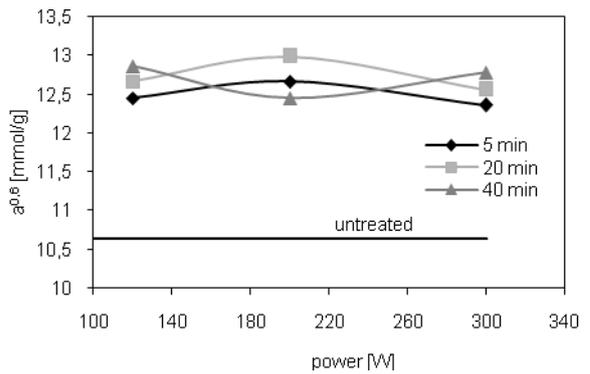


Fig. 5. Plots of calculated values of water adsorption for relative pressure 0.6 for R1Ex carbon treated with carbon dioxide plasma

Experimental data related to adsorption of water vapor in relative pressure 0.6 show that in the case of argon plasma treatment the adsorption of water vapor decreases. In comparison the adsorption of water for carbon dioxide plasma treated carbon are relatively better.

The breakthrough time for untreated R1Ex carbon was the following:

- for acetone: 11 min;
- for cyclohexane: 18 min.

The experimental results of breakthrough time for acetone and for cyclohexane obtained for the R1Ex carbon treated with Ar plasma are presented in Figures 6 and 7.

The experimental results of breakthrough for acetone and for cyclohexane obtained for the R1Ex carbon treated with CO₂ plasma are shown in Figures 8 and 9.

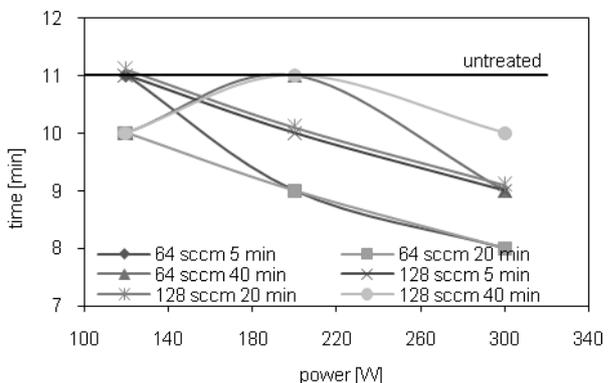


Fig. 6. Breakthrough times of acetone through R1Ex carbon treated with Ar plasma as a function of various process parameters

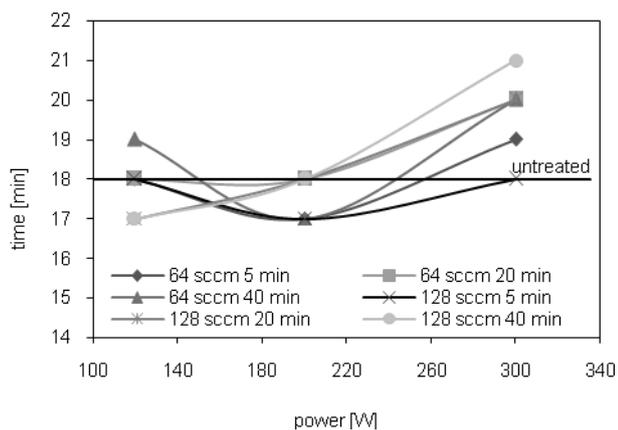


Fig. 7. Breakthrough times of cyclohexane through R1Ex carbon treated with Ar plasma as a function of various process parameters

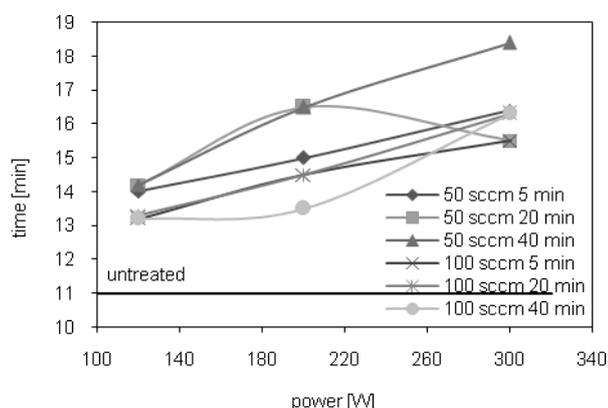


Fig. 8. Breakthrough times of acetone through R1Ex carbon treated with CO₂ plasma as a function of various process parameters

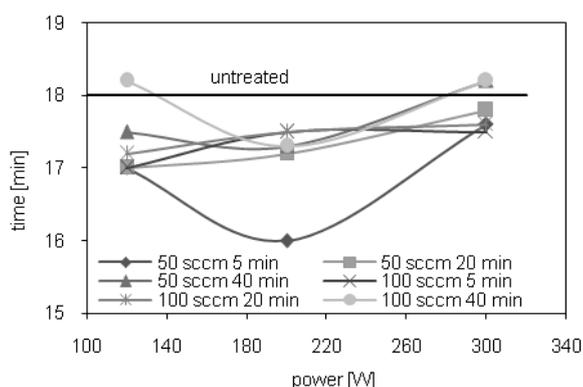


Fig. 9. Breakthrough times of cyclohexane through R1Ex carbon treated with CO₂ plasma as a function of various process parameters

Experimental data related to obtained breakthrough time results show that in the case of argon plasma treatment the adsorption of acetone vapor decreases in most cases and adsorption of cyclohexane vapor increases, especially in case of 300 W power. In comparison in the case of carbon dioxide treatment the breakthrough time for acetone significantly increases in all cases and adsorption of cyclohexane is slightly worse.

4. CONCLUSION

The initial studies related to the effects of plasma treatment for one of the commercially available activated carbon (R1Ex) commonly used in respiratory protection to protect workers against harmful vapors has been carried out. Two different plasma gases were used: argon and carbon dioxide. Based on the water vapor results it was found that argon plasma could treat the carbon surface only physically – the same or slightly decreased the geometrical surface of micropores walls. On the other hand, the CO₂ plasma could treat the surface chemically – relatively more increased the geometrical surface of micropores walls.

The influence on dynamic adsorption expressed by the breakthrough time of acetone and cyclohexane vapors in carbon bed made of the plasma treated carbon has been shown. In the case of carbon treated by CO₂ plasma, improvement in the adsorbability has been achieved for acetone vapors only. Similar influence has been obtained for carbon treated with Ar plasma, but in the case of cyclohexane vapor adsorption. Based on the results obtained for water vapor sorption and the breakthrough times it is possible to conclude that CO₂ plasma leads to the change in the surface chemical structure of the commercial activated carbon rather than the modification of the surface physical structure.

Based on the performed experiments, it is possible to underline that plasma technology could give us some advantages of improving or modeling activated carbon properties. However, further works related to the influence of plasma treatment on carbon properties need to be carried out for example studies related to detailed investigation of surface functional group (XPS, SEM studies) as well as detailed tests regarding the porosity of the carbon and dynamic adsorption of various activated carbons.

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