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Scinetific paper

ACTIVATED CARBONS OBTAINED BY PYROLYZING OF RESORCINOL FORMALDEHYDE GELS

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Abstract

Activated carbon is used in different industrial domains due to highly developed specific surface area and its specific chemistry. Properties of activated carbons obtained by pyrolyzing formaldehyde gels are presented in this paper. The gels were synthesized on several temperatures in order to follow the kinetics of gelling process. The relationship between gel synthesis conditions and properties of activated carbons was examined especially in terms of its influence on value of specific surface area and porosity. Carbon was activated with water vapor and cited activation was examined in terms of influence of water vapor on the value of specific surface area and porosity. The capability of modifying activated carbon surface by $HN0_3$ *oxidation was examined. Characterization of activated carbons was carried out using methods of BET and SEM, IR spectroscopy and by determination of surface electric density.*

Key words: *Activated carbons, gels, kinetics.*

1. INTRODUCTION

Activated carbon is one of the most significant commercial sorbents. Thanks to its huge specific surface area it is widely used in industry and particularly in environmental protection as well as in preparation processes of potable water and air and waste water treatment. The production of activated carbon consists of two phases: carbonization of starting material (which is carbon based) and subsequent physical or chemical activation of so obtained carbon. By selecting starting material and by controlling the process of carbonization and activation, activated carbon with the desired properties i.e. carbon with the defined structure and sorption characteristics can be obtained.

2. EXPERIMENTAL

Synthesis of resorcinol formaldehyde gels

Resorcinol formaldehyde (RF) gels were synthesized by polycondenzation process under base conditions [1]. For syntheses of RF gels these chemicals were used: 35 mass % formaldehyde (HCHO, "Fluka"), resorcinol (1,3 - dihydroxybenzene, "Merck") and anhydrate sodium carbonate (Na_2CO_3, "Fluka"). It was prepared a water solution of mentioned chemicas in molar ratio: resorcinol: formaldehyde: sodium carbonate as 1 : 2 : 0,01. The polycondenzation process and RF gels synthesis from the starting solution were achieved in autoclave. The conditions of RF synthesis in autoclave from the solution with starting PH= 7,05 are given in Table 1.

Tab. 1. The conditions of RF synthesis in autoclave

Sample	temperature	time	RF
1	150 ^{0}C	3h	A
2	150 ^{0}C	2h	B
3	150 ^{0}C	1h	C
4	130 ^{0}C	3h	D
5	110 ^{0}C	4h	E

Carbonization of RF gels and their activation by water vapor

The RF gels were put in tube furnace within nitrogen flow (6,5cm^3/min) at 25^{0}C and the temperature was raised with ratio of 10^{0}C/min until 400^{0}C.This temperature was constant for 10 min. and then it was rasised with the ratio of 10^{0}C/min until 800^{0}C. These temperatures were taken because at 400^{0}C most of volatile substances will be eliminated and at 800^{0}C is necessary for achieving larger porosity and specific surface area.Upon completed carbonization the activation was conducted by entering water vapor under the same conditions of temperature and velocity of flow. Table 2. contains the conditions under which the activated carbons were synthesized from corresponding RF gels as well as cabonisation and activation times.

Tab. 2. The conditions of activated carbon synthesis

1. RF gel A was carbonized 30 min
2. RF gel A was carbonized 30 min and activated 15 minutes
3. RF gel A was dried on air (25^{0}C) for 15 min and then carbonized 30 min
4. RF gel A was dried on air (25^{0}C) for 15 min and then carbonized 30 min and activated 15 min
5. RF gel A was carbonized 30 min and activated 10 min.
6. RF gel A was carbonized 10 min and activated 5 minutes
7. RF gel D was carbonized 30 min
8. RF gel D was carbonized 30 min and activated 15 minutes

Activated carbon No. 2. was oxidized using HNO_3. It was mixed with 20% HNO_3 and then the suspension was kept at the boiling temperature for 4h. After cooling, activated carbon was separated from HNO_3. It was rinsed using 1% NaOH and then washed using distillated H_2O until neutral reaction was reached.

Characterization of synthesized activated carbons

The characterization of activated carbons included:

1. The determination of specific surface area, pore size and its distribution, using BET method (five spots) and micro / mesoporosity using the instrument Sorptomatic 1990.
2. The particle morphology using SEM microscopy type JEOLT-20.
3. FT IR spectroscopy by MB Boman Hartmann MB 100 (4000 –400 cm^{-1}).
4. Potentiometric titration and determination of surface electric density.

3. RESULTS AND DISCUSSION

During the gel synthesis in the moment of gel formatting the color change was observed varying from colorless to brown. Table 3. contains description of conducted experiments under the conditions given within Table 1.

Tab. 3. The description of gels

1.	Hard dark gel was obtained keeping the shape of a vessel in which it was formed.
2.	Orange extremely soft gel was obtained which did not keep the shape of a tank in which it was formed.
3.	The gel was not formed. It is observed the change in color of starting solution from colorless to yellow.
4.	It was formed a strong orange extremely soft gel.
5.	Gel was formed only on the sample surface while yellow color fluid remained in the interior.

As has been presented, pH value was constantly decreasing during the synthesis of RF gels. The results of experiments 1 – 5 confirmed that temperature had a very large influence on polycondenzation process velocity and gelling process. Hard compact gel was obtained after 3h at temperature 150^{0}C. Gels 1. and 4. were used in further experiments, partly being dried on air and then pyrolyzed and activated and partly being pyrolyzed and activated without drying. The BET method determined specific surface area (five spots) is given in Table 4.

Tab. 4. Determined specific surface area using BET method

Activated carbon No.	Specific surface area, Sp (m^2/g)
1. (150 °C, 3h, P30, A0)	130
2. (150 °C, 3h, P30, A15)	544
3. (150 °C, 3h, S*, P30, A0)	125
4. (150 °C, 3h, S*, P30, A15)	286
5. (150 °C, 3h, P30, A10)	380
6. (150 °C, 3h, P10, A5)	280
7. (130 °C, 3h, P30, A0)	< 10
8. (130 °C, 3h, P30, A15)	222

*S is a gel, which is dried before pyrolysing and activation.

According to obtained experimental results it can be concluded that the specific surface area grows up with activation process. Process of polycondenzation and interconnecting RF gels becomes more intensive when temperature rises and with longer gelling time. That is a reason why the specific surface area becomes larger when temperature rises and gelling time is longer. The pore number grows up as well. If the gel was not dried before pyrolyzing process, larger specific surface area was developed due to presence of water in pores. The water in pores does not allow shrinking of gel and closing of pores. The maximum possible porous structure can be obtained by pyroliyzing gels without previous drying.Adsorption and desorption isotherm of activated carbon No. 2. determined by adsorption of gaseous nitrogen at the temperature of liquid nitrogen was given at Fig. 1.

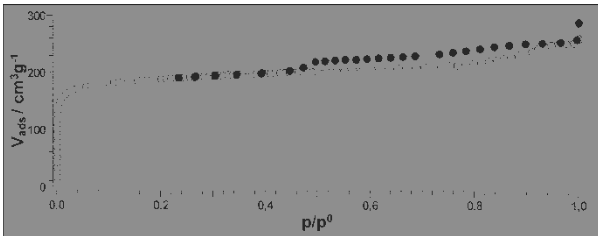

Fig. 1. Adsorption – desorption isotherm of activated carbon No. 2.

Pore volume at p/p_0 = 0,998 is 0,398 cm^3/g and specific surface area is 571m^2/g. Latter value is different from the value determined by BET method in five spots. This is expectable because in the first case more than five spots were used for drawing BET graph thus enabling more precise determination of specific surface area.

Adsorption and desorption isotherm of oxidized activated carbon determined by adsorption of gaseous nitrogen at the temperature of liquid nitrogen was given at Fig. 2.

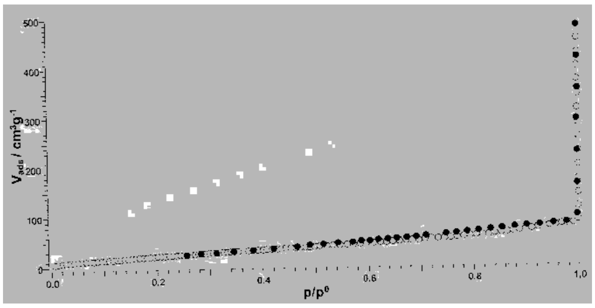

Fig. 2. Adsorption – desorption isotherm of oxidized activated carbon.

Pore volume at p/p_0 = 0,998 is 0,157 cm^3/g and specific surface area is 96,5 m^2/g. These values are considerably lower than the same values at the activated carbon No. 2. These cases are described in literature [2] and they indicate that acid activation can in some way decrease the specific surface area of activated carbons, because it leads to destruction of porous structure.

Adsorption-desorption isotherm presented at picture 1 has a hysteresis, which indicates the mesoporosity, but it also has a significant adsorption at low relative pressures which indicate the micro porosity. The volume of micro pore at activate carbon No. 2 is larger than the volume of meso pores so this sample can be treated as a micro porous with some extent of meso pores whose dimensions are at a line between micro and macro. The distribution of mesoporosity of activated carbon No. 2. is given at Fig. 3.

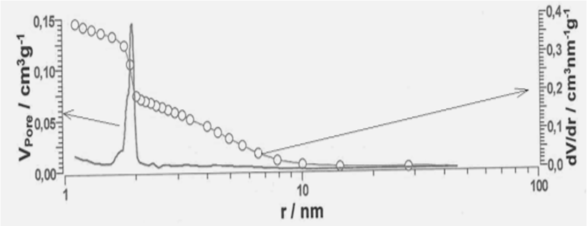

Fig. 3. Distribution of mesoporosity of activated carbon No. 2.

The maximum at the distribution of mesoporosity curve of activated carbon No. 2. is at 1,94 nm and average value of mezzo pores is 2,02 nm. The cumulative mezzo pores volume of activated carbon No. 2. is 0,1455cm^3/g. The distribution of mesoporosity of oxidized activated carbon is given at Fig. 4.

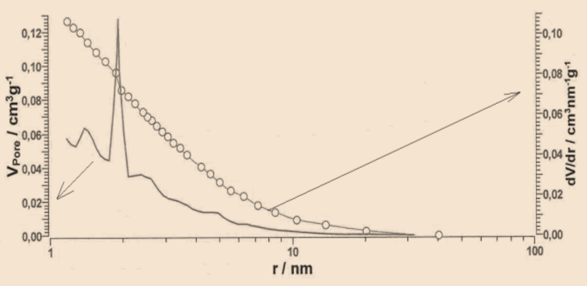

Fig. 4. Distribution of mesoporosity of oxidized activated carbon.

The maximum at the distribution of mesoporosity curve of oxidized activated carbon is at 1,91 nm and average value of mezzo pores is 2,73 nm. The cumulative mezzo pores volume of oxidized activated carbon is 0,1256 cm^3/g.

The distribution of micro porosity of activated carbon No. 2. is given at Fig. 5.

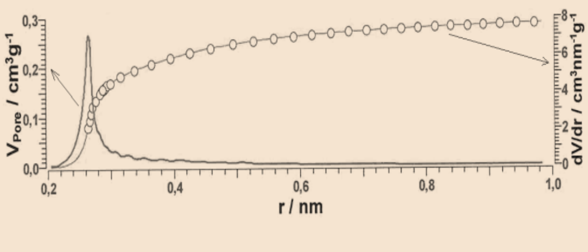

Fig. 5. Distribution of micro porosity of activated carbon No. 2.

The maximum at the distribution of micro porosity curve of activated carbon No. 2. is at 0,264 nm and average value of micro pores is 0,280 nm. The cumulative micro pores volume of activated carbon No. 2. is 0,2884 cm^3/g. The distribution of micro porosity of oxidized activated carbon is given at Fig. 6.

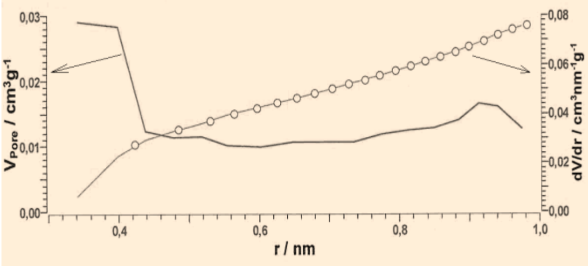

Fig. 6. Distribution of micro porosity of oxidized activated carbon.

There is no maximum on the curve of micro porosity of oxidized activated carbon and the distribution is very irregular. The cumulative micro pores volume is extremely low and reaches 0,0283 cm^3/g. which is ten times less than at activated carbon No. 2.

The above mentioned values of specific surface area, especially the values of pore volume distribution, show that activated carbon No 2. is micro – mezzo porous material, with higher micro pore volume but also with significant part of mesoporosity as well.

The shape of micro and mezzo pore distribution curves as well as the ratio of maximum values of the mentioned curves and average pore size show that in activated carbon No 2. exist very narrow distribution of micro and mezzo pore size.

In the case of the oxidized activated carbon the specific surface area is very small as a result of small micro pores quantities in sample. This activated carbon is dominantly mezzo porous. These results obtained from determinations show that described oxidation process of activated carbon practically leads to closing of micro pores.

The morphology of activated carbon No 2. and oxidized activated carbon is shown in Fig. 7. and Fig. 8.

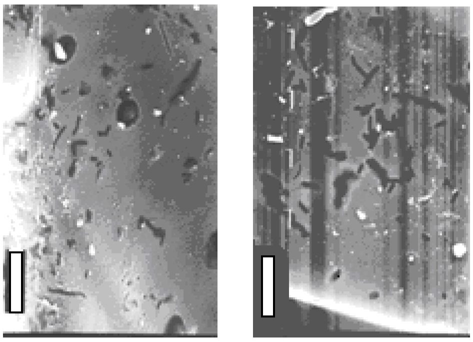

Fig. 7. SEM pictures of activated carbon No 2. (scale: 1 bar = 7 μm)

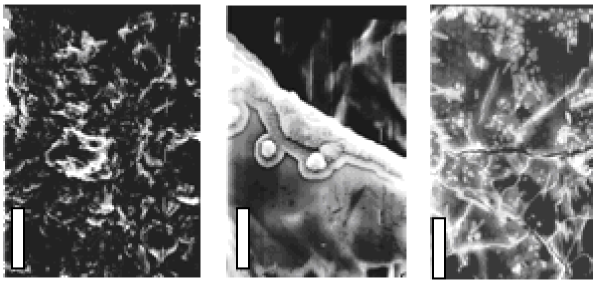

Fig. 8. SEM pictures of oxidized activated carbon (scale: 1 bar = 7 μm)

These pictures show that particles of activated carbon No 2. has very smooth surface, with small notching/s and furrows alternatively distributed over the surface. Such texture (morphology) provides good mechanical features to activated carbons. The surface of oxidized activated carbon particles is more like broken relief than in the case of activated carbon No 2., which probably resulted from oxidation.

Fig. 9. shows FTIR spectrum of activated carbon No 2. and oxidized activated carbon respectively.

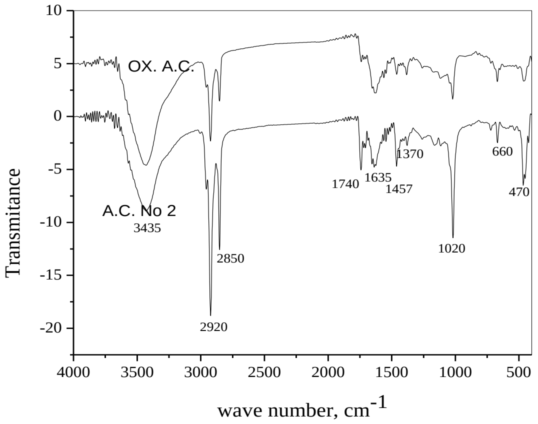

Fig. 9. FTIR spectrum of activated carbon No 2. and oxidized activated carbon.

By comparing FTIR spectra of activated carbon No 2. and oxidized activated carbon, the same lines are observed at both spectra but the intensities of peaks slightly differ. Based on data from literature [2 - 5] a wide line at 3440 cm^{-1} corresponds to elongated vibrations of OH group and adsorbed water. The lines at 2920 and 2840 cm^{-1} correspond to elongated vibrations of C – H bond in CH_2 group of alifation chain. Lines which would correspond to C – H bond in aromatic structures are not observed (i.e. lines 3050 and 3022 cm^{-1} which would correspond to elongated C – H bond vibrations and deformation vibrations lines of C – H bond at 885, 818, 756 and 700 cm^{-1} of aromatic rings). Based on certain literature quotes, line at 670 cm^{-1} could correspond to aromatic C – H bonds. Based on data from literature [2 - 5], lines from 1450 till 1750 cm^{-1} correspond to oxidized groups, primarily of carboxyl and carbonyl groups. However, some of these lines are attributed to C – H bonds from alifation chains (line at 1460 cm^{-1}) as from aromatic structures (line at 1634 cm^{-1}). The line at 1020 cm^{-1} could correspond to C – O – C bond between resorcinol molecules. These considerations of FTIR spectra of activated carbon No 2. and oxidized activated carbon show that obtained activated carbons are not totally pyrolyzed. Intensive lines can be observed in spectra which correspond to C – H bonds as well as some other lines which correspond to gel bonds. By extending pyrolyzing time and with higher pyroliyzing temperature, better pyrolyzing effect could be achieved and activated carbons would have larger specific surface areas. By comparing quoted spectra, it can be seen that both spectra possess lines which show presence of oxide groups, first of all carboxile and carbonile groups. It tells us that described synthesis process creates activated carbons with acid surface functional groups. Washed activated carbon No 2. and oxidazed activated carbobn are titrated with base under different ionic strengths. Washed activated carbon No 2. was also titrated with acid under different ionic strengths. Fig.10. and 11. show potentiometric titration curves of washed activated carbon No 2 with “blind trial” and oxidized activated carbon also with “blind trial” in KNO_3 0,01 mol/dm^3 solution.

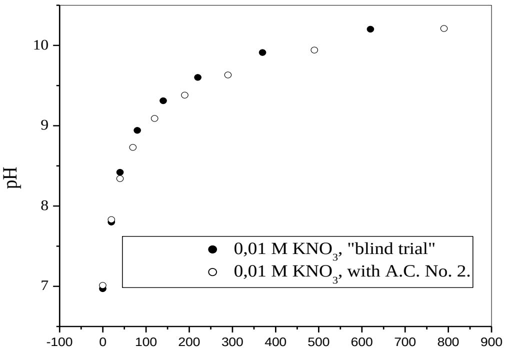

Fig. 10. Potentiometric titration curve of activated carbon No. 2 and "blind trial" in KNO_3 *0,01 mol/dm*^{3} *solution.*

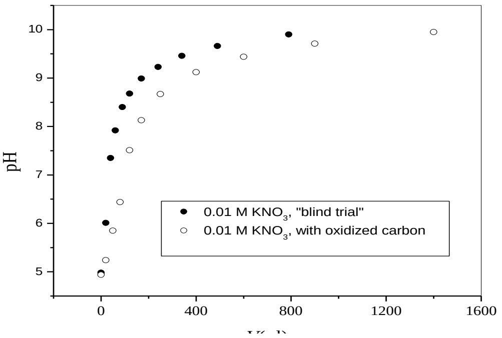

Fig. 11. Potentiometric titration curve of oxidized activated and "blind trial" in KNO_3 *0,01 mol/dm*^{3} *solution.*

By comparing the results of potentiometric titration of washed activated carbon No 2. and oxidized activated carbon it can be concluded that the surface of oxidized activated carbon is participating more in titration process (it takes more base) than activated carbon No 2. This result shows that the surface area of oxidized activated carbon contains more acid groups than the surface area of activated carbon No 2.

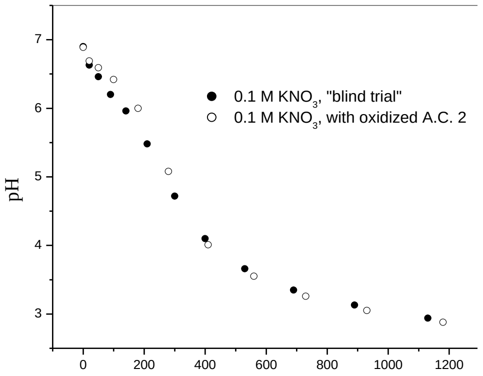

Fig. 12. Potentiometric titration curve of activated carbon No. 2 and "blind trial" in KNO_3 *0,1 mol/dm*^{3} *solution.*

From Fig. 12. it can be seen that while titrating suspension of washed activated carbon No 2. using acid there is no difference in consumption of titration acid in comparison with consumption of acid titration at "blind trial". This tell us that solid faze is not included in titration. Such results tell us that the surface of activated carbon No 2. do not posses groups of base character. Using equation

$\sigma_0 = \frac{100\Delta VcF}{SAV}$ and the results of potentiometric titrations with base in KNO_3 0,01 mol/dm^3 solution, the surface electric density for different PH values for activated carbon No 2 and oxidized activated carbon are determined. These values are given in Table 5. and Table 6.

Tab. 5. Dependence of surface electric density of activated carbon No.2 and oxidized activated carbon from PH value.

Activated carbon No. 2.		
pH	ΔV	σ_0
-	-	-
-	-	-
9	20.51	-0.34
9,25	35.9	-0.61
9,5	56.41	-0.95
9,75	76.92	-1.30
10	117.95	-2.00

Oxidized activated carbon		
pH	ΔV	σ_0
6	46.5	-4.65
6,5	65.11	-6.51
7,5	93.02	-9.31
8	111.63	-11.17
8,5	130.23	-13.03
9	148.84	-14.90
9,5	223.25	-22.35

Table 5 shows that the surface electric density of oxidized carbon is significantly higher related to activated carbon No. 2 thus indicating that by oxidation of activated carbon No. 2 number of ionized acid surface groups per unit surface is significantly higher.

4. CONCLUSION

Based on experimental outputs presented in this paper it can be concluded that high quality activated carbons can be created by pyrolizing resorcinol formaldehyde gels. These materials can find wide application as sorbents.

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