Investigation of Modified Activated Carbons Structural Parameters and Adsorption Capacity

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This paper presents experimental data concerning the influence of microwave irradiation upon the samples of activated carbons obtained from nut shells through activation with water vapours oxidated with hydrogen peroxide and impregnated with guanidine. Experimental data demonstrate that, following the microwave irradiation of activated carbon oxidized and impregnated with guanidine, its specific surface decreases substantially relative to the non-irradiated sample and a shift of the maximum of the pores distribution curve occurs towards higher values of pores size. The role of water bonding with functional groups of oxidized activated carbon, of humic acids available in the mezopores, as well as of water molecules from micropores subjected to some enormous pressures upon the transformations occurring in the adsorbent structure following the irradiation with microwaves, has been analyzed and quantified.

Keywords: modified active carbons, microwave irradiation, adsorption capacity, guanidine

Modified activated carbons are of great importance in making water potable as well as in catalysis where a predominant role is played by the specific surface and the presence of functional groups (carboxilic, phenolic, carbonilic, quinonic etc.) on their surface.

It is well known that as a result of oxidation of activated carbon obtained from nut shells through chemical activation with hydrogen peroxide, and later impregnated with nitrogen heteroatoms, the specific surface of activated carbon significantly increases [1].

Irradiation of activated carbon (saturated with pentaclorphenol) with microwaves leads to the increase of the specific surface from 896.5 m²/g to 983.7 m²/g [2].

In [3] it is ascertained that as result of irradiation of activated carbon fibres with microwaves the specific surface of the adsorbent decreases significantly, except of only one fibre sample in which the specific surface displays some increase (from 433 m²/g to 453 m²/g). The authors explain this result through the fact that this sample was heated up to ~ 800°C during irradiation, while the other samples have been heated up to 900°C.

Microwave irradiation of carbon fibres in nitrogen at P = 1000 w, t = 5 – 30 min leads to the reduction of micropore volume [4].

From the given data, it follows that the problem concerning the impact of microwaves on the structural parameters of carbon adsorbents is not univocally treated. The aim of this paper is to investigate the influence of microwave irradiation of activated carbon (oxidized and impregnated with nitrogen containing organic compounds) upon its structural parameters and adsorption capacity.

Experimental part

Benzene vapours adsorption isotherms on activated carbons samples CAN-7 oxidized with H₂O₂ and impregnated with guanidine at room temperature, and CAN-oxidized with H₂O₂ impregnated with guanidine and irradiated with microwaves (P = 450 W, t = 5 min) have been measured using the installation with vacuum at various relative pressure.

The pores distribution curve by dimensions has been figured out applying the Kelvin equation based on the vapours adsorption isotherms activated carbon CAN-7 oxidized with H₂O₂ and impregnated with guanidine at room temperature, and that irradiated with microwaves (P = 450 w, t = 5 min) within the BET equation coordinates:

\[
\frac{P}{P_s} = \frac{1}{a_mC} + \frac{C-1}{a_mC} \cdot \frac{P}{P_s}
\]

where:
- \(P/P_s\) = the relative pressure of benzene vapors;
- \(a = \) the values of adsorption at different values of benzene vapors pressure, mmol/g;
- \(a_m = \) the maximal value of benzene vapors adsorption;
- \(C = \) a constant equal to the difference between the total adsorption heat in the first layer and the condensation heat.

From figure 1, it follows that as a result of microwave irradiation of such modified activated carbons, the specific surface of the adsorbent decreases significantly from 907 m²/g to 543 m²/g. This result is most probably explained by the fact that at microwave irradiation, the continuous activation of the modified activated carbon occurs and a great part of micropores turn into mezopores, while a part of mezopores turn into macropores. This phenomenon is confirmed by the curve of pore size distribution on these two samples of modified activated carbons (fig. 2).

The above data show a clear shift of the maximum towards higher values of pore size. The same behaviour is found in [5].

It is worthwhile mentioning that in the microwave furnace the heating of the adsorbent occurs due to the
adsorption of microwave energy by water molecules and by other dielectrics contained. At the high frequency field of electromagnetic waves, the direction of the electric field changes with a very high frequency (more than one billion times per second) and the water molecule (dipole) is in a permanent rotation. At the collision of the rotating water molecules, a part of the rotation energy turns into translation energy. Finally, this leads to an increase of the water temperature in the modified activated carbon pores. On the surface of the activated carbon CAN-7, oxidized and modified with guanidine, there are free carboxylic groups that did not react with guanidine molecules due to their inaccessibility. This is also the case of modified activated carbon CAN-7 oxidized with H2O2 and impregnated with melamine [6]. The inaccessibility of some carboxylic functional groups for melamine molecules has been demonstrated through the adsorption of Pb2+ ions on activated carbon CAN-7 oxidized with H2O2 and impregnated with melamine. The size of hydrated Pb2+ ions is less than that of melamine molecules. Water molecules can be adsorbed on free carboxylic groups, thus forming primary adsorption centres so that water existent in the pores of activated carbon CAN-7 oxidized with H2O2 and impregnated with guanidine at microwave irradiation leads to the heating of the zone where these groups are available (these functional groups are practically absent in small micropores).

Moreover, in the large micropores of modified activated carbon a certain amount of water could exist as a result of oxidation, impregnation and drying processes (105°C). Its specific is specific since it is subjected to some enormous pressure due to forces of adsorbate – adsorbate and adsorbate – adsorbent interactions. It is possible that in the electromagnetic field the orientation of water molecules in the direction of the field will occur with substantial delay which will also lead to the heating of the modified activated carbon sample subjected to irradiation.

In the activated carbon with the characteristic energy $E_o = 20$ kJ/mol, the pressure variation in micropores is approximately 2000 bar for benzene. In the activated carbon CAN – 8, the characteristic energy for benzene is also equal to 21.69 kJ/mol, while the pressure variation in micropores will be a bit higher than 2000 bar. Pressure variation in micropores is calculated by relationship:

$$P = \sqrt{\frac{n}{2}} \cdot E_o / V_{o,liq}$$

(1)

where:

- $E_o$ = the characteristic energy;
- $V_{o,liq}$ = the molar volume of the adsorbate (benzene) [7].

As for the pressure variation in micropores following the water vapours adsorption, it will, probably, be not less than in the case of benzene vapours adsorption. In any case, the characteristic energy of activated carbon CAN-7 oxidized with H2O2 and impregnated with melamine, calculated based on water vapours adsorption isotherms is 10.25 kJ/mol, which is half than in the case of benzene. However, the molar volume of water is $V_w = 0.018$ cm3/mmol and is about five times less than that of the benzene. Thus, the pressure variation in the micropores of modified activated carbon, in which the water molecules is adsorbed, can exceed the value of 2000 bar.

Following the oxidation of the activated carbon CAN-7, along with strong and weak carboxylic groups, there are other functional groups (phenolic, carboxylic, quinonic etc.) on its surface which, due to the thermal oscillations, can move chaotically in different directions at distances that do not exceed the ions size. In the electromagnetic field the movements become field oriented. As a result of this process, an asymmetry in the distribution of electric charges appears in the carbon sample (dielectric) thus creating an electric momentum. Movement requires time, thus polarization occurs with some delay – relaxation in relation to the field variation. Therefore, an ion – relaxation polarization occurs. The stabilization time lasts from tenths second to several seconds. Stabilization is energy consuming. It disperses in the form of heating and this kind of polarization results in dielectric losses.

It is also necessary to take into consideration the fact that, following the oxidation of the activated carbon with hydrogen peroxide and its later treatment with NH4OH of 2% the humic acids washed off the activated carbon surface [8]. Since the humic acids do not dissolve in water, but in base media (NH4OH, 2%), it can be supposed that as a result of activated carbon CAN – 8 oxidation, the humic acids will be adsorbed only in mesopores as their size exceeds those of the micropores and superpores. Naturally, in the electromagnetic field they will delay the polarization in respect to the field change. This will lead to the substantial heating of the modified activated carbon mesoporous space.

Figure 3 shows the dependence of the statistical average thickness of benzene adsorption layer ($t, \AA$) upon relative pressure on the samples of activated carbon CAN-7, oxidized with H2O2 and impregnated with guanidine at room temperature and of that later irradiated with microwaves ($P = 450$ W, $t = 5$ min).

From the above data, it follows that, at P/P0 > 0.35, on both samples of modified activated carbons the $t, \AA$ value is higher than 3.7Å, which is the thickness of the benzene ring in the monolayer at its orientation parallel to the adsorbent surface. The fact that this value for the sample
irradiated with microwaves is a little higher than for the sample before irradiation, demonstrates that the microwave irradiation determines the increase of the inclination angle of benzene molecule plane in the newly formed porous structure.

In the figure 4 is shown the dependence of benzene vapours adsorption volume in the two samples studied, upon the statistical average thickness of the adsorption layer \( t, \AA \), based on the equation from [9]:

\[
\alpha V^* = V_1 + S_{me} t
\]  

From data of figure 4, the mezopores surface of these two samples of modified activated carbons has been calculated, being numerically equal to the tangent in the right-winged angle in the \( t - V^* \) coordinates.

Since the value of mezopores surface, calculated based on the \( t - \) method, is about twice that of the film surface [9], we obtain \( S_{me} = 440 \text{ m}^2/\text{g} \) for the sample not irradiated and \( S_{me} = 250 \text{ m}^2/\text{g} \), for the sample after microwave irradiation.

Conclusion

As a result of microwave irradiation (\( P = 450\text{ w}, t = 5 \text{ min} \)) of the activated carbon \( \text{CAN} - 7 \), oxidized with \( \text{H}_2\text{O}_2 \), impregnated with guanidine, the specific surface of the adsorbent decreases substantially from 907 \( \text{ m}^2/\text{g} \) to 543 \( \text{ m}^2/\text{g} \).

The modification process of activated carbons samples by heating as a result of microwave irradiation is due to the delay of humic acids polarization in relation to the field change, as well as due to the delay of the orientation of polar water molecules available in micropores and those bonded by the functional groups on the adsorbent surface.

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