INTRODUCTION

Porous structure, shape and surface area of carbon sorbents are dominant parameters in the physical adsorption of non-polar organic molecules. For the inorganic and organic polar molecules adsorption, both porous structure and surface chemistry of sorbents are important. The surface chemistry of carbon sorbents is determined by the chemical composition of precursor, the way of production, the presence of additives in the carbonization and activation processes and by post treatment with gaseous and liquid agents commonly used to develop specific surface structures.

The oxidation treatment is mostly used method for surface activation of carbon materials involving a number of possible agents: air, oxygen, ozone based gas mixtures, acids (nitric, sulphuric, phosphoric) alone or in combination, hydrogen peroxide, sodium hypochlorite, potassium and sodium permanganate, chromate and dichromate, transition metals nitrates etc [1].

In present work, activated carbon cloth have been oxidized by air, nitric acid, hydrogen peroxide and iron nitrate crystal hydrate melt treatments. Obtained samples have been analysed by TGA, electrical resistance measurement and by selective neutralization method. Adsorption of Cd(II) ions on modified cloth samples has been investigated.

EXPERIMENTAL

Viscose rayon cloth (fiber producer Viskoza-Loznica) was carbonized (N2 flow) and activated (CO2) at 850°C for 1h. The impregnants usually applied prior to carbonization and activation were mixtures of NH4Cl and ZnCl2 both these additives producing activated materials with a low ash content. The activated cloth samples were washed to remove traces of chlorides and other soluble impurities and then heat treated in Ar flow up to 1000°C to ensure the decomposition of possibly present surface complexes. Oxygen surface groups were produced: by air oxidation at 415°C (2.5h), samples denoted as OX-415; by conc HNO3 (90°, 1h) treatment, samples OX-HNO3; by conc. H2O2 (90°, 1h), samples OX-H2O2; by Fe(NO3)3-9H2O (140°, 1h), samples Fe(NO3)3-60. The wet oxidized samples were thoroughly washed and dried at 60°C for 24h. Prepared samples were kept in a desiccator until use.

TGA was performed by Stanton thermobalance with Ar flow and heating rate of 7°/min up to 1100°C. In the neutralization method freshly obtained samples were brought into contact with 0,1 mol/dm3 NaHCO3, 0,05 mol/dm3 Na2CO3 and 0,1 mol/dm3 NaOH solutions. After reaching the equilibrium (24h minimum) the excess of each base was neutralized with 0,05 M H2SO4.

Electrical resistance measurements were performed according to Barton [2]. Electrical resistance at 25°C of samples heat treated in Ar flow to different temperatures up to 900°C has been measured.

Cadmium adsorption (Co= 10 mg/dm3) has been measured by atomic absorption spectrophotometry (PYE UNICAM SP9 unit) at 20°C.

RESULTS AND DISCUSSION

TGA curves of starting P and oxidized samples (Fig.1) show mass losses under 150°C what can be attributed to moisture evaporation. Sample OX-420 is exception as a consequence of preparation procedure. Mass changes above 200°C originating from surface groups degradation are different: 7% for P sample, 19% for OX-420, 22% for OX-HNO3, 33% for Fe(NO3)3-60 and 5% for OX-H2O2 (curve is not presented in the figure).
because of similarity with P. Different mass changes and degradation temperatures indicate that different amounts and kinds of oxygen surface groups have been formed during oxidation procedures.

Electrical resistance data presented in Fig.2 are generally in accordance with TGA results. Investigated samples show extremely different resistance values ranging from about 500 Ω for starting and OX-H2O2 samples to about 30,000 Ω for OX-Fe(NO3)3-60 sample. The resistance enhancement of oxidized samples is evidently result of surface oxygen groups formation during oxidative treatments. Different resistance decreasing during heat treatment is again evidence for different nature of surface groups.

The selective neutralization method gives more detailed information on oxygen surface functionality of the carbons studied. According to Boehm [3] only the strongly acidic carboxylic groups can be neutralized by NaHCO3, whereas those neutralized by Na2CO3 are believed to be lactones, more likely lactols, and carboxylic groups. The weakly acidic phenolic hydroxyl groups are neutralized by NaOH, as are all other mentioned surface groups, so the evidence of total acidity is obtained in this way. Table I presents the neutralization data giving the fraction of each postulated group in total acidity determined by NaOH neutralization. Cadmium adsorption data are also presented.

Results of cadmium adsorption (performed at optimal pH value of 5.2) show the adsorption increase on oxidized samples, especially on OX-420 and OX-HNO3 samples with pronounced acidity. That indicates that cadmium ion adsorption probably takes place by the ion exchange mechanism on acidic oxygen groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total acidity, mmol/g</th>
<th>Phenolic hydroxyl groups, %</th>
<th>Lactone+lactol groups, %</th>
<th>Carboxylic groups, %</th>
<th>Cd(II) ads. μmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2.27</td>
<td>33</td>
<td>5</td>
<td>62</td>
<td>10.5</td>
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<tr>
<td>OX-420</td>
<td>5.07</td>
<td>3</td>
<td>9</td>
<td>88</td>
<td>34.7</td>
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<tr>
<td>OX-H2O2</td>
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<td>73</td>
<td>0</td>
<td>27</td>
<td>14.3</td>
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<tr>
<td>OX-HNO3</td>
<td>7.29</td>
<td>34</td>
<td>29</td>
<td>37</td>
<td>35.6</td>
</tr>
</tbody>
</table>

Sample Fe(NO3)3-60 has not been investigated because of low mechanical properties.

CONCLUSION

Surface modification of activated carbon cloth with air, HNO3, H2O2 and Fe(NO3)3·9H2O treatment results in the formation of different amount and kind of acidic oxygen groups. The amount of Cd(II) ions adsorbed is directly proportional to the number and acidity strength of oxygen groups present on the activated carbon cloth.

REFERENCES