

STUDIES OF ADSORPTION OF ORGANIC SOLUTES FROM AQUEOUS SOLUTIONS ON THE OXIDISED ACTIVE CARBON THERMALLY TREATED AT VARIOUS TEMPERATURES

A. Deryo-Marczewska^a, A. Witkowski^b, H. Grajek^b, S. Biniak^c, Z. Witkiewicz^d

^a Maria Curie-Skłodowska University, Department of Chemistry, 20-031 Lublin, Poland

^b Military Technical Academy, Institute of Chemistry, 00-908 Warsaw, Poland

^c Nicolaus Copernicus University, Department of Chemistry, 07-100 Toruń, Poland

^d Witokrzyska Academy, Department of Chemistry, 25-020 Kielce, Poland

Corresponding Author – hgrajek@zchem.wat.edu.pl

Introduction

Adsorption on active carbon is one of the main methods of removing various organic impurities from liquid solutions. The adsorption properties of active carbons are mainly determined by their pore structure and surface characteristics [1,2]. In adsorption from liquid phase the character of surface functional groups influences the process to a large extent [3]. Knowledge of the influence of these properties on adsorption process is, therefore, of fundamental importance.

The adsorption process from aqueous solutions is of great importance in industrial practice. The processes of water and wastewater treatment are widely applied to protect the environment. The problems concerning the effectiveness of carbonaceous adsorbents in removing the pollutants from waters were often discussed. The effect of adsorbent and adsorbate properties on adsorption uptake was analyzed [1,4]. Despite numerous experimental and theoretical studies many problems still remain to be resolved. Among various effects the role of surface functional groups in adsorption mechanisms was considered. The surface chemistry of carbons depends on the content of complexes formed on adsorbent surface in the modification processes, that determines its charge, hydrophobicity, and the electronic density in the graphene layers. Various mechanisms by which the carbon surface functional groups influence the adsorption from aqueous phase were proposed: dispersive (electrostatic)/repulsive interactions, hydrogen bonding, water adsorption, donor-acceptor interactions. The adsorption processes are also influenced by the properties of the solute functional groups: ability for hydrogen-bonding, activating/deactivating effect on the aromatic ring. Many experimental works concerned the adsorption behavior of aromatic derivatives on active carbons possessing different surface chemical characteristics.

In the present work the effect of acid/basic properties of active carbon on adsorption of organic solutes from dilute aqueous solutions is investigated. The activated carbon obtained from plum stones and previously oxidized was modified by a gradual heating under vacuum in order to obtain the materials characterized by different surface properties.

Experimental

An active carbon obtained from the plum stones was used in the experiments. The commercial carbon was demineralized with concentrated hydrofluoric and hydrochloric acids and oxidized with concentrated nitric acid at 80°C during 2h. Then eight separate carbon samples were thermally modified at different temperatures (180, 260, 340, 420, 500, 580, 740, and 900 °C). As a result eight types of active carbons of differentiated chemical nature of their surfaces were obtained (C180, C260, C340, C420, C500, C580, C740, and C900) [4,5].

In order to investigate the differences in chemical properties of the studied carbons the thermogravimetric (TG) measurements were performed using the thermoanalyzer Setsys 16/18 (Setaram, France). The carbon samples were heated from 30°C to 800°C (5°C/min) in argon atmosphere.

Additionally to estimate hydrophobic/hydrophilic character of carbon surface water vapor adsorption isotherms were measured for three samples C180, C500 and C900.

The Boehm method was applied to determine the content of oxygen surface functional groups. Neutralization with four kinds of bases of various strength (NaHCO₃, Na₂CO₃, NaOH, C₂H₅ONa) was used to estimate the acidic centers. In the case of basic functional groups the neutralization with hydrochloric acid was applied.

The total oxygen content in the investigated carbon samples was determined by the elemental analysis using the analyzer CHNS-O model 1108 (Carlo Erba, Milan, Italy).

Nitrogen adsorption/desorption isotherms at 77 K were determined volumetrically by using ASAP 2405N analyzer (Micromeritics Corp., USA). Before the experiment the adsorbents were outgassed (10⁻⁴ mm Hg) at 393 K.

The 4-nitrophenol and nitrobenzene adsorption isotherms from aqueous solutions at the ionic strength I=0.1 and pH=2.2 were measured by static method. The equilibrium solute concentrations were determined spectrophotometrically.

For the analysis of experimental data for adsorption of organic solutes from aqueous solutions the linear form of well-known Langmuir-Freundlich (LF) isotherm equation, taking into account the energetic heterogeneity of solids [6], was chosen.

RESULTS AND DISCUSSION

In order to study the influence of thermal modification of oxidized and heat treated carbons on their porous structure, the adsorption/desorption isotherms of nitrogen were measured for all the obtained carbon samples. We found only small differences in the pore structure of the analyzed carbons. The observed small differences are a result of successive removal of surface functional groups (the changes in quantity and character of surface oxides) during thermal treatment. The increase of adsorption on the carbons heated at higher temperatures is connected with a decrease of the amount of surface groups that could block smaller micropores or, to a certain extent, some micropores may be widened (in fact eliminated) during oxidation.

The water vapor adsorption isotherms on the carbons C180, C500 and C900 are presented in Figure 1.

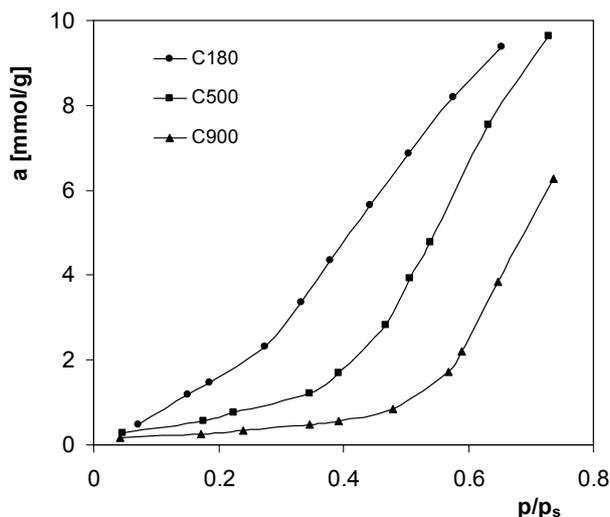


Figure 1. The water vapour adsorption isotherms for the oxidized carbon thermally treated at various temperatures C180, C500 and C900.

The initial course of water vapour isotherm becomes steeper with the increase of total oxygen content in the carbon sample studied.

The thermal treatment of previously oxidized carbons leads to a strong differentiation of their surface properties with respect to the content of oxygen functional groups. In the Table a quantitative analysis of acidic and basic surface groups is presented for all the carbons studied; the total oxygen content is also given.

Table. Surface functional groups on modified carbons [5]

Carbon sample	Content of the surface functional groups [mmol/g]		Parameters of Dubinin-Serpinsky equation			Total oxygen content [wt. %]
	<i>acidic</i>	<i>basic</i>	<i>a_o</i> [mmol/g]	<i>c</i>	<i>k</i> [g/mmol]	
C180	2.29	0.07	3.19	1.81	0.038	10.34
C260	2.13	0.11				8.50
C340	1.91	0.13				7.49
C420	1.75	0.16				6.60
C500	1.12	0.31	1.12	1.72	0.029	5.49
C580	0.83	0.42				4.68
C740	0.46	0.53				2.08
C900	0.23	0.64	0.62	1.37	0.014	0.95

As it is seen from the Table the thermal treatment successively reduces the concentration of surface acidic groups, especially the concentration of strong groups (in the case of carboxyl groups, even to zero) [5]. Simultaneously, this process

increases the amount of basic groups as a result of oxygen removing from the activated carbon surface what results in creating the electron-rich Lewis base sites. The acidic groups decrease the basicity of activated carbons by attracting and thus localizing π -electrons in the graphene layers. It was proved that the basic character of activated carbons arises primarily from delocalized π -electrons. The total amount of surface groups decreases almost three times in the process. Moreover, the amount of oxygen decreases about tenfold.

The observed differences in carbon surface chemistry influence the process of adsorption from liquid phase. In order to study their influence on adsorption from liquids the measurements of isotherms were performed for aqueous solutions of nitrobenzene and 4-nitrophenol. The experimental isotherms are shown in Figure 2 for all the studied adsorption systems.

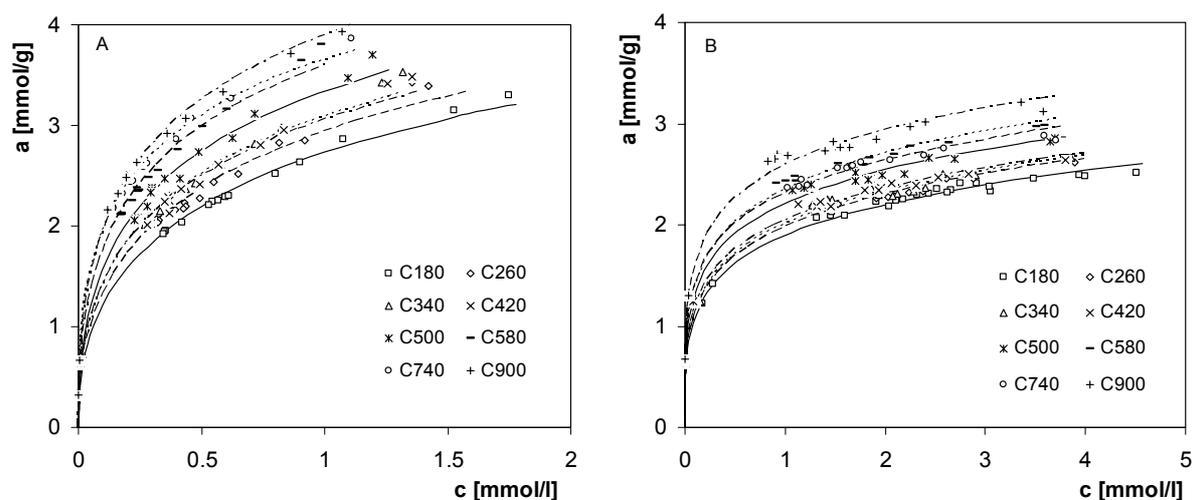


Figure 2. The experimental data of nitrobenzene (A) and 4-nitrophenol (B) adsorption on the oxidized carbon thermally treated at various temperatures.

In the case of both solutes the increase of adsorption is observed with the decrease of concentration of acidic surface groups (the total amount of functional groups also decreases), as it was also observed by the other authors [1,3]. In order to find the explanations of this strong effect of surface oxygen groups on solute uptake one should regard the properties of adsorbent, solvent and adsorbate, and consider the possible interactions between carbon surface and solute molecules. Adsorption of organic molecules on carbonaceous materials is a result of the electrostatic and non-electrostatic interactions between the solute ionic or molecular forms and sorbent surface. Thus, the solution pH determining the adsorbent surface charge and ionization of weak organic electrolyte is one of important factors influencing adsorption process.

The other factors influencing the process of sorption are the properties of adsorbate: size which may limit its accessibility to the pores, molecular form (ionized or non-ionized), solubility determining the hydrophobic interactions, and finally, its chemical character in general. In the case of nonionic substances of similar sizes the effect of the last two factors on adsorption mechanism should be regarded. For aromatic substances of hydrophobic character their sorption is mainly driven by their dislike of water, however, their diverse affinity to the surface being a result of type of substituent has also to be taken into account. In Fig. 3A, C the adsorption isotherms of nitrobenzene and 4-nitrophenol on the acidic C180 and basic carbon C900 are compared in linear and logarithmic scales. For both carbons whose surfaces have

different chemical character nitrobenzene is adsorbed stronger than 4-nitrophenol. These differences in adsorption uptakes for both adsorbates may be a result of the difference in their hydrophobicity determined by their solubilities: ($c_{s,NPh}=0.087$ mol/l, $c_{s,NB}=0.015$ mol/l), and the effect of adsorbate functional groups and their specific interactions with active sites on carbon surface [1]. In order to consider the influence of aromatic solute substituent on adsorption mechanism it is necessary to eliminate the differences in hydrophobicity by normalizing the procedure bringing about the presentation of the isotherms in the reduced co-ordinates (solute concentration divided by its solubility). In Fig. 3B, D the adsorption isotherms for nitrobenzene and 4-nitrophenol are drawn in these reduced co-ordinates in linear and logarithmic scales.

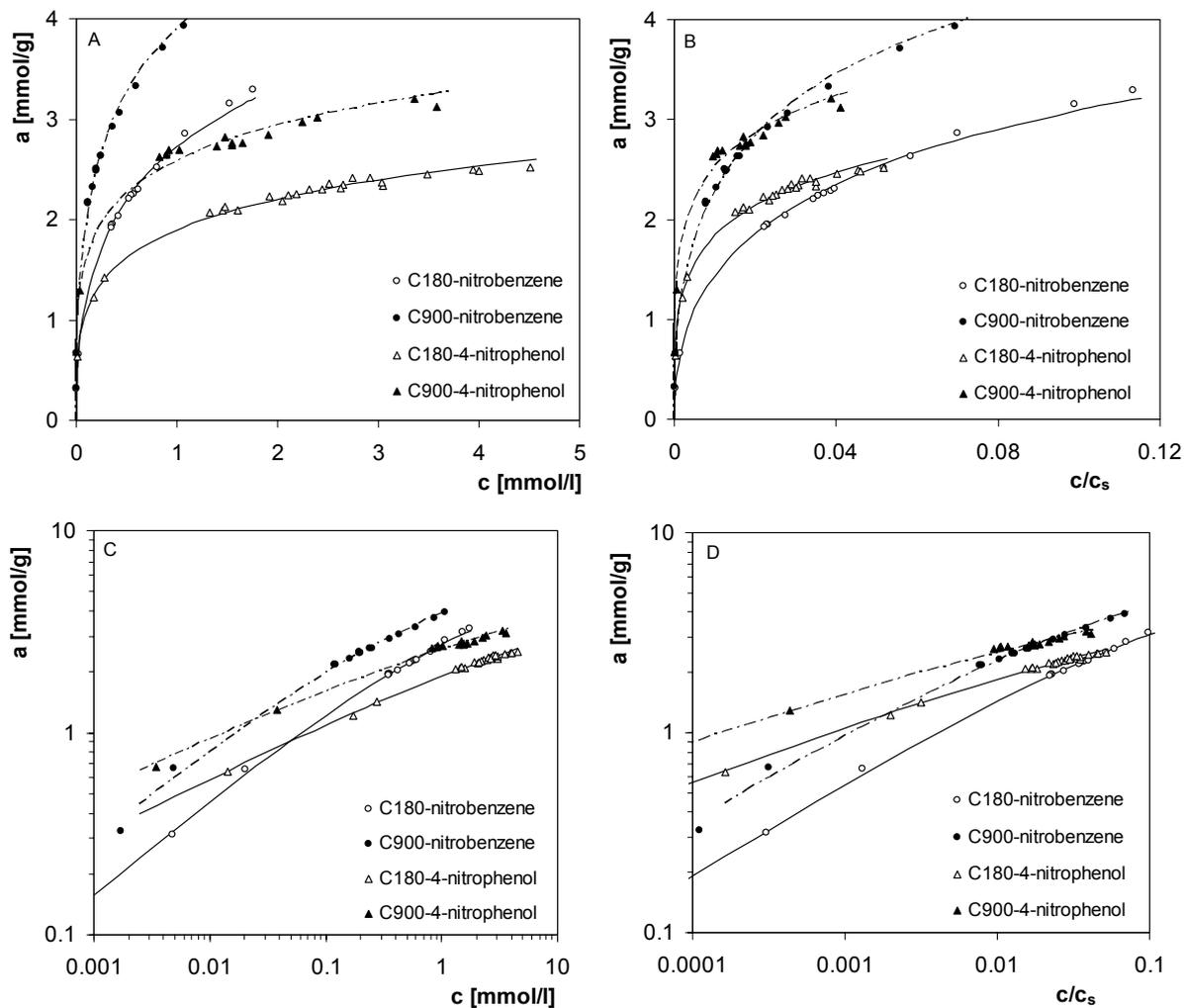


Figure 3. The isotherms of nitrobenzene and 4-nitrophenol adsorption on the oxidized carbons C180 and C900 drawn in standard a vs. c (A, C) and reduced a vs. c/c_s (B, D) co-ordinates, in linear (A, B) and logarithmic (C, D) scales.

In the case of both carbons one can find that 4-nitrophenol has stronger affinity for the adsorbent surface in the range of lower concentrations. Such a behavior may be explained by the consideration of the properties of functional groups for both adsorbates. Similarly as in the case of carbon surface groups the substituent of the aromatic solute ring can withdraw or release electrons from the ring affecting its dispersion interactions with the carbon graphene layers. The functional group

being the electron donor activates the benzene ring by pushing the electrons towards it, and creating a partially negative charge. However, the deactivating group being the electron acceptor creates a partially positive charge. The nitrobenzene molecule has a deactivating $-\text{NO}_2$ group, which produces a positive charge of the aromatic ring. Therefore, the interaction of such molecules is decreased with the surface of oxidized carbon from which the chemisorbed oxygen removes electrons creating positive holes in the conductive π -band of the graphitic planes (Radovic *et al.* 1997; Franz *et al.* 2000). The 4-nitrophenol molecule has an additional $-\text{OH}$ group of activating character, which partly reduces the effect of NO_2 group increasing its dispersive interactions with graphene layers. Thus, for a wide range of lower concentrations stronger 4-nitrophenol adsorption is observed in comparison to nitrobenzene. Such relation is reversed for high concentrations when the condensed phases are formed and the solute molecules may alter their orientation from parallel to vertical. Adsorption (expressed in mol/g) of 4-nitrophenol from concentrated solutions is lower because of its larger molecular size. The same tendencies are observed for the basic carbon C900; in this case it is a result of protonation of electron-rich regions within the graphene layers acting as Lewis basic centers at experimental $\text{pH}=2.2$.

Conclusions

Eight samples of active carbons of differentiated surface properties were obtained in the process of gradual thermal modification of previously oxidized carbon. The thermal treatment successively reduces the concentration of surface acidic groups, and increases the amount of basic groups. The total amount of surface groups decreases almost three times and the amount of oxygen decreases about tenfold. The influence of acid/base properties of active carbons on adsorption of nitrobenzene and 4-nitrophenol from dilute aqueous solutions was investigated. The increase of adsorption is observed with the decrease of concentration of acidic surface groups for both adsorbates. The differences in adsorption uptakes for both adsorbates were found as a result of the difference in their hydrophobicity determined by their solubilities, and the effect of adsorbate functional groups and their specific interactions with active sites on carbon surface. As a result of the differences in adsorbate structure (the amount and chemical character of functional groups) strong non-homogeneity effects were found in the case of 4-nitrophenol adsorption, however, the adsorption system with nitrobenzene shows moderate heterogeneity effects. The correlations between the chemical character of carbon surfaces and parameters characterizing adsorption from solutions were found. Stronger correlation between the equilibrium adsorption constants and the content of acidic and basic groups was found for nitrobenzene adsorption as well for acidic as for basic surface groups.

Acknowledgments

This work was partly supported by the Polish State Committee for Scientific Research, Grant No. 4 T09B 025 24.

References

- [1] Radovic LR, Moreno-Castilla C, Rivera-Utrilla J. In Radovic LR, editor. *Chemistry and Physics of Carbon*, Vol. 27, New York, Basel: Marcel Dekker, , 2001; 227.
- [2] Deryło-Marczewska A. Jaroniec M. In Matijević, E, editor. *Surface and Colloid Science*, Vol. 14, New York, London, Plenum Press, 1987; 301.
- [3] Moreno-Castilla C. Adsorption of Organic Molecules from Aqueous Solutions on Carbon Materials. *Carbon* 2004; 42(1); 83-94.
- [4] Grajek H, Świątkowski A, Witkiewicz Z, Pakuła M, Biniak S. Changes in the Surface Chemistry and Adsorptive Properties of Active Carbon Previously Oxidised and Heat-treated at Various Temperatures. I. Physicochemical Properties of the Modified Carbon Surface, *Ads. Sci. Technol.* 2001; 19: 565-576.
- [5] Świątkowski A, Grajek H, Pakuła M, Biniak S, Witkiewicz Z. Voltammetric studies of the gradual thermal decomposition of activated carbon surface oxygen complexes, *Colloids Surf.A*, 2002; 208: 313-320.
- [6] Jaroniec M, Madey R. *Physical Adsorption on Heterogeneous Solids*, Amsterdam, Elsevier, 1988.