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Adsorption of Phenol and 2,4-Dinitrophenol on Activated Carbon Cloth: The Influence of Sorbent Surface Acidity and pH

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Abstract: In this work the effect of the activated carbon cloth surface acidity and pH of the solution on phenols adsorption has been studied. Two phenols, widely different in the terms of their pKa values (phenol and 2,4-dinitrophenol), have been chosen as the model compounds. It has been shown that phenol adsorption was favored by low pH values of solution and high point of zero charge values of activated carbon cloths. The adsorption of 2,4-dinitrophenol was promoted at very low pH values of solution and it was less influenced by activated carbon cloth surface acidity.

Keywords: Adsorption, activated carbon cloth, phenols, surface properties

INTRODUCTION

There has been an increasing interest in the study of adsorption of organic molecules on activated carbon materials. This is due to the importance of the removal of organic pollutants from water streams and the atmosphere (1–5).

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The adsorption of phenol and substituted phenols from aqueous solution on activated carbons has been intensively investigated for decades, because the phenol molecule, which is relatively simple and well characterized, is frequently used as a model for the adsorption of more complicated organic compounds (6). However, this subject remains highly controversial as described in a recent review by Radović et al. (2) A general concept in adsorption assumes that the surface area is directly proportional to the adsorption capacity. Nevertheless, with microporous activated carbons, a part of the surface can be inaccessible. Among many other subjects discussed in the literature, the nature of the adsorption sites for substituted phenols is a major source of discrepancies. The surface of activated carbons can be divided into three main parts (7):

1. The carbon basal planes, which constitute the majority of the carbon surface (more than 90% of the surface);
2. Sites formed by heterogeneous oxygen-containing groups, which are mainly located at the edges of the graphitic basal planes;
3. Metal impurities (ash).

Coughlin and Ezra (8) suggested that adsorption of phenol takes place between the phenol aromatic ring and the π electron system of carbon basal planes, while Mattson et al. (9) proposed that phenol forms strong donor–acceptor complexes between carbonyl groups located at the carbon surfaces and the phenol aromatic ring. Superficial carboxylic groups, which are able to form a hydrogen (10) or ester (1) bond with the OH function of phenols, are another possible adsorption sites. The presence of oxygen-containing basic groups (e.g., chromene-type, pyrone-type), as a key factor in promoting phenol irreversible adsorption on carbon materials, has been reported as well (11). Vidić et al. (12) investigated the influence of metal impurities (Al, Ca, Cu, Mg, Mn, and Fe) on phenol adsorption on activated carbon. They concluded that metal impurities content was not the key parameter in phenol uptake.

In the recent paper Terzyk (13) emphasized the role of the so-called "solvent effect" on the phenol adsorption on carbon surfaces. Hydrophilic surface groups caused water blockage of carbon active surface sites. The same author reported that adsorption of phenol at the acidic pH (1.5) was lower for all studied carbons than at neutral one. Moreno-Castilla et al. (14) reported that the adsorption capacity of the activated carbons towards phenols depended on the solution pH in the following way: at acid pH the amount adsorbed remained practically constant or increased slightly with increasing pH. When the pH increased further, there was a decrease in the amount of phenolic compound adsorbed. The pH at which this decrease occurs depended on the difference between the external and internal surface charge density determined by electrophoretic and titration measurements, respectively. Laszlo et al. (15) studied adsorption of phenol and tri-chlorophenol on basic activated carbon at different pH. The order of the monolayer capacities in phenol adsorption was: unbuffered $>$ pH $= 3 >$ pH $= 11$, while in the case of tri-chlorophenol the order was: pH $= 3 >$ unbuffered $>$ pH $= 11$. Radovic and co-workers (16) investigated the influence of pH on aniline and nitrobenzene adsorption on activated carbons. They found out that both electrostatic and dispersive adsorbate/adsorbent interactions could have a significant influence on the equilibrium uptakes of ionic and non-ionic adsorbate species. Dispersive interactions in general are promoted by conducting the experiments at solution pH values near the adsorbate's PZC, at which the repulsive interactions between charged surface groups and uncharged molecules are minimized.

Activated carbon is the most commonly used and studied adsorption material, although carbon fibers and carbon cloth are found to be very efficient phenol adsorbents (3, 5). In this work the effect of the surface acidity of activated carbon cloth (ACC) and pH of solution on the phenols adsorption has been studied. The object of this study was to get deeper insight into the mechanism of phenols adsorption on ACC aimed towards use of ACC for phenols removal. Two phenols widely different in the terms of their pKa values (phenol and 2,4-dinitrophenol) have been chosen as the model compounds.

Surface acidity of ACC samples was determined in the terms of their intrinsic ionisation constants (pK_a^{int} values) and point of zero charges (PZCs). The pK_a^{int} values and PZC have been considered as an excellent reference index for correlating changes in the surface acidity of carbons to the degree of surface oxidation (7, 17–19). PZC is shifted to lower pH values as the degree of oxidation increases due to the introduction of acidic groups such as carboxyl, phenolic, carbonyl and lactonic (20, 21).

pK_a^{int} and PZC values were calculated from the potentiometric titration studies using site-binding model (22, 23).

EXPERIMENTAL

Characterization of Activated Carbon Cloth Samples

Three samples of ACC were produced in the "Vinča" Institute of Nuclear Science, Belgrade, Serbia and Montenegro. The process of carbonization and activation were described elsewhere (23, 24). ACCs were impregnated prior to carbonization, using either mixture of NH_4Cl and $ZnCl_2$ (samples C1 and C3) or the mixture of NH_4Cl and $CuCl_2$ (sample C2). These additives produce activated materials with low ash content (23). ACC samples were washed several times with deionized boiling water to remove traces of chlorides and other soluble impurities, dried in an oven at 110°C and stored in a desiccator until used.

Specific Surface Area

BET specific surface areas of ACC were determined by benzol adsorption at 295.15 K. Benzol was used, rather than nitrogen, for the reason that its molecular radius is much closer to the molecular radius of phenol.

Pore size distribution of ACC was determined from nitrogen adsorption isotherms measured at 77 K by a Micromeritics ASAP 2020 computer-controlled surface analyzer. The Micropore analysis (MP) method (25) was used to determine micropore size distributions. The mesopore volume distribution was calculated according to the Barrett, Joyner and Halenda (BJH) theory (25).

Surface Acidity

Surface charge densities of ACCs were determined by potentiometric titrations in aqueous solutions of KNO_3. Two parallel runs were carried out:

a. In the presence 0.1 g of ACC (in 50 ml of 0.001, 0.01 or 0.1 mol/dm^3 KNO_3) and
b. In the same electrolyte in the absence of ACC (blank). A 0.1 mol/dm^3 solution of HNO_3 or KOH was used as a titrant.

Volume increments of 0.01 ml of titrant were added to the solution successively. Each addition was followed by 10 minutes equilibration. To prevent O_2 and CO_2 absorption from the air, purified N_2 was bubbled through the solution throughout the titration run. The solutions were stirred by a magnetic stirrer in all experiments. All experiments were carried out at 298 K.

The surface charge (σ_o) ($\mu C \cdot cm^{-2}$) was estimated from the net titration curves by the following expression:

$$\sigma_o = \frac{\Delta v \cdot M \cdot F \cdot 100}{S \cdot A \cdot V} \tag{1}$$

where V(cm^3) is the volume of KNO_3 solution, A ($g \cdot dm^{-3}$) is the amount of ACC used for titration, S ($m^2 \cdot g^{-1}$) is the specific surface area of the ACC, F is Faraday's constant (96500 C), M is the molarity of the titrant used, and Δv is the difference between the volume of the titrant used for the solution with ACC and the blank at given pH values. Intrinsic ionisation constants were calculated based on 2-pK model by Hou and Song (22) proposed for amphoteric solids. The detailed procedure for calculation of the pK_a^{int} values from experimental data for the surface charge is presented elsewhere (23). PZC values were calculated according to the following equation (23).

$$PZC = 0.5(pK_{a1}^{int} + pK_{a2}^{int}). \tag{2}$$

Phenols Adsorption

The adsorption of phenols was carried out by immersing 50 mg of ACC into 50 ml of 100 ppm aqueous solutions of phenol or 2,4-dinitrophenol in tightly closed glass flasks. pH values of phenols solutions were adjusted by the addition of 0.1 mol/dm^3 HCl or 0.1 mol/dm^3 NaOH. Flasks were shaken at 298 K in a thermostated bath until equilibrium was reached. Phenols solutions were separated by filtration and their concentrations were evaluated by reversed-phase high performance liquid chromatography (Spectra-Physics HPLC system model SP8810, Lichrosorb RP-18 column, mobile phase: 50% methanol–50% water acidified with 0.1% acetic acid, $\lambda = 280$ nm). Quite a few of the experiments were repeated at least three times and the results were reproducible. The average deviation was <3%.

RESULTS AND DISCUSSION

Activated Carbon Cloth Surface Characterization

Surface Area and Pore Size Distribution

Benzol adsorption isotherms were analysed using the Brunnauer, Emmett and Teller (BET) (26) method in order to determine the surface area of the ACC samples. The measurements were performed for several samples and for further consideration three samples having significantly different surface areas were chosen: sample C1–1138 m^2/g, C2–481 m^2/g and C3–684 m^2/g.

According to the pore size distribution (Table 1) ACC samples have predominantly microporous surfaces, as expected for fibrous carbon materials (14). The total micropore volume decreases with the surface areas of the samples, C1 (0.582 cm^3/g) > C3 (0.491 cm^3/g) > C2 (0.386 cm^3/g). All ACC samples have similar average micropore radius: C1–0.323 nm, C2–0.331 nm and C3–0.316 nm.

Table 1. Surface characteristics of ACC samples

ACC	Surface area (m^2/g)	Mesopore volume (cm^3/g)	Micropore volume (cm^3/g)	Average micropore radius (nm)	pK$_{a1}^{int}$	pK$_{a2}^{int}$	PZC
C1	1138	0.0054	0.582	0.323	5.8	7.6	6.7
C2	481	0.0056	0.386	0.331	7.1	8.1	7.6
C3	684	0.0057	0.491	0.316	4.0	6.4	5.2

Surface Acidity

The plots of surface charges versus pH, in Fig. 1, have a trend similar to that reported (27) for amphoteric oxides, with σ_o increasing with an increase in ionic strength and acidity at pH $<$ PZC, and negative σ_o increasing with an increase in ionic strength and basicity of the solution at pH $>$ PZC. The shapes of σ_o versus pH curves are typical for amphoteric surfaces, and are not symmetrical with respect to PZC, which means NO_3^- and K^+ ions exhibit different complexation affinity toward the ACC surfaces.

Numerical pK_a^{int} values were obtained from the dependence $pQ_{a1} = pH + \log(\alpha_+/1 - \alpha_+)$ and $pQ_{a2} = pH - \log(\alpha_-/1 - \alpha_-)$ versus fraction of surface positive and negative charged sites, α_+ and a_- respectively. The double-extrapolation technique proposed by James et al. (28) (illustrated in Fig. 2) was used to extrapolate pQ_{a1} and pQ_{a2} to the zero α_+ and α_- values Obtained results are presented in Table 1.

The results obtained for C3 sample confirmed predominantly acidic nature of that sample surface. The sample C3 has the lowest value of PZC (5.2) and that is in agreement with the highest amount of carboxyl groups ($0.421\,\mathrm{mmol\,g^{-1}}$) found on that sample by Boehm method of selective titration (29), published in our previous paper (30). As a matter of fact the pK_{a1}^{int} value for C3 surface (4.0) lies very close to the benzoic acid pKa value ($pKa_{benzoic\ acid} = 4.19$). The sample C2, having lowest total amount of surface acidic groups ($0.545\,\mathrm{mmol\,g^{-1}}$), consequently has the highest PZC value (7.6). The sample C1 having the highest amount of total acidic surface groups ($0.928\,\mathrm{mmol\,g^{-1}}$) but smallest amount of most acidic carboxyl groups ($0.168\,\mathrm{mmol\,g^{-1}}$) has the intermediate PZC value (6.7). Therefore, the PZC value proved to be in exceptional correlation with the surface acidity of carbons.

The numerical values for pK_{a1}^{int} and pK_{a2}^{int} obtained enabled a schematic illustration of the variations in charged-site density with local pH_s, for studied ACCs, to be drawn (Fig. 3). Here, a program employing the stehiometric equations describing association-dissociation and counterion binding reactions at the amphoteric ACC/electrolyte interface, written in MATHCAD ver. 2001 commercial software package, was used. As might be expected, amphoteric and basic single-site surfaces are dominated by positively charged sites if the system is very acidic ($pH_s < pK_{a1}^{int}$). Similarly, amphoteric and acidic single-site surfaces are dominated by negatively charged sites if the system is alkaline ($pH_s > pK_{a2}^{int}$). In the range between pK_{a1}^{int} and pK_{a2}^{int}, a great majority of the uncharged sites at the surface are evident.

Phenols Adsorption at Different pH Values of Solution

A change in solution pH influences the charge properties of ionizable phenols molecules and, hence, their adsorption. With a p*K*a of 9.99 (31), phenol is

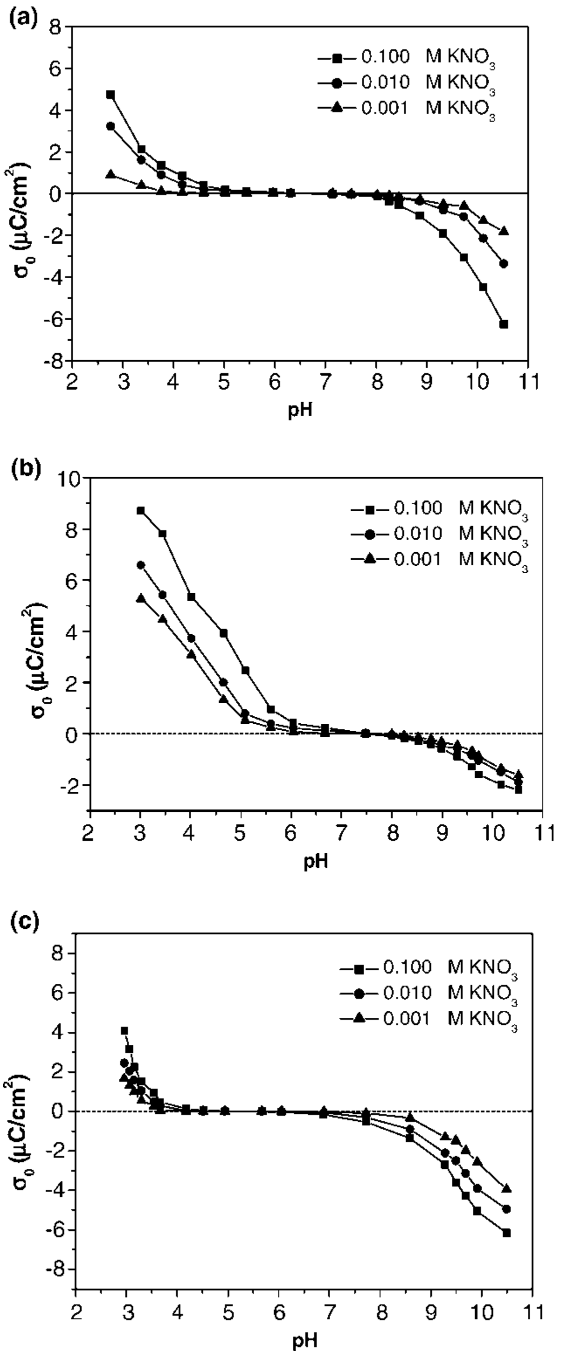

Figure 1. Surface charge densities of ACC samples a) C1, b) C2, and c) C3 in KNO_3 solutions as a function of pH.

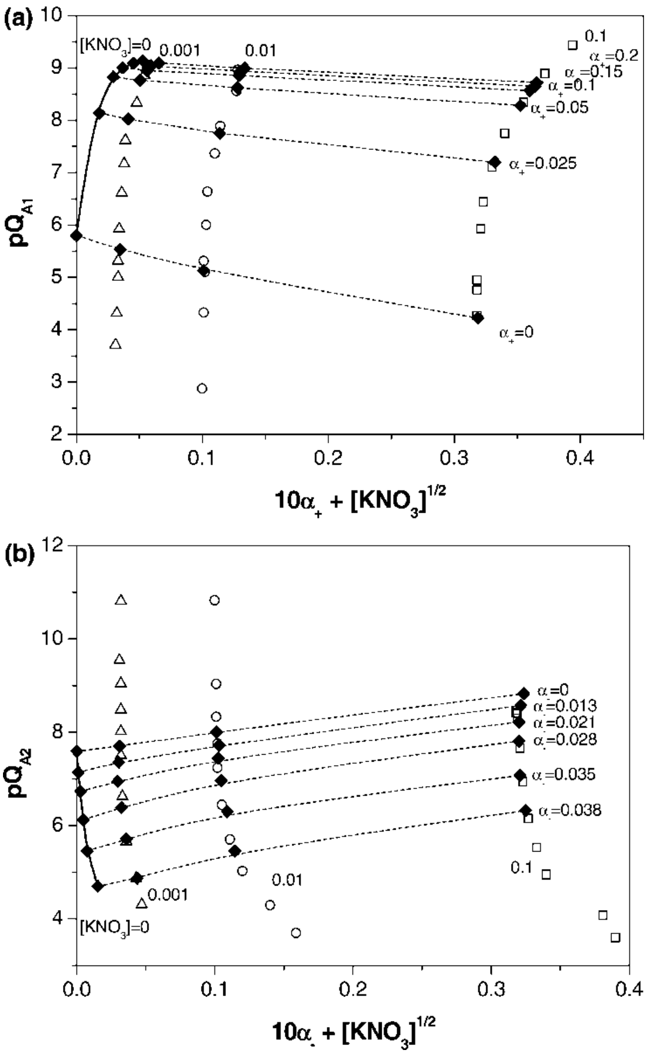

Figure 2. Calculation of (a) pQ_{a1} and (b) pQ_{a2} values for sample C1 by the double-extrapolation technique. Hollow symbols represent experimental data while dashed lines and filled diamonds are the extrapolated ones. Explanation: $pQ_{a1} = pH + \log(\alpha_+/1 - \alpha_+)$, $pQ_{a2} = pH\ -\log(\alpha_-/1 - \alpha_-)$, where α_+ and α_- denote fraction of charge sites for the positive and the negative surface respectively.

present in solution predominantly in the molecular form at $pH < 9.99$ or as an anionic species at $pH > 9.99$. More acidic 2,4-dinitrophenol ($pKa = 4.09$) (31) is preferably in anionic form at $pH > 4.09$. Fig. 4 illustrates the distribution of the molecular form of phenol and 2,4-dinitrophenol in the solutions with pH values ranging from 0–14.

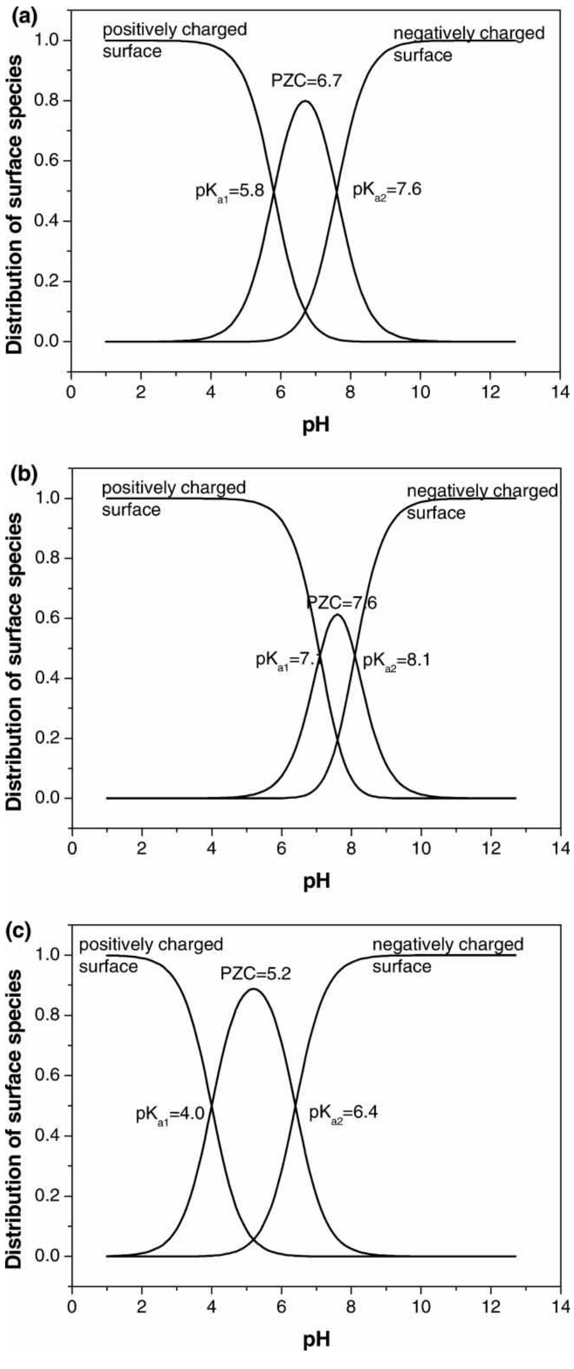

Figure 3. The schematic illustration of the variations in charged-site density with local pHs for ACC samples a) C1, b) C2, and c) C3 surface.

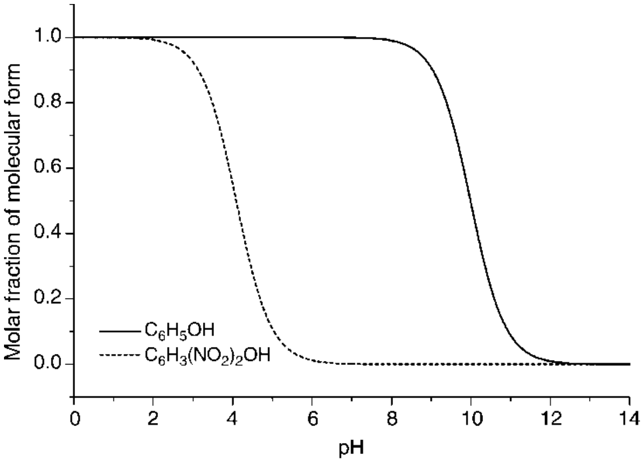

Figure 4. Distribution of phenol and 2,4-dinitrophenol molecular forms versus pH.

The effect of the solution pH on the adsorption capacity of ACCs for phenol is shown in Fig. 5. At the lowest observed solution pH value ($pH = 2$) phenol uptake is similar on all ACC samples. Generally phenol uptake decreases as the pH of the solution increases. The exception is observed on the sample C2 in the pH range 2–7, where gradual increase of phenol adsorption is observed. The decrease in phenol uptake is more pronounced at basic pH values. The distinct decrease in phenol adsorption at

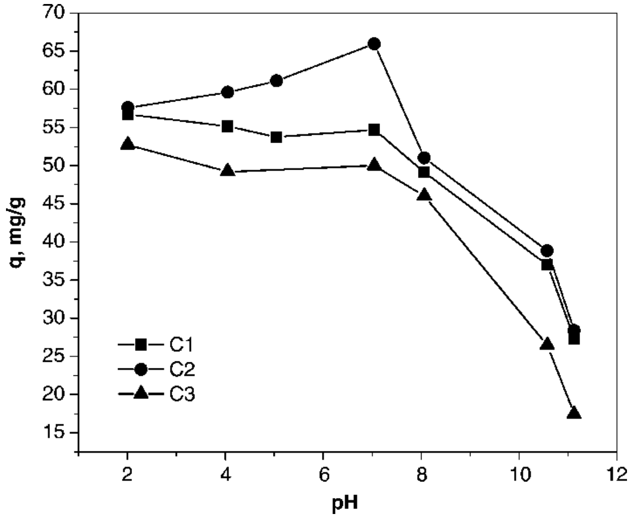

Figure 5. Phenol adsorption on ACC samples at various pH.

$pH > 8$ can be explained by repulsion of phenolate anions by the negative charge at the ACCs surfaces, as described in reference data (15, 16).

By comparing Fig. 4 with Fig. 5. it can be noticed that the trends of the phenol adsorption curves on samples C1 and C3 (Fig. 5.) followed the trend of the phenol molecular fraction curve (Fig. 4). These results indicate that phenol is preferentially adsorbed at the surfaces of C1 and C3 sample in its molecular form. Keeping in mind that at the low values of solution pH ACCs surfaces are neutral to positively charged, it can be assumed that phenol molecules are adsorbed on samples C1 and C3 mainly trough dispersive forces (π-π interactions), as suggested by Coughlin and Ezra (8).

However, the amount of phenol adsorbed depends also upon the surface charge of the carbon. Thus, the adsorption is highest at the sample C2 surface and the lowest at the sample C3 surface having the highest and the lowest PZC values, respectively. The decrease of phenol adsorption with the increase of surface carboxylic groups density (i.e. decrease of PZC value) have been reported in literature (32). The proposed explanation was that carboxylic groups withdrew electrons from graphene layers and consequently reduced the number of adsorption sites. This behavior is in favor of the π-π interaction argument. The additional argument is that surface oxygen groups, particularly carboxylic groups, adsorb water, creating water clusters through H-bonding, which reduces the accessibility and affinity for aromatic adsorbates, and therefore reduces the adsorption capacity (10, 13).

The basic functional groups at the carbon surface increase electron density in the graphene layers of the activated carbons, and thus dispersive interactions between electrons are stronger (17). That explains the highest phenol uptake on sample C2.

The shape of the adsorption curve for the most basic C2 sample in acidic pH range differs from corresponding curves for C1 and C3 samples. The highest amount of phenol is adsorbed on ACC C2 at $pH = 7$. The similar results were reported by Laszlo et al. (15) on basic activated carbon. There are at least two possible explanation of that phenomenon:

1. $pH = 7$ is lower than C2 PZC value and the sample C2 surface is charged slightly positive (Fig. 2.). It can be assumed that positively charged C2 surface cause phenol dissociation at some extent and subsequently adsorption of phenolate anion by electrostatic attraction forces, as suggested by Aksu and Yener (33).
2. At more acidic pH values the ACC C2 surface becomes more hydrophilic due to the adsorption of protons on basic groups as suggested by Terzyk (13). Increased adsorption of water on ACC surface blocks some active adsorption sites and in that way diminishes the phenol uptake.

These results demonstrate that the role of the surface area is not dominant in phenol adsorption. The sample C2, with the lowest surface area (481 m^2/g)

adsorbed more than samples C1 ($1138\,m^2/g$) and C3 ($684\,m^2/g$) through out the whole pH range.

Equilibrium pH values of the phenol solution in contact with all ACC samples were closely related to the initial pH values (± 0.3). The similar trends were observed with 2,4-dinitrophenol in the pH region were adsorption was significant ($pH = 2-5$), as well as in the pH range 8–11. In the pH interval 5–8 there were some discrepancies due to the buffer effect, but irrelevant for the adsorption process.

The adsorption capacities for 2,4-dinitrophenol on ACC samples obtained in the pH range 2–11 are presented in Fig. 6. The adsorbed amount of 2,4-dinitrophenol on all ACC samples is highest at the lowest observed pH value of the solution ($pH = 2$). By comparing Fig. 5 and Fig. 6 it can be noticed that 2,4-dinitrophenol uptake is less influenced by the surface chemistry of the ACC samples and more sensitive to the pH solution change than uptake of phenol. In the pH range 2–4, the adsorption capacity for 2,4-dinitrophenol is rapidly decreasing. The similar trend for Bromoxymil (a phenol derivate having very similar pKa, 4.06, to 2,4-dinitrophenol pKa, 4.09) adsorption on carbon black was report by Yang et al. (34). In the same pH range there is a rapid decrease in the molar fraction of molecular form of 2,4-dinitrophenol (Fig. 4). These results strongly support the assumption that the mechanism of phenols adsorption is based mainly on the unpolar interactions, that can be weaken by the ionisation of phenols molecules. In the pH range 4–7 2,4-dinitrophenol is predominantly in anionic form and the surfaces of ACC samples C1 and C2 are positively charged (Fig. 3). If the electrostatic forces had dominant influence on phenol adsorption the

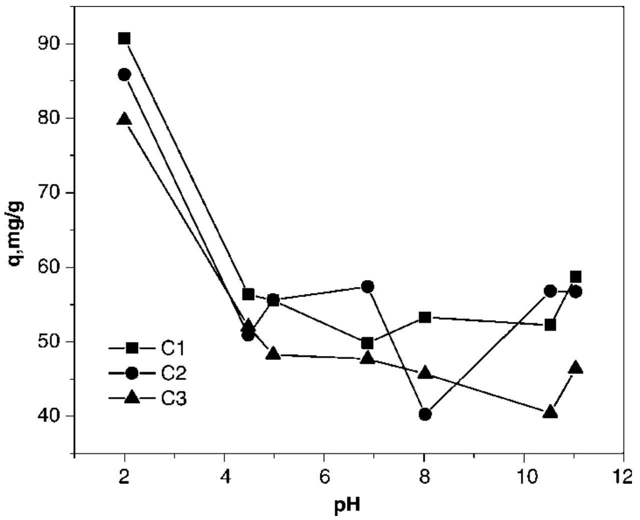

Figure 6. 2,4-dinitrophenol adsorption on ACC samples at various pH.

maximum of C1 and C2 adsorption curves would be expected in that range. Only one local maximum can be observed at $\mathrm{pH} = 7$ in C2 adsorption curve confirming that electrostatic attraction forces are present but less important than π-π interactions. At high pH values ($\mathrm{pH} = 8-11$) some increasing trend at adsorption curves can be noticed for all ACC samples, the most significant on ACC C2 adsorption curve. However in this pH interval the overall adsorption of 2,4-dinitrophenol is insignificant.

CONCLUSIONS

It has been shown that phenol adsorption was favoured by low pH values of solution and high PZC values of ACCs. The adsorption of 2,4-dinitrophenol was promoted at very low pH values of solution and it was less influenced by ACC surface acidity. The results obtained support the hypothesis that phenols were adsorbed on the carbon materials mainly through dispersion forces between π electrons in phenol aromatic ring and π electrons from the basal carbon planes. Electrostatic attraction forces were present but less significant in the phenols adsorption mechanism.

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