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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Adsorption Properties of Modified Multilayer Carbon Nanotubes with Respect to Benzoic Acid

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Abstract—Multilayer carbon nanotubes were modified by ultrasonic treatment in nitric acid and subsequent calcination in an inert atmosphere of argon at temperatures of 500, 800, and 1200°C. The dependence of the adsorption of benzoic acid on carbon nanotubes on the temperature of their calcination was analyzed.

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The discovery of carbon nanotubes (CNT) by S. Iijima in 1991 initiated a steadily increasing number of studies in this area. Active development of methods for synthesis of CNTs with prescribed properties and structure and a search for their promising application areas were commenced [1–3]. At present, CNTs are successfully used as sorbents, which is due to their high specific surface area of up to 2000 $m^2 g^{-1}$ [4].

Benzoic acid (C_6H_5COOH) belongs to permitted synthetic preservatives most frequently used in Russia, Ukraine, and other countries. The solubility of benzoic acid is about 0.34 g per 100 g of water at 25°C. The maximum permissible concentration of (C_6H_5COOH) for various food products is 150 to 2000 mg per gram of a product [5]. Together with parabens, salicylic acid, and 4-hydroxy benzoic acid, benzoic acid is used in the cosmetic industry and can penetrate into organisms from various makeup preparations via respiratory tracts and skin [6]. Benzoic acid is a component of bottled sweet water and juices, added to prolong their storage life. In natural water basins, (C_6H_5COOH) is formed in the life activities of various aquatic organisms and in their decomposition. Industrial wastewater is a source of synthetic benzoic acid found in surface water [7]. Numerous human diseases are caused by consumption of water containing toxins, radionuclides, pathogenic microorganisms, and substances whose content exceeds the maximum permissible concentration. Some researchers believe that (C_6H_5COOH) is a carcinogen because, when reacting with vitamin C, it forms benzene frequently found in tap and bottled water. Benzene can cause malignant changes in organs of a human organism. Therefore, there presently exists the problem of a search for effective sorbents for extraction of benzoic acid from water [8].

The adsorption activity of carbon nanotubes with respect to polar organic molecules has been studied [9]. In [10, 11], experiments were performed on adsorption of benzoic acid from aqueous solutions on activated carbon. Single- and multilayer nanotubes have been used for adsorption of zinc ions from aqueous solutions [12]. CeO_2 particles deposited onto the CNT surface have been used to purify water to remove arsenates [13]. In [14], the advantage of carbon nanotubes over activated carbon as sorbents for dioxins was demonstrated. The adsorption of *o*- and *p*-xylene from water by carbon nanotubes oxidized with nitric acid was studied in [15]. The adsorption of resorcin, phenol, catechine, hydroquinone, and pyrogallol from water by oxidized multilayer was analyzed in [16] in order to develop new adsorbents for water purification to remove contaminants.

The aim of the present study was to examine the adsorption of benzoic acid from water by modified multilayer carbon nanotubes and to determine the dependence of the adsorption of the acid by CNTs on the temperature of their thermal treatment.

EXPERIMENTAL

Certified multilayer carbon nanotubes (Nanothinx S. A.; diameter 12–31 nm, length >10 μm, number of

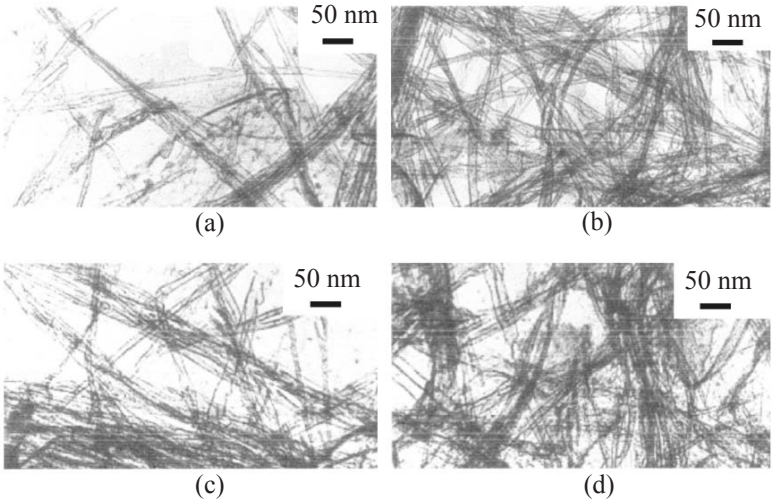

Fig. 1. TEM images of carbon nanotubes: (a) initial and (b–d) calcined in the atmosphere of argon for 1 h at (b) 500, (c) 800, and (d) 1200°C.

layers 15–35, purity 97%) produced by catalytic pyrolysis were used in the study. The CNTs were modified by the procedure described in detail in [17]. The nanotubes were subjected to ultrasonic treatment in concentrated nitric acid for 12 h (CNT^{in}) and then were calcined in the inert atmosphere of argon at temperatures of 500 (CNT^{500}), 800 (CNT^{800}), and 1200°C (CNT^{1200}) for 1 h.

Carbon nanotubes were identified by transmission electron microscopy (TEM, JEMOOCX-II instrument). The specific surface area of the samples was measured by the chromatographic method on the basis of the low-temperature desorption of argon [carrier-gas helium (93.5%), adsorbate-gas argon (6.5%)]. The adsorption of benzoic acid was performed as follows: carbon nanotubes (0.05 g) were brought in contact with 100 ml of an aqueous solution of benzoic acid with a concentration of 0.164 M (20 mg l^{-1}) for 1–200 min, with the amount of adsorbed benzoic acid measured at regular intervals of time. To construct the isotherm of C_6H_5COOH adsorption, 100 ml of the acid (concentration 0.082–0.492 mM) was adsorbed onto CNTs in the course of 2 h. Data on the dependence of the amount of adsorption on the pH value were obtained by bringing a weighed portion of CNTs with benzoic acid solutions with a concentration of 0.164 mM. The pH values of the acid solutions were varied from 2.8 to 10.6 by addition of HCl or NaOH. After the equilibrium was attained, pH values of the equilibrium solutions were measured. The concentration of benzoic acid in aqueous solutions was determined by titration with a standard NaOH solution in the presence of phenolphthalein as indicator (pH range of color transition, 8.2–9.8). The solutions were titrated under agitation until a stable weakly pink coloration appeared. The adsorption of benzoic acid was calculated from the difference of the concentrations of the initial and equilibrium solutions. The experimental error was 6%.

Figure 1a shows TEM micrographs of carbon nanotubes modified with nitric acid under ultrasonic treatment conditions and then calcined at 500, 800, and 1200°C to obtain samples with varied content of chemisorbed oxygen on the nanotube surface (Figs. 1b–1d). The joint treatment of the CNT samples with ultrasound and nitric acid was performed in order to raise the content of oxygen on the surface and make larger the specific surface area [9].

For CNT^{in}, CNT^{500}, CNT^{800}, and CNT^{1200}, the specific surface areas were calculated from desorption of argon to be 525, 320, 263, and 245 $m^2\ g^{-1}$, respectively. The observed sequence can be attributed to occurrence of aggregation and sintering of nanotubes under the action of high temperatures, up to 1200°C. According to the results of temperature-programmed desorption (TPD) of CO and CO_2, with mass-spectrometric monitoring, the amount of chemisorbed oxygen on the samples decreases in the order $CNT^{in} > CNT^{500} > CNT^{800} > CNT^{1200}$. Only trace amounts of chemisorbed oxygen were found in nanotube samples calcined at 1200°C.

The dependence of the amount of benzoic acid adsorbed from an aqueous solution with a concentration of 0.164 mM on the time of contact between the solution and carbon nanotubes, obtained in the study, is shown in

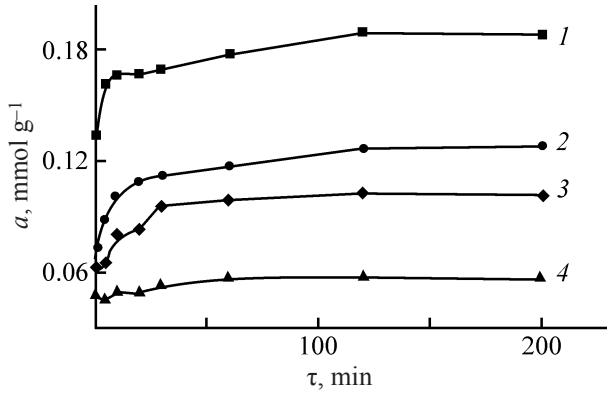

Fig. 2. Adsorption of benzoic acid, a, vs. the time τ of contact between its aqueous solution with (*1*) CNT^{in}, (*2*) CNT^{500}, (*3*) CNT^{800}, and (*4*) CNT^{1200} samples. T = 20°C, c = 0.164 mmol g^{-1}.

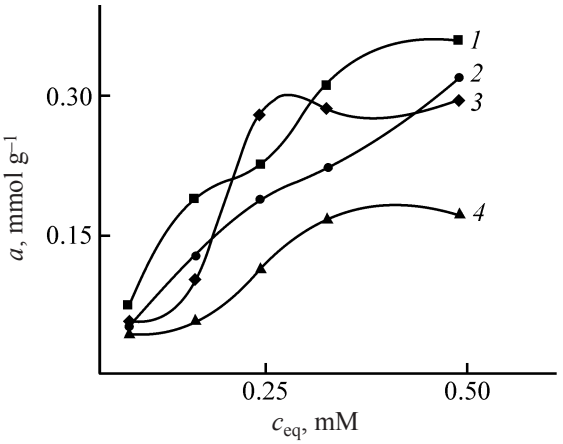

Fig. 3. Isotherms of benzoic acid adsorption on (*1*) CNT^{in}, (*2*) CNT^{500}, (*3*) CNT^{800}, and (*4*) CNT^{1200} samples. T = 20°C, τ = 2 h. (*a*) Amount of adsorbed acid and (c_{eq}) equilibrium concentration of the benzoic acid solution.

Fig. 2. The amounts of the adsorbate on CNT^{in}, CNT^{500}, CNT^{800}, and CNT^{1200} after 1 and 200 min of contact are 0.134, 0.072, 0.062, 0.046 and 0.189, 0.128, 0.102, 0.056 mmol g^{-1}, respectively. The adsorption equilibrium is attained in 2 h. For all the nanotube samples, the adsorption of the acid increases with the time of contact; by 29, 44, 39, and 18% for CNT^{in}, CNT^{500}, CNT^{800}, and CNT^{1200}, respectively. The decrease in the amount of adsorbed benzoic acid in the order $CNT^{in} > CNT^{500} > CNT^{800} > CNT^{1200}$ (Fig. 2) is probably due to the decrease in the same order in the specific surface area of the nanotube samples. A comparison of the adsorption activities of modified CNTs (in terms of the amount of adsorbed benzoic acid per unit surface area) demonstrated that close values are obtained for CNT^{in}, CNT^{500}, and CNT^{800}: 0.36×10^{-3}, 0.4×10^{-3}, and 0.38×10^{-3} mmol m–2. According to the TPD data, chemisorbed oxygen is present on the surface of these tubes. For CMT^{1200}, on whose surface chemisorbed oxygen is completely absent, this value decreases by 40% (0.23 10–3 mmol m^{-2}). Removal of polar oxygen-containing groups diminishes the adsorption of benzoic acid molecules because of the decrease in the affinity of the nanotube surface for polar molecules.

In [18], the adsorption of phenol and 4-nitrophenol by granulated activated carbon was studied. In this process, the adsorption equilibrium was attained in 48 h. The adsorption equilibrium in adsorption of phenol was attained in 1 h on activated carbon and in 7 h on ash and charcoal [19]. The time necessary for equilibrium to be attained in the adsorption of benzoic acid on carbon nanotubes, examined in this study, was 2 h, which is substantially shorter than the above published values. Thus, the high adsorption activity of CNTs with respect to benzoic acid is confirmed.

For all of the CNT samples synthesized, the amount of adsorbed benzoic acid increases with its concentration in the aqueous solution (Fig. 3). As the acid concentration is changed from 0.082 to 0.492 mM, the amount of the adsorbate on the CNT surface becomes 4–6 time larger.

The isotherms of acid adsorption on the surface of carbon nanotubes (Fig. 3) have the form characteristic of monomolecular processes and can be described by the Langmuir equation

$$a = a_m K c_{eq}/(1 + K c_{eq}),$$

where a is the adsorption of benzoic acid; a_m, amount of adsorbate necessary for covering the whole adsorbent with a monolayer of the adsorbate; K, adsorption equilibrium constant; and c_{eq}, equilibrium concentration of the acid.

The values of a_m and K were calculated by the Langmuir equation to be (mmol g^{-1} and mM^{-1}, respectively): 2.83 and 0.436 for CNT^{in}, 2.01 and 0.408 for CNT^{500}, 0.97 and 0.717 for CNT^{800}, 0.78 and 0.481 for CNT^{1200}.

The maximum adsorption of the acid on activated carbon with a specific surface area of 2500 m^2 g^{-1} is 0.83 mmol g^{-1}, which substantially exceed the value for the nanotube samples synthesized: 0.172–0.361 mmol g^{-1} [10]. As recalculated to unit surface area, the maximum adsorption was 0.332×10^{-3} and 0.112×10^{-2} mmol m^{-2} on carbon and nanotubes, respectively. It can be stated that CNTs and activated carbon have comparable adsorption activities with respect to benzoic acid. A valuable property

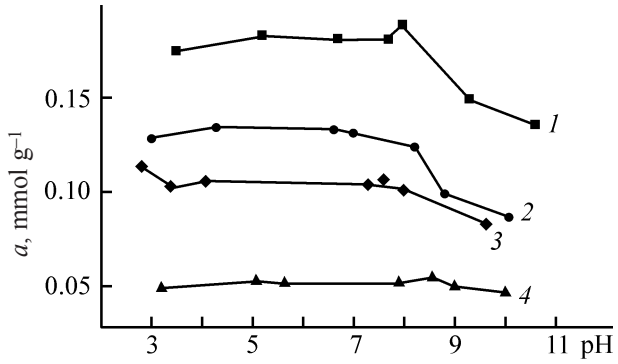

Fig. 4. Adsorption of benzoic acid, *a*, on (*1*) CNT^{in}, (*2*) CNT^{500}, (*3*) CNT^{800}, and (*4*) CNT^{1200} samples vs. the pH of the medium. $T = 20°C$, $c = 0.164$ mM, $\tau = 2$ h.

of nanotubes is their structural homogeneity, which makes them advantageous over activated carbon because of the manifestation of the molecular-sieve effect.

Analytical calculations using the pK_a value of benzoic acid (4.2) [10, 11] demonstrated that the degree of dissociation of the acid depends on the pH of the medium. The experimental results indicate that, in a solution at pH 3.7, the acid is present as anions (~45%) and in the neutral molecular form (~55%). In a more acid medium, the acid is in solution mainly (up to 100%) in the form of molecules, whereas in the alkaline medium, benzoate anions are formed (>99%). Researchers experimentally found the zero-charge point (pH_{zcp}) of the surface of activated carbon to be 7.4. The carbon surface is charged positively at pH values of the medium lower than pH_{zcp}, and negatively at pH higher than pH_{zcp}. It can be assumed that, at varied pH, the surface charge of carbon nanotubes will coincide with that of activated carbon because their chemical compositions and surface structures are similar.

Figure 4 shows how the amount of adsorbed acid depends on the pH of the medium. The largest amount of the adsorbate is observed on the surface of CNT_{in} in acid and neutral media. In an acid medium at pH 2.8–5.2, the amount of adsorbed acid on nanotube samples is 0.052–0.182 mmol g^{-1}, and in the neutral range, it slightly decreases, to 0.051–0.18 mmol g^{-1}. As pH increases from 9 to 10.6, the amount of the adsorbate on the surface of the CNT samples decreases by 10–26% (to 0.046–0.134 mmol g^{-1}). A similar dependence of the amount of benzoic acid on the surface of activated carbon on the pH of the medium, specifically, a decrease in the amount of adsorbed acid upon an increase in the pH value, was observed in [10, 11].

Weak dispersion and induction dipole interactions occur in acid, neutral, and alkaline media for CNT samples of all types. As the pH of the medium is varied from 2.8 to 9, the amount of adsorption on carbon nanotubes changes by only 10%. This confirms the predominant contribution of nonspecific interactions in adsorption of benzoic acid.

In an acid medium, the carbon surface of CNTs is positively charged, and benzoic acid is present in solution as molecules in the dissociated state. Therefore, the adsorption of the acid also occurs under the action of the electrostatic attraction between the nanotube surface and acid anions. In a neutral medium, the carbon surface is almost not charged at all. In this case, the amount of adsorbed acid becomes smaller because of the decrease in the electrostatic attraction between the surface and the acid. In an alkaline medium, the CNT surface is charged negatively, and benzoic acid is present predominantly in the form of anions. The decrease in the amount of adsorbate on nanotubes at high pH values is due to the electrostatic repulsion of the negatively charged carbon surface and $C_6H_5COO^-$ anions.

Hydrogen bonds are formed in adsorption of the acid on nanotubes containing a considerable amount of chemisorbed oxygen (CNT^{in} and CNT^{500}). Changes in the pH value affect the adsorption of the acid on CNT^{1200} only slightly. The reason is that the surface of nanotubes has no functional group s and many types of specific interactions are absent.

CONCLUSIONS

(1) The maximum adsorption of benzoic acid on carbon nanotubes (0.361 mmol g^{-1}) is observed on CNT^{in} samples, which is due to their large specific surface area of 525 m^2 g^{-1}.

(2) Raising the calcination temperature of carbon nanotube samples results in that the specific surface area becomes smaller and the adsorption of benzoic acid decreases to 0.172 mmol g^{-1}.

(3) On passing from acid to alkaline medium, the adsorption of benzoic acid decreases, which is due to mutual repulsion of the negatively charged surface of carbon nanotubes and acid anions.

(4) Varying the pH value affects the adsorption of the acid on the surface of CNT^{1200} only slightly. This occurs because the surface of nanotubes bears no functional groups.

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