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Mass and surface changes of activated carbon treated with nitric acid. Thermal behavior of the samples

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Abstract

The mass and surface changes produced when a commercial activated carbon is treated with HNO_3 solutions and in the subsequent heat treatment of the resulting samples are investigated. In the preparation of samples, acid solutions of varying concentration were used. The outgassing, first of activated carbon, and the contact, then of the acid solution with the resulting intermediate product, were effected under controlled temperature and temporal conditions. The starting carbon and some HNO_3-treated samples were examined by Fourier transform-infrared spectroscopy. Brunauer–Emmett–Teller (BET) surface areas were determined by nitrogen adsorption at −196°C. Heat treatments were carried out between 30° and 800°C in nitrogen. The oxidation of the activated carbon resulted in a significant mass increase. This was dependent on the method of preparation of the samples. Also, the surface chemistry of the activated carbon modified. Additionally, the surface area of the carbon underwent slight changes, this textural parameter increasing for a number of samples. The mass loss in the heat treatment of the samples was higher than the mass gain produced in their preparation. The mass loss was greater in the 30°–180°C range than in the 180–500° and 500–800°C ranges. In the various temperature ranges, the mass loss generally increased with increasing concentration of the HNO_3 solution and the outgassing and contact temperature or time.

Keywords: Activated carbon; HNO_3; Mass; Surface

1. Introduction

Nitric acid is widely used in the chemical industry, e.g. in fertilizer production. This inorganic acid may take part in undesired processes such as corrosion. HNO_3 reacts with most metals [1]. Accordingly, the removal of HNO_3 from a contaminated medium may be of interest. Activated carbon is the most common adsorbent for gases, liquids and solutes in solution. In recent years, such a carbon material has received considerable attention as a means of preventing the emission of pollutants into the environment. Usually, the removal of pollutants from waste streams only adds to the cost of an industrial operation. For this reason, granular activated carbon, having sufficient mechanical stability to withstand repeated regenerations and re-use, has been developed. The development of technology for regenerating the spent carbon makes the use of activated carbon viable as a pollution control measure. The various regeneration techniques used are thermal, chemical, solvent, vacuum, biolo-

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gical and wet oxidation methods [2]. In the thermal method, the temperature has a definite influence in the degree of regeneration. The higher the temperature, the more will be the carbon regenerated. Temperatures of ~ 1000°C are required to produce a regenerated product equal in adsorptive capacity to that of the starting carbon. However, high temperatures will affect the carbon particles adversely, hence, the usual procedure is to operate at the lowest possible temperature. For maximum process economy, low temperatures may be also desirable [2].

The study of mass changes, produced when aqueous solutions of HNO_3 are contacted with activated carbon and the resulting samples heated in nitrogen, provides valuable information on the feasibility of using activated carbon for the removal of HNO_3 and the thermal technology for regeneration of the spent product. Accordingly, the main objective of this work is to determine the possible influence of concentration of the acid solution, outgassing conditions of the activated carbon, and contact conditions of the acid solution with the carbon on the mass of sample, both in the preparation and heat treatment. The thermal behavior of samples prepared using the same activated carbon and solutions of different substances, including hydrogen peroxide and sulfuric acid, was studied in earlier reports [3–5]. On the other hand, carbons treated with HNO_3 have been used in the removal of inorganics from dilute aqueous solutions [2]. Therefore, the results obtained in studies with HNO_3-activated carbon may also apply in improving the adsorptive behavior of the carbon.

Table 1
Codes and preparation of the samples

Sample code [a]	Dilution of HNO_3	Outgassing conditions of activated carbon		Contact conditions of carbon and HNO_3 solution [b]	
		T/°C	t/h	T/°C	t/h
D-4	4	250	2	30	2
D-2	2	250	2	30	2
D-0	0	250	2	30	2
OT-30	2	30	2	30	2
OT-150	2	150	2	30	2
OT-250	2	250	2	30	2
OT-350	2	350	2	30	2
Ot-0	2	250	0	30	2
Ot-2	2	250	2	30	2
Ot-6	2	250	6	30	2
Ot-12	2	250	12	30	2
CT-0	2	250	2	0	2
CT-30	2	250	2	30	2
CT-50	2	250	2	50	2
CT-70	2	250	2	70	2
Ct-2	2	250	2	30	2
Ct-6	2	250	2	30	6
Ct-12	2	250	2	30	12

[a] Key: D – dilution; O – outgassing; T – temperature; t – time; and C – contact.

[b] The contact between the phases was established with the system at the indicated temperature.

2. Experimental

Activated carbon from Merck (average particle size, 1.5 mm) was used in this study. Oxidizing solutions of varying concentration were prepared from commercial HNO_3 (Carlo Erba; 65 wt%, 1.400 g cm^{-3}) solution. The experimental set-up used in the preparation of the samples was described previously [6]. The general method consisted of several successive steps in which ~ 5g of activated carbon (after being oven-dried at 110°C for 24 h) were first outgassed at 250°C for 2 h (heating rate 5°C min^{-1}) and cooled to 30°C in nitrogen (purity > 99.998 vol%). Then, the acid solution (50 cm^{-3}) was brought into contact with the outgassed product, the contact between the solid and liquid phases being established for 2 h. After that, the supernatant liquid was filtered and the remaining carbon particles were oven-dried at 60°C for 24 h. The resulting samples were finally stored in a desiccator containing $CaCl_2$. The specific conditions of preparation of the samples as well as their notations are shown in Table 1. The concentrations of the HNO_3 solutions used in the preparation of the D samples were 3.6 mol l^{-1} for D-4, 7.2 mol l^{-1} for D-2 and 14.4 mol l^{-1} (i.e. commercial HNO_3 as such) for D-0. Although activated carbon is commonly used to clean up dilute solutions, it is thought that with these high-concentration solutions some effects of the HNO_3 treatment (for example, those connected with its oxidizing power) can be stronger. It should also be pointed out that OT-250, Ot-2, CT-30 and Ct-2 are in fact the same sample.

Adsorption isotherms for nitrogen at −196°C were determined with a conventional gravimetric apparatus. Adsorbent samples were first oven-dried at 110°C for

24 h and then outgassed in the adsorption system at 150°C for 12 h, at a pressure of 133×10^{-6} Pa. Equilibration time given to each isotherm measurement was 1 h.

Infrared spectra of the activated carbon and selected HNO_3-treated samples were recorded on a Perkin–Elmer 1720 Fourier transform-infrared spectrometer in the 450–4000 cm^{-1} wave number range, with 10 scans being taken at a scan speed of 0.1 and 2 cm^{-1} resolution. Subtraction of a previously recorded background spectrum, from that of each sample, was made automatically. Disks were prepared by first thoroughly mixing 1 mg of sample with 500 mg of KBr in a agate mortar, then by pressing the resulting mixture at 10 tons for 3 min with a Perkin–Elmer hydraulic press. The disks were oven-dried at 50°C for 1 h for the removal of hygroscopic water taken up by KBr.

The heat treatments of the samples were carried out in a thermogravimetric apparatus, Mettler TA-3000, consisting of a TG-50 thermobalance (precision: ±2°C in temperature; ±1 µg in weight) and a TG-10 processor. About 100 mg of each individual sample were heated from 30° to 800°C (heating rate 5°C min^{-1}; flowing nitrogen > 99.998 vol%, flow rate 200 cm^3 min^{-1}).

3. Results and discussion

3.1. Mass changes in the preparation of samples

As shown by the values of percentage of mass increase (PMI) originated in the preparation of the samples (Table 2), the treatment of activated carbon with HNO_3 solutions caused a significant increase in the mass of sample. The percentage of mass increase varies between 3.6 for CT-50 and 9.3 for D-0. Nevertheless, the percentage of mass increase is much smaller than that for the samples prepared under identical conditions but using H_2SO_4 solutions [5]. In this case, the percentage of mass increase amounted to 70.1 for OT-350. The mass gain produced with HNO_3 solutions denotes formation of surface groups in activated carbon, although water or other chemical

Table 2
Mass and surface changes for the samples prepared with HNO_3 solutions

Sample	PMI [a]	PML [b,c]				S_{BET} [d] (m^2 g^{-1})
		30–800°C	30–180°C	180–500°C	500–800°C	
D-4	5.5	13.2	5.3	3.6	4.3	831
D-2	7.7	20.4	8.1	4.3	5.0	908
D-0	9.3	20.5	9.3	5.3	5.9	901
OT-30	6.0	13.6	4.9	4.0	4.7	890
OT-150	7.5	16.5	7.3	4.3	4.9	852
OT-250	7.7	17.4	8.1	4.3	5.0	908
OT-350	8.9	18.5	8.9	4.3	5.3	958
Ot-0	7.1	14.7	6.0	4.0	4.7	953
Ot-2	7.7	17.4	8.1	4.3	5.0	908
Ot-6	6.8	20.1	7.6	5.9	6.6	929
Ot-12	7.3	17.4	8.1	4.3	5.0	922
CT-0	5.7	13.1	5.2	3.6	4.3	959
CT-30	7.7	17.4	8.1	4.3	5.0	908
CT-50	3.6	16.3	5.7	5.0	5.6	968
CT-70	6.1	18.2	6.0	5.7	6.5	928
Ct-2	7.7	17.4	8.1	4.3	5.0	908
Ct-6	6.7	18.2	7.3	5.1	5.8	829
Ct-12	8.7	20.4	9.0	5.4	6.0	822

[a] $[(m_f - m_i)/m_i] \times 100$, where m_i is the initial mass of activated carbon and m_f the final mass of sample.

[b] $[(m_1 - m_2)/m_0] \times 100$, where m_1 and m_2 represent the mass at T_1 and T_2 ($T_1 < T_2$), respectively, and m_0 is the initial mass of sample.

[c] The PML values were obtained from the TG data, i.e. mass of sample (m) a function of temperature (T).

[d] S_{BET} was calculated from the nitrogen adsorption isotherms at −196°C by application of the BET equation to p/p^0 (relative pressure) ≈ 0.30, and taking a_m (the average area occupied by a molecule of adsorbate) $=16.2$ Å^2 [23].

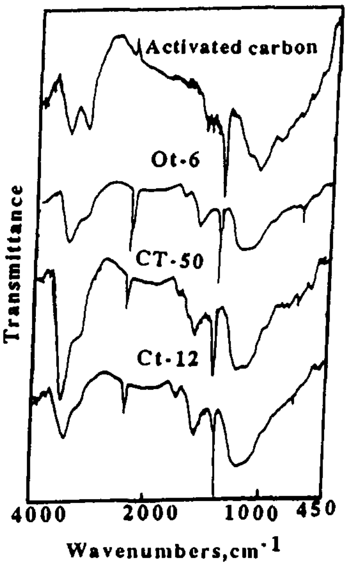

Fig. 1. Fourier transform-infrared spectra of activated carbon and various HNO_3-treated samples.

species may remain in the samples because of the mild drying conditions of the HNO_3 solutions-treated products. The former is clearly brought out by data of the chemical analyses. The values of the nitrogen content, the oxygen content (obtained by difference) and the volatile matter content for the activated carbon are 0.5, 11.6 and 2.7 wt%, whereas for the samples of oxidized carbon they fall in turn in the 1.5–2.1, 14.7–21.0 and 10.7–16.4 wt% ranges (for the individual samples such values are omitted for the sake of brevity; proximate analysis determinations were effected by a thermogravimetric method [7]). Particularly, the great differences in the volatile matter content of the activated carbon and the HNO_3-treated samples are really meaningful since they are in line with the fact that, in the HNO_3 treatments of the carbon, relatively thermally stable surface complexes were formed. The Fourier transform-infrared spectra of the activated carbon [6] and selected HNO_3-treated samples are shown in Fig. 1. The spectra for the samples of oxidized carbon display absorption bands centered in the 1800–1600 cm^{-1} wave number range, which are compatible with the presence of oxygen structures and of N–O-containing structures [8]. Changes in the relative intensity of bands appearing between 1300 and 900 cm^{-1} indicate that structures with C–O bonds were also affected. About the changes produced in the surface chemistry of carbons upon treatment with HNO_3, it has been suggested that they are due to the formation of various oxygen surface groups [9–11] and of structures containing N–O bonds (nitro-groups and nitrate complexes) [10] as well as of oxygen species mainly of a discrete nature [12]. According to Vinke et al. [13], the HNO_3 oxidation of activated carbon may have some analogies to aromatic hydrocarbons. The oxidation reaction was thought to proceed by a radical mechanism [14–16]. Not and Schwarz [17] concluded that the HNO_3 treatment increases the surface acidity of activated carbons. Furthermore, the HNO_3 oxidation of a gas-activated carbon and a chemically activated (H_3PO_4) granular carbon resulted in a larger amount of surface acid groups than in the calcium hypochlorite oxidation [13].

The mass of sample suffers a steady increase with increasing concentration of the HNO_3 solution. This behavior is attributed to the strong concentration dependence of the oxidizing power of HNO_3, Whereas HNO_3 of concentration below 2 M has little oxidizing power [18], concentrated HNO_3 can either oxidize, or nitrate organic compounds. In the latter case, the nitro group ($-NO_2$) enters the compound in place of hydrogen. The mass increase is also markedly favored with increasing outgassing temperature. Then, the loss from activated carbon of surface groups and of adsorbed species facilitated the subsequent oxidation of material by HNO_3. The mass of sample is, however, almost insensitive to the increase in outgassing time, as shown by the nearly constant values of the percentage of mass increase for the Ot samples. The rather irregular variation of the percentage of mass increase for the CT samples is surprising since warm HNO_3, particularly in the vapor phase, is frequently used in the oxidation of organic molecules, the reaction being promoted by molecular oxygen and retarded by nitric oxide.Perhaps, other factors influenced the mass of sample. The fluidity of the HNO_3 solution and hence its diffusion in pores of the carbon should be greater with rising contact temperature between the phases. However, the thermal agitation of the oxidizing solution might hinder its entrance in pores of the material. The values of the percentage of mass increase for the Ct samples show no variation trend, the differences between them being small.

3.2. *Surface area of the samples*

When investigating the effect of HNO_3 treatment on the surface acidity of activated carbons, Not and Schwarz [17] reported that the method was effective in altering the surface chemical properties of the activated carbon without affecting the surface area significantly. The values of the Brunauer–Emmett–Teller (BET) surface area (S_{BET}, $m^2 g^{-1}$) for the samples are given in Table 2. Comparison with the value of the surface area of 912 $m^2 g^{-1}$ for the activated carbon shows that the HNO_3 oxidation of the carbon produced slight changes in the surface area, which varies between 831 $m^2 g^{-1}$ for D-4 and 968 $m^2 g^{-1}$ for CT-50. The expected behavior for all samples was a decrease in surface area owing to the mass increase associated with the treatments of the activated carbon. Also, the effect of surface loss should be larger with increasing percentage of mass increase. However, the surface area increases for a number of samples compared to the activated carbon and, in addition, a correlation between the percentage of mass increase and the surface area as a rule is not observed. An exception to the rule is the series CT, although for these samples the surface area is generally higher than for the activated carbon. The results suggest that not only the amount of matter incorporated into the samples, but also other factors influenced the surface area. One of the presumable factors may be connected with the method of preparation of the samples as the concentration of the HNO_3 solution and the outgassing or contact conditions varied. Another factor may be related to the determination of the surface area by N_2 adsorption at −196°C. Concerning the series D, the lower the concentration of the HNO_3 solution, the smaller is its viscosity [19], and hence the greater the diffusion of oxidizing solution in pores of the activated carbon and the larger the detrimental effect of the HNO_3 treatment on the accessibility to smaller size pores (i.e. for microporous solids such as activated carbon, the surface area largely concentrates in micropores) of the samples. For the series OT, as a second example, it seems likely that the outgassing of the activated carbon at 350°C resulted in creation of porosity by removal of chemical species from the material and that, in spite of the subsequent HNO_3 treatment of the intermediate outgassed product, the pores involved are accessible to nitrogen. However, their accessibility to N_2 molecules seems to be partly prevented with increasing outgassing time of the activated carbon, thus to a general decrease in the surface area for the series Ot. Perhaps, in the same direction of variation in outgassing time, firstly, the HNO_3 solution diffused to a larger extent in pores of the activated carbon (this should cause the mass of sample progressively to increase) and, subsequently, the removal of species by outgassing effect during measurement of the adsorption isotherms took place less favorably. As a final comment, it is worth mentioning that in relation to the effect of outgassing – during the preparation of samples and during the determination of adsorption isotherms – on the surface area, the important factor may be the location of the matter removed (i.e. in pore entrances or on the surface of pore walls) rather than the amount of species evolved. A very small amount of matter, when found in pore narrowings, may constitute a constriction and, in this way, to block the entrance to a large pore volume. The mass loss corresponding to the outgassing stage when measuring the nitrogen isotherms was ≈ 3.5wt% for the activated carbon and on an average 3.1 wt% for the HNO_3-treated samples.

3.3. *Thermal behavior of the samples*

Fig. 2 illustrates derivative (D) thermogravimetric (TG) analysis curves for the HNO_3-treated samples. These curves display a markedly different shape from that previously reported for the HNO_3-treated activated carbon, though the samples were not prepared in the same way [3]. The curve for the activated carbon was reported previously [4]. The strongest effect of weight loss in the curves in Fig. 2 is centered between 120° and 135°C. At higher temperatures, weak effects of weight loss occur (some of them are almost imperceptible). The thermogravimetric analysis curves (these are omitted for the sake of clarity) show that the decrease in the mass of sample is first greater, up to ≈ 150°C, and then gradual to 800°C. The mass loss at the lowest temperatures is neither attributable to the release of HNO_3 from the samples, as the boiling point of anhydrous liquid HNO_3 is 82.6°C [20], nor of reduction products of HNO_3, as they are gases at room temperature. Most likely, it is due to the evolution of chemical species such as water which were adsorbed in the samples. In connection with the

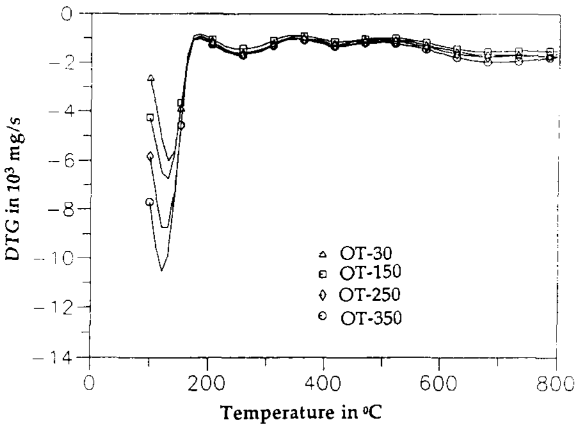

Fig. 2. Thermal behavior of the samples prepared by cotrolling the outgassing tempeature of activated carbon.

thermal stability of the oxygen surface structures formed as a result of the interaction of oxidizing agents with carbons it has been stated [21] that, in general, they are stable at temperatures below 200°C. At higher temperatures, the oxygen structures decompose to produce CO_2 and steam, or CO and hydrogen, depending on temperature. Also, in the course of heating a carbon sample under vacuum or in a neutral gas, particular surface compounds decompose at different temperatures [22]. Accordingly, in this study the thermal behavior of the HNO_3-treated samples shows decomposition of various surface complexes. This agrees with the results obtained previously by Otake and Jenkins [11] who concluded that the oxygen groups present in HNO_3-oxidized and air-oxidized carbons can be divided into four groups depending on the decomposition temperature (the oxygen complexes are essentially completely decomposed by heat treatment of the samples at 1000°C in nitrogen) and on whether they yield carbon monoxide or carbon dioxide. Using intermittent temperature-programmed desorption (ITPD), Joly et al. [12] found seven steps in the energy vs. CO or CO_2 evolved curves. Finally, it should be noted that for hydrogen peroxide-treated samples a strong effect of weight loss was located between 150° and 400°C [4]. For the samples prepared with H_2SO_4 solutions, the maximum mass loss was centered at $\sim$ 300°C [5].

The values of the percentage of mass loss (PML, Table 2) produced in the heat treatment of the HNO_3-treated samples between 30° and 800°C range between 13.1 for CT-0 and 20.5 for D-0. They are much larger than the values of the percentage of mass increase, which argues for contributions to the mass loss (e.g. the removal species adsorbed by the samples after their preparation) other than those due to treatments of the carbon. In this connection it is relevant to indicate that the moisture content for the HNO_3-treated samples, as determined by a thermogravimetric method [7], is relatively small. It is lower than 5.0 wt%, whereas for the activated carbon the moisture content is 7.7 wt%. On the other hand, the mass loss depends on the method used in the preparation of the samples and also on the temperature range. The normal trend is an increase in the mass loss with increasing concentration of the HNO_3 solution, outgassing temperature and time of activated carbon, and contact temperature and time between the liquid and solid phases. The mass loss is greater in the 30°–180°C range than in the 180–500° and 500–800°C ranges (for the activated carbon it was 10.5, 7.8, 0.6 and 2.1 wt% in the 30–800°, 30–150°, 150–400° and 400–800°C ranges, respectively [4]). Furthermore, it is slightly higher between 500° and 800°C than between 180° and 500°C. The mass loss in the several temperature ranges generally varies for all series of samples as the whole mass loss between 30° and 800°C. An exception to the rule is observed for the series OT between 180° and 500°C and also, though less, between 500° and 800°C. The close values of the percentage of mass loss for the OT samples indicate that the thermal stability of the surface state in such temperature ranges was practically independent on the outgassing temperature of activated carbon.

From the aforementioned results it can be concluded that the treatments of activated carbon with HNO_3 solutions produced mass and surface changes, depending on the solution concentration and on the outgassing and contact conditions. The thermal behavior of the samples is also influenced by the method of preparation of the samples.

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