Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 945–953

UTILIZATION OF THERMAL ANALYSIS TO ESTABLISH THE OPTIMAL CONDITIONS FOR REGENERATION OF ACTIVATED CARBONS

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Abstract

Thermoanalytical methods (TG, DTG and DTA) were used to determine the temperature interval (140–350°C) in which *p*-nitroaniline undergoes thermal desorption from the surface of activated carbons obtained from the shells of oxidized plum stones and impregnated with aqueous solutions of Cu, Fe and Ti salts, which simulate the processes of activated carbon regeneration. It was established that the impregnation of the activated carbons facilitated the regeneration processes in the sense that they can occur at lower temperatures: 135–320 (Cu), 150–340 (Ti) and 130–320°C (Fe). The utilized activated carbons were preliminarily characterized by BET surface area, DSC and scanning electron microscopic methods.

Keywords: activated carbons, BET surface area, DSC, DTA, DTG, scanning electron microscopy, TG

Introduction

Activated carbons are characterized by a wide area of application: technologies for the purification of gases, the cleaning of various categories of sewage, the conversion of surface water into drinkable water, etc. In most cases the purification methods are based on procedures involving the use of adsorbent materials. From the point of view of economy, therefore, it is very important that the utilized sorbents be regenerated so as to allow their repeated use. From this aspect, it is important to conduct research aimed at establishment of the optimal conditions for activated carbon regeneration. As procedures for the regeneration of various types of sorbents, use has been made of chemical and thermal methods based on desorption and destruction processes. Literature data indicate that the thermal methods prove more efficient for these purposes [1].

It is well known that TA methods may be successfully used to characterize various types of chemical substances and materials.

The characterization of the activated carbons, which possess specific properties, by means of TA methods is often accompanied by difficulties of various types, such

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

as the overlapping of thermal effects, catching fire at low temperatures, etc. Nevertheless, the data in the literature reveal that TA methods are used both to establish the thermal behavior of activated carbons [2–5] and to study the sorption–desorption processes on their surfaces [6–8]. In the latter case, the works of Staszczuk and Glazewski [6, 7] deserve special mention.

TA methods have also been applied to investigate activated carbons subjected to oxidation processes by means of phosphoric and nitrogen acids [9, 10]. The possibility of regenerating activated carbons obtained from olive stones has been examined. Matatov-Meytal *et al*. [13] studied the processes of regeneration of activated carbons impregnated with Cu(II), Fe(III) and Cr(III) mixtures as oxide catalysts which were later saturated with phenol. It was established that the impregnated catalysts contribute to the regeneration processes, which in this case occur at lower temperatures: 220–240 and 320–370°C, respectively.

Dawson *et al.* [14] mentioned that the catalytic effect of copper on carbon gasification was noted at a lower reaction temperature for both linear heating (380 as compared to 500°C) and constant rate experiments (320 as compared to 400°C).

Activated carbons obtained from nut shells, peach stones and plum stones have been characterized by TA and BET methods [15].

We previously applied TA methods to study the possibility of thermal and chemical regeneration of activated carbons obtained from the shells of peach stones, which were saturated with aniline derivatives (regeneration conditions 300–370°C) [16], and the possibility of regeneration of activated carbons obtained from nut shells and the shells of peach stones, which were saturated with phenol derivatives (regeneration conditions 300–360°C) [17].

The purpose of the present work is to make use of TA to determine the optimal conditions of regeneration of vegetal activated carbons.

Experimental

The process of obtaining activated carbons from vegetal raw material is usually based on the carbonization and activation of celluloid materials. In our case, an activated carbon (CA-36-in) prepared from plum stones (Republic of Moldova) as previously described [18] was used.

The oxidation was performed with 50% nitric acid under heating on a water bath for 8 h at an activated carbon:HNO_3 ratio of 50 g:150 ml. The resulting samples of oxidized carbons were washed with distilled water, and next treated with 0.1 N NaOH to remove humic substances, followed by HNO_3 to transform them into the H form, which was washed to remove acid and dried at 105°C to constant mass.

Impregnated samples were obtained from oxidized activated carbons by using aqueous solutions of the $TiOSO_4 \cdot 2H_2O$, $CuSO_4$ and $FeCl_3 \cdot 6H_2O$ in appropriate concentration (0.1 g ml^{-1}) as support. The solutions were then heated and constantly stirred until total elimination of the liquid. The sample impregnated with the Ti salt was treated with HNO_3 or HCl to prevent hydrolysis.

For saturation of the samples of the investigated carbons, use was made of aqueous solutions of *p*-nitroaniline, for which the ratio of the solution volume to the carbon mass was maintained constant. The temperature, 25°C was maintained with a thermostatic automatic shaker during 3 days. The adsorbent particles were separated from the liquid phase by filtration through a paper filter. The carbon samples were later dried in the open air at 25°C to constant mass. *p*-Nitroaniline was used without additional purification. For TG, DTG and DTA, a derivatograph OD-102 and a Q-1000D (MOM, Hungary) were used. 100 mg samples were heated up to 1000°C at a rate of 10°C min^{-1}. Dried alumina powder was taken as a standard for DTA. DSC measurements were made with Perkin–Elmer DSC No. 1 equipment. Microphotos of carbon samples were made with a Cambridge S 500 scanning electronic microscope. Gemini 2370 equipment (BET method) was used to determine the specific surfaces (Table 1) of the investigated carbons.

Results and discussion

Table 1 shows the BET surface area data for the initial activated carbon and those modified by oxidation and impregnation. The obtained data demonstrate that, in consequence of the impregnation process, there is a reduction in the specific surface, this probably being due to the blocking of some micropores. Figure 1 shows a DSC curve of CA-36ox+Cu, which demonstrates that no essential thermal effects are manifested within the given temperature interval. Comparative analysis of the DTA curves (Fig. 2) reveals that their shapes differ for the different carbon samples, which demonstrates their different surface and thermal stabilities. The DTA curves are modified as a result of the oxidation and impregnation processes. This is confirmed by the micrograph obtained by means of the electron microscope (Figs 3a, b).

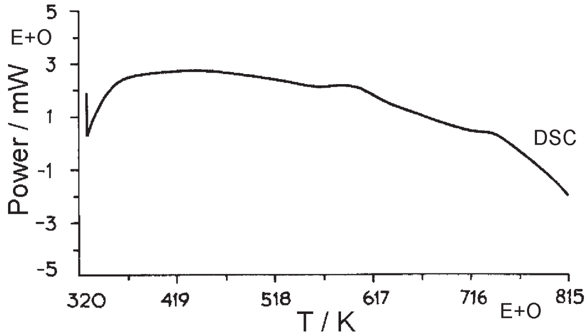

Fig. 1 DSC curve of CA-36ox+Cu

Figures 4–6 depict the TG, DTG and DTA curves of the impregnated activated carbon samples (1), and the same carbon saturated with an aqueous solution of *p*-nitroaniline (2).

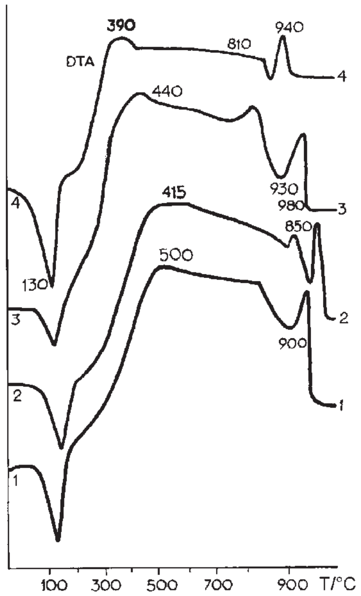

Fig. 2 DTA curves of 1 – CA-36ox+Ti; 2 – CA-36ox+Fe; 3 – CA-36in; 4 – CA-36ox+Cu

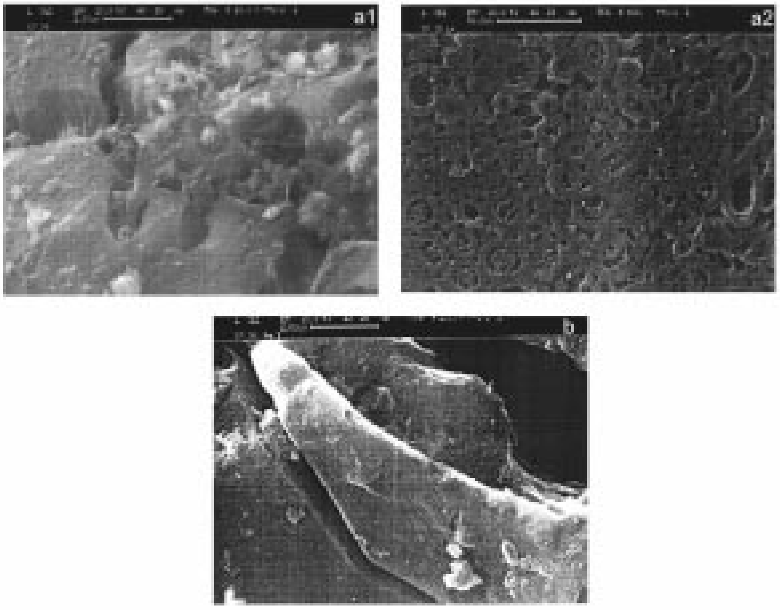

Fig. 3 Scanning electron microscopy: a – CA-36-initial[1] and oxidized[2]; b – CA-36ox+Fe

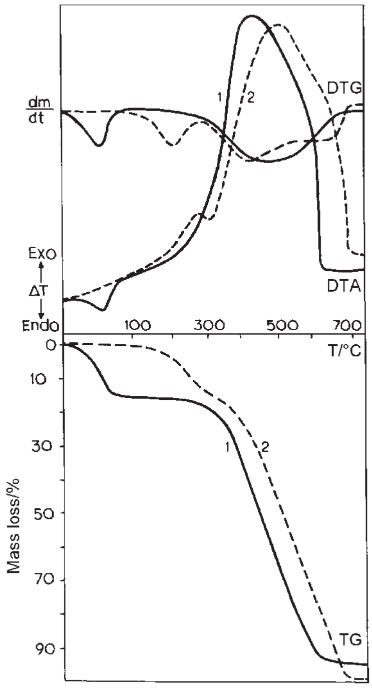

Fig. 4 TG, DTG and DTA curves (derivatograph OD-102) of 1 – CA-36in; 2 – CA-36in+*p*-nitroaniline

Table 1 BET* surface areas of oxidized and impregnated activated carbons

Sample	BET ($m^2 g^{-1}$)
CA-36in (initial activated carbon)	1130
CA-36ox (oxidized)	1160
CA-36ox+Cu (Cu-impregnated)	1010
CA-36ox+Fe (Fe-impregnated)	1070
CA-36ox+Ti (Ti-impregnated)	1020

*The accuracy of the Gemini equipment is about 3%

From Figs 4–8 and Tables 2 and 3, it may be seen that, in comparison with the TA curves for the *p*-nitroaniline-free carbons, new endothermic effects due to *p*-nitroaniline oxidation appear within the temperature interval 130–360°C. Endothermic effects were identified within the temperature interval 30–150°C; these correspond to the desorption of water and other volatile compounds, e.g. carbon dioxide adsorbed from the atmosphere [19, 20]. For the different samples of carbon, the process of *p*-nitroaniline oxidation starts at different temperatures: 150, 135 and 130°C for the impregnation with Ti, Cu and Fe, respectively. The temperatures of oxidation of carbon, T_c, and burning, T_g, start within the intervals 290–520 and 460–865°C, respectively.

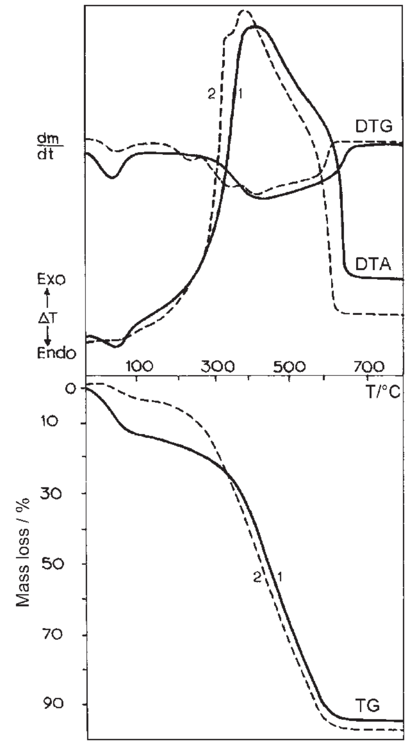

Fig. 5 TG, DTG and DTA curves (derivatograph OD-102) of 1 – CA-36ox; 2 – CA-36ox+*p*-nitroaniline

The results of analysis of the TG/DTG/DTA curves are presented in Tables 2 and 3. They allow conclusions on the thermal behavior in the system activated carbon – catalyst – *p*-nitroaniline.

Table 2 Temperatures** of desorption of water and other volatile compounds, $T_{w,v}$, of *p*-nitroaniline oxidation, T_a, oxidation of the carbon surface, T_c, and burning of carbon, T_g, obtained from TG, DTG and DTA measurements with derivatograph OD-102

Sample	$T_{w,v}$/°C	T_a/°C	T_c/°C	T_g/°C
CA-36in*	30–130	–	290–730	
CA-36in+*p*-nitroaniline	30–140	140–320	320–510	520–740
CA-36ox*	30–150	–	360–700	
CA-36ox+*p*-nitroaniline	30–150	150–260 260–360	360–440	440–660
CA-36ox+Fe*	30–130	–	360–650	
CA-36ox+Fe+*p*-nitroaniline	–	130–320	320–500	500–645

*Without *p*-nitroaniline; **the accuracy is about 10°C

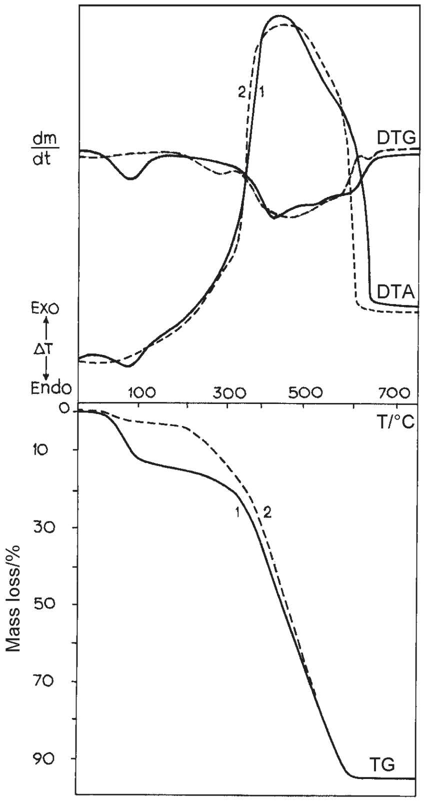

Fig. 6 TG, DTG and DTA curves (derivatograph OD-102) of 1 – CA-36ox+Fe; 2 – CA-36ox+Fe+*p*-nitroaniline

Table 3 Temperatures of desorption of water and other volatile compounds (CO), $T_{w,v}$, oxidation of *p*-nitroaniline, T_a, oxidation of the carbon surface, T_c, and burn-off of carbon, T_g, obtained from TG, DTG and DTA experiments with derivatograph Q-1000D

Sample	$T_{w,v}$/°C	T_a/°C	T_c/°C	T_g/°C	100% burn-off
CA-36in*	35–180	–	360–480	480–830	930–980
CA-36ox+Ti*	35–200	–	300–520	520–740	790–970
CA-36ox+Ti+*p*-nitroaniline	35–150	150–340	340–465	465–730	740–950
CA-36ox+$CuSO_4^*$	35–190	–	210–460	460–810	810–940
CA-36ox+$CuSO_4$+*p*-nitroaniline	35–130	135–320	320–510	510–865	865–970

*Without *p*-nitroaniline

The catalytic impact allows the process of *p*-nitroaniline oxidation to occur at lower temperatures: 135–320 (Cu), 150–340 (Ti) and 130–320°C (Fe). The catalytic effects are stronger in the presence of *p*-nitroaniline.

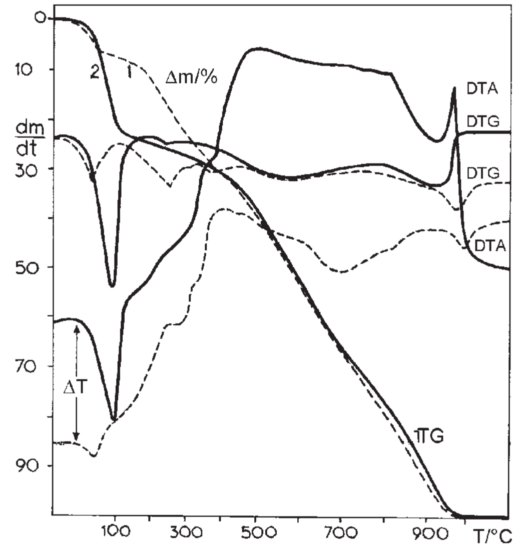

Fig. 7 TG, DTG and DTA curves (derivatograph Q-1000D) of activated carbons: 1 – CA-36ox+Ti; 2 – CA-36ox+Ti+*p*-nitroaniline

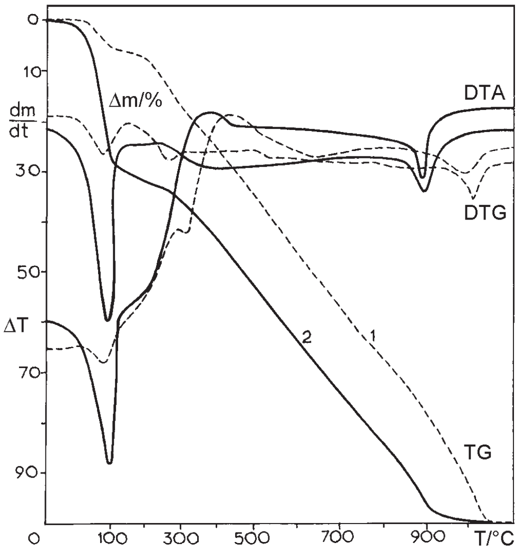

Fig. 8 TG, DTG and DTA curves (derivatograph Q-1000D) of activated carbons: 1 – CA-36ox+Cu; 2 – CA-36ox+Cu+*p*-nitroaniline

Thus, the data obtained from TA allowed the optimal conditions to be established: for the investigated carbons 130–360 (T_a) and 320 –510°C (T_c).

The results demonstrate that TG, DTG and DTA methods based on the Derivatograph permit the investigation (simulation) of processes for the regeneration of activated carbons obtained from vegetal material (shells and stones of fruits).

The system CA-36ox+*p*-nitroaniline is characterized by two thermal effects, with DTA peaks in the intervals 150–260 and 260–360°C, this being conditioned by two types of pores in the adsorbent material according to [13].

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