Thermochimica Acta, 30 (1979) 247–253

THERMOANALYTICAL STUDY OF ACTIVATED CARBON REGENERATION. I. DESORPTION OF PHENOL AND ANILINE*

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(Received 22 May 1978)

ABSTRACT

During a thermoanalytical investigation to determine the mechanism and desorption energies of common pollutants, a complex pattern has been demonstrated when activated carbon loaded with phenol or aniline is heated up to 950°C in a dynamic nitrogen atmosphere. Water is completely removed before 150°C. Four and three consecutive steps appear when phenol and aniline are released, respectively.

INTRODUCTION

Further developments of adsorption on activated carbon (AC) for treatment of industrial or civil wastewaters are mainly dependent on regeneration economics. Restoration of exhausted AC is made almost exclusively by thermal regeneration, at a temperature close to 1000°C. In spite of the relative ease of operation (fully automatic process control, no harmful solvents employed, etc.), which makes it preferable to biological or chemical regeneration, the high cost of thermal regeneration actually prevents a widespread application of AC[1, 2].

On the other hand, while thermal regeneration is a well defined technology[3], relatively poor advancements have been made on the fundamental knowledge of the adsorption–desorption mechanism. Major contributions to this aim have been provided, among others, by the direct investigations of Mattson et al.[4–7] based on IR internal reflectance spectroscopy, and of Puri[8, 9] on thermal modifications of the surface chemistry of AC.

However, the main question of why such a high temperature should be needed to thermally desorb weakly bound systems (adsorption energy averages a few tenths of kcal mole^{-1} for the most common adsorbates) still remains unsolved.

In order to obtain more information on desorption mechanisms, a thermo-

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* Work supported by IRSA–CNR, contract No. 76.00066.11.

analytical study on AC loaded with various pollutants has been systematically undertaken, with the special aim to evaluate the desorption energy requirements associated with each pollutant. Phenol, aniline and their three mono-nitro (*ortho, meta, para*) isomers, adsorbed on a commercial granular carbon, have been preliminary selected as representative of pollutants encountered in industrial wastewaters.

In this paper the thermoanalytical results of the desorption of phenol and aniline are presented.

EXPERIMENTAL

After a preliminary screening to 16–25 (US) mesh, the carbon, Filtrasorb 400 from Calgon Corp., Pittsburg, Pa. (surface area about 1100 m^2 g^{-1})[10], was kept for 3 h at 110°C in an oven, then stored over anhydrous $CaCl_2$.

Previous investigations seemed to indicate a possible role of initial moisture content on carbon thermoanalytical behaviour[11]. Accordingly, 20 samples of dry carbon (about 100 mg each) were equilibrated by continuous shaking at room temperature in stoppered Erlenmayer flasks with 100 cc of an aqueous solution at 300 p.p.m. of the selected pollutant. The same procedure was repeated using only distilled water, thus making an overall amount of $20 \times 3 = 60$ samples.

Once the supernatant solution showed no appreciable concentration variations (usually after 5 days), each sample was vacuum filtered, with filtration time varying from 1 to 150 min, to obtain various degrees of moisture content.

Accurate mass balance on the aqueous phase allowed the adsorption capacities for each adsorbate to be determined. The samples were then quantitatively transferred in a Pt crucible, loaded in a Model TA_1 Thermoanalyzer from Mettler AG, Zurich, Switzerland, and progressively heated up to 950°C in a dynamic nitrogen atmosphere, Al_2O_3 calcinated at 1200°C for 24 h being used as reference material.

In order to ensure that water is completely removed, an isothermal stop (omitted in the drawings) for 60′ at 150°C was performed on all samples.

Operating conditions during heating were as follows. Pt specimen-holder assembly with Pt 10% Rh–Pt ΔT thermocouple (DTA 20 from Mettler); cold junction temperature 25°C; heating rate 10°C min^{-1}; flow rate 5 l h^{-1} of N_2 dried on P_2O_5; DTG and DTA range 0.5 mg min^{-1} and 200 μV, respectively. Calorimetric sensitivity

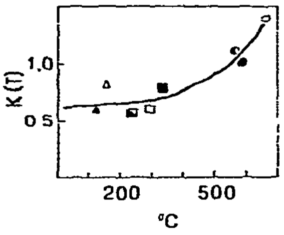


Fig. 1. Calorimetric constant of apparatus $K(T)$ (mcal μV sec^{-1}) vs. temperature. ▲, KNO_3; △, $AgNO_3$; ◪, NH_4ClO_4; □, $KClO_4$; ■, KNO_3 (m.); ●, K_2SO_4; ◐, SiO_2; ○, K_2CrO_4.

of thermoanalyzer, *K*, for quantitative evaluation of DTA peaks was determined by reference to N.B.S. standards (see Fig. 1).

Solution concentrations were measured with a double beam Model 1750 spectrophotometer from Pye Unicam Ltd., Cambridge, Gt. Britain at 270 and 230 nm for phenol and aniline, respectively, using distilled water previously shaken with carbon as blank.

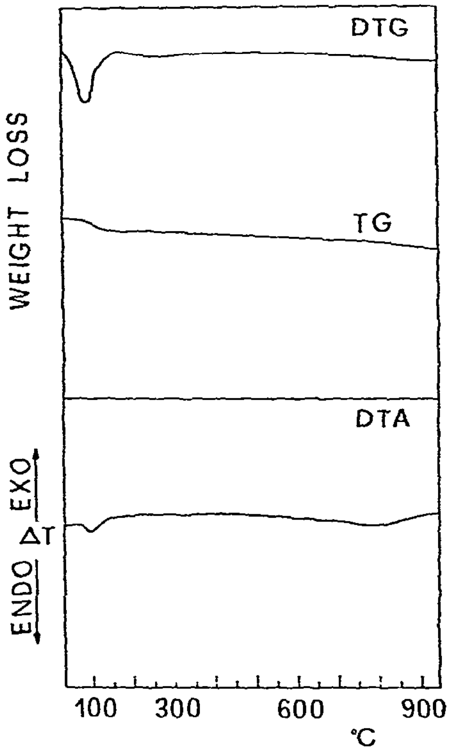
Solutions were prepared using analytical grade reagents and deaerated distilled water.

RESULTS AND DISCUSSION

TG, DTG

In the absence of specific information about the gaseous phase originating during heating, particular attention was paid to relating energy requirements to mass balance throughout the experiments. This applied to the "matrix blank" problem, i.e. the heating of virgin activated carbon (VAC), dry or wet, required that a preliminary unambiguous solution with affordable conclusions should be obtained.

As shown by Figs. 2 and 3, where some typical thermoanalytical curves for wet and dry VAC are reported, the weight loss presented by the latter from 25 to 150°C (about 1.5%) could be attributed to residual moisture still present after the



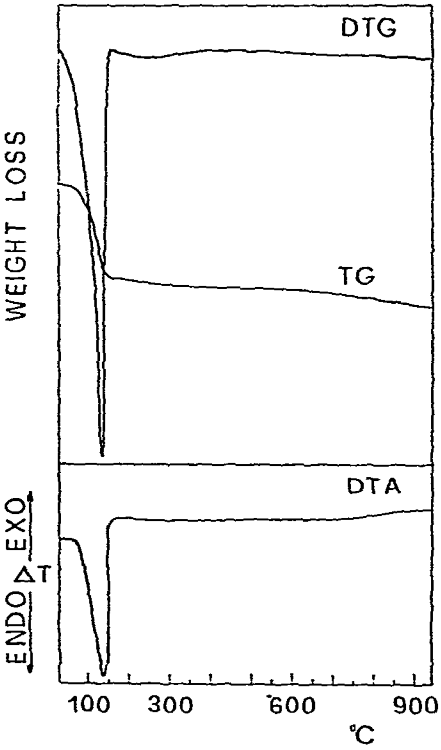


Fig. 2. TG, DTG and DTA curves of dry virgin activated carbon.

Fig. 3. TG, DTG and DTA curves of wet virgin activated carbon.

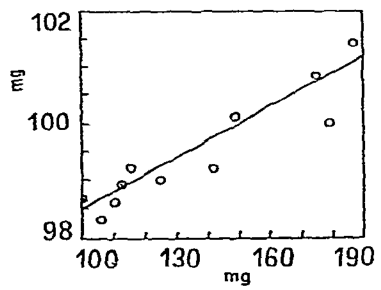
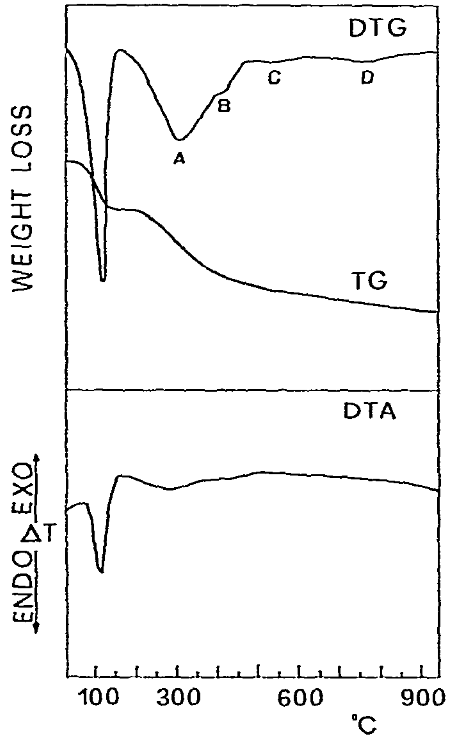


Fig. 4. Weight at 150 °C as a function of initial sample weight.



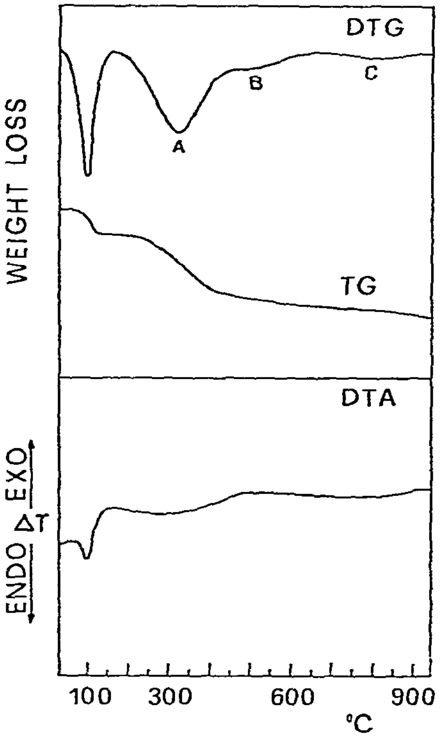


Fig. 5. TG, DTG and DTA curves of phenol loaded activated carbon.

Fig. 6. TG, DTG and DTA curves of aniline loaded activated carbon.

drying procedure. A further decrease of approximately 2.5% occurs in the subsequent heating from 150 to 950 °C.

As for weight losses from wet VAC, a quite constant value of approximately 3% occurs in the 150–950 °C range, while anomalous figures are obtained in the 25–150 °C interval, weight losses being somewhat less than expected on the basis of moisture content.

As shown by Fig. 4, however, a straight correlation has been obtained between the weight loss of the wet VAC at the end of the isothermal plateau at 150 °C and its initial moisture content. This provided the basis for any mass balance in future developments of this study.

The thermoanalytical curves of phenol and aniline loaded AC are reported in Figs. 5 and 6.

Experimental data for weight losses from 25 to 150°C, determined according to the proposed procedure for both series of samples, are in good agreement with the expected moisture release, thus indicating that only water is removed in this interval.

As for phenol and aniline desorption, a qualitative inspection of the corresponding TG and DTG curves shows this to be a rather complex process. In no cases did complete adsorbate release occur even at 950°C, as shown by the definite increase in the final experimental weight, quite independently of moisture content.

Overall weight losses average 65 and 55% of adsorbate for phenol and aniline, respectively, partially due to the chemically inert atmosphere (N_2) adopted in the investigated conditions, in agreement with baking performances reported by Juhola[12].

Furthermore, thermal behaviour shows a different complexity for phenol and aniline loaded AC.

Four separate steps are evident when phenol loaded AC is heated (A, B, C and D, Fig. 5) with desorption starting just after the dewatering isothermal stop. A large part of mass release occurs at moderate temperature, with about 95% of desorption being associated with the first two steps (peak tip temperature at 310 and 420°C, respectively, which close around 500°C). As shown by Fig. 6, thermodesorption of aniline starts around 160°C passing through three separate steps (A, B, C). The first two terminate before 650°C with definite peak tip temperatures around 310 and 530°C respectively, while no definite maximum could be associated with the third step. The largest part of aniline overall desorption, however, occurs during the first two steps (more than 90% of desorption attained before 450°C), with only minor release being associated with further heating up to 950°C.

DTA

As for energy variations associated with phenol and aniline thermodesorption, DTA curves show two distinct endothermic peaks below 150°C and around 300°C, respectively, while only the former appears when dry or wet virgin carbon is heated (Figs. 2 and 3). The first peak can be clearly related to water release, and the experimental figure (about -9.0 kcal mole^{-1}) is in good agreement with the theoretical value of -10.0 kcal mole^{-1} for the heat of evaporation of water[13] and the reported value of $+10.6$ kcal mole^{-1} found by Mahajan and Walker[14] for water adsorption on different carbonaceous materials. Relating the mass release to aniline and phenol molecular weight, the energy associated with the second DTA peak amounts to about -25 kcal mole^{-1} for phenol loaded AC, while a markedly lower value (~ -15 kcal mole^{-1}) is obtained for aniline.

Following Coughlin and Ezra[15], indeed, equal energy requirements should be expected for desorption of similar benzo-derivative adsorbates, due to electrostatic donor–acceptor interactions between AC surfaces and the π-electron system of aromatic rings. Furthermore, a somewhat higher adsorbability for aniline than for phenol has been experimentally found[16] as confirmed by the higher final temperature of its B peak (about 500 and 600°C for phenol and aniline, respectively).

Thus one should eventually expect higher energy requirements for aniline than for phenol desorption, while the contrary was found experimentally.

According to the several steps shown by the DTG behaviour of these products, DTA figures can be hardly related to phenol and aniline desorption per se, suggesting the occurrence of consecutive energetic processes (desorption, pyrolysis, readsorption, etc.) during the heating which presumably necessitate the high temperatures required. Useful information on this could be provided by a kinetic analysis of the process, as recently pointed out by Kirchhof and Hobert[17] for complex thermodesorption processes from zeolitic materials.

CONCLUSIONS

Thermoanalytical data obtained between 25 and 950°C show that the thermal behaviour of phenol and aniline loaded carbons in a chemically inert (N_2) atmosphere follows a complex pattern, with the possible formation of four or three subsequent pyrolytic by-products. Weak energy requirements seem to be associated with desorption of adsorbates per se while a considerable part of heat consumption should concern the pyrolytic reactions occurring on the side cracking by-products formed during heating.

Furthermore, 95 to 90% of desorption is associated with a milder heating (up to 500 and 450°C for phenol and aniline, respectively) compared with ordinary industrial practice.

Further investigations, based on the use of nitro-derivatives of phenol and aniline, are expected to provide more information about the possible simultaneous phenomena comprehensively involved with DTA and DTG effects shown by thermal analysis.

ACKNOWLEDGMENT

The Authors are indebted to Mr. L. Calabrese for skilfull contribution to experimental work.

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