

INVESTIGATION OF LOW-TEMPERATURE REGENERATION OF ACTIVATED CARBON*

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(Received March 12, 1979)

Granular activated carbon loaded with aniline, *o*-nitroaniline or *o*-nitrophenol, regenerated at relatively low temperature (450° in N₂ atmosphere), shows losses of cyclic adsorption performances (about 5% per cycle) comparable to those occurring with standard thermal regeneration (950° in controlled atmosphere). Adsorbate build-ups and related surface modifications have been determined.

Alternative regeneration techniques (i.e. chemical, biological, etc.) or substantial economic improvements of standard thermal regeneration are required to expand the application of active carbon (AC) in the field of pollution control. With this aim, promising implications have been associated to massive adsorbate release at relatively low temperatures (400–500°), as already evidenced in previous articles of this series [1–3]. In the present paper the cyclic performances of AC loaded with aniline (A), *o*-nitroaniline (ONA) or *o*-nitrophenol (ONF), thermally regenerated up to 450° in N₂ atmosphere, are presented.

Experimental

The progressive decay of the adsorption capacity of AC thermally regenerated to about 450° was followed by alternately submitting it to several adsorption-thermodesorption steps. About 100 mg of 16–25 (US) mesh dry AC (Filtrisorb 400 from Calgon Corp., Pittsburg, Pa.) was equilibrated with 100 ml of aqueous solution containing 300 ppm of aniline (A) or *o*-nitroaniline (ONA) or *o*-nitrophenol (ONF). The adsorbed amount was determined spectrophotometrically by analysis of the aqueous phase. After vacuum filtration, the samples were submitted to thermal analysis up to 450° in a dynamic N₂ atmosphere, using a model TA₁ Thermoanalyzer from Mettler AG, Zürich, Switzerland, with a heating rate of 6°/min. A new adsorption cycle was then started and the decrease of adsorption capacity of each sample progressively recorded. In order to follow surface and porosity modifications through the cycles, 6 AC samples, equilibrated with each solute and routinely submitted to heating-readsorption treatment, were discharged after the 1st, 2nd, 4th, 5th, 8th and 10th cycle, respectively,

* Work supported by IRSA-CNR, contract no. 77.01823.11.

and analyzed with a Series 1800 Sorptomatic from Carlo Erba, Milan, Italy following the B.E.T. method. Other experimental details are described elsewhere [1-3].

Results and discussion

The thermal behaviour (DTG and DTA) over the number of cycles for the three investigated systems is reported in Fig. 1. As already shown [1], the weight loss before 150° closely corresponds to the calculated water content (see Fig. 2), so that phenomena at $T > 150^\circ$ are clearly referable to adsorbate only. It is interesting to observe from Fig. 1 how the exothermic peaks in the DTA curves of nitro

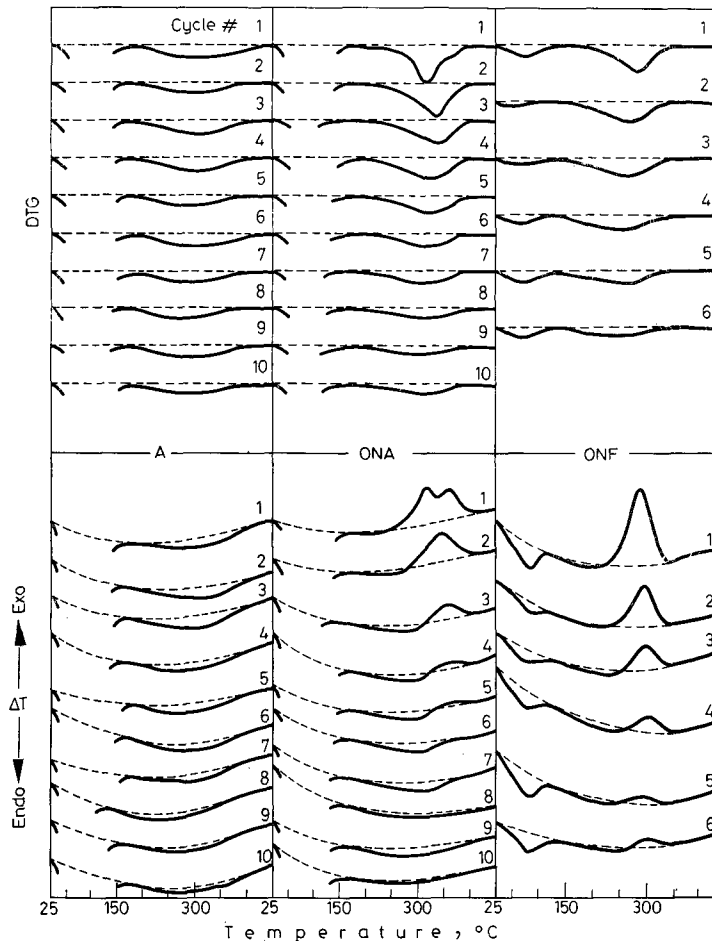


Fig. 1. Cyclic DTG and DTA behaviour of the investigated systems

compounds progressively vanish as the number of cycles increases, showing that neither the ease of release (DTG and DTA) nor the specific heat released (kcal/g desorbate) remain constant through the runs. While not readily explainable, this further confirms the multiform energy utilization during AC heating (pyrolysis, local surface modifications under strongly oxidative conditions, etc.), only the net effect of which is measured with this procedure.

As for the possibility of maintaining acceptable performances on low-temperature regenerated AC, Fig. 3 shows a progressive decay of adsorption capacities for the three investigated systems. As anticipated by Suzuki et al. [4], large amounts

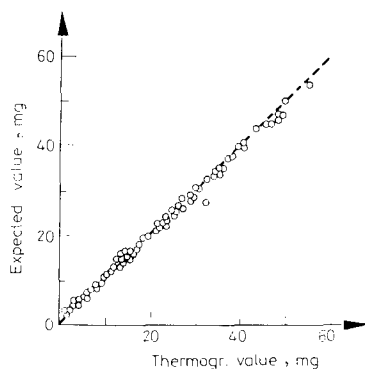


Fig. 2. Water removal at $< 150^{\circ}$ for all tested samples

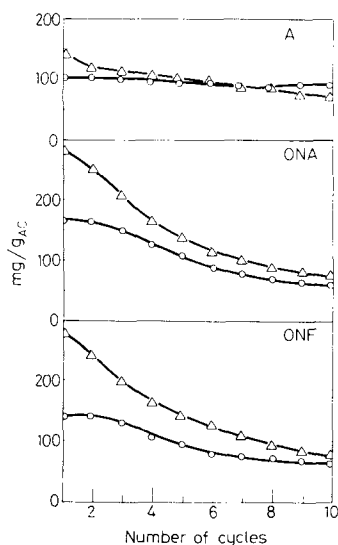


Fig. 3. Progressive variation of adsorption (Δ , \bar{C}_{ads}) and desorption (\circ , \bar{C}_{des}) capacities

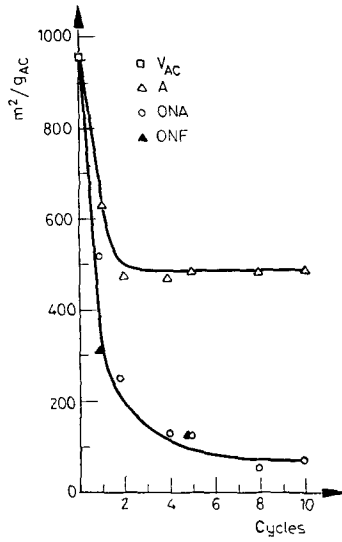


Fig. 4. Progressive total surface variation

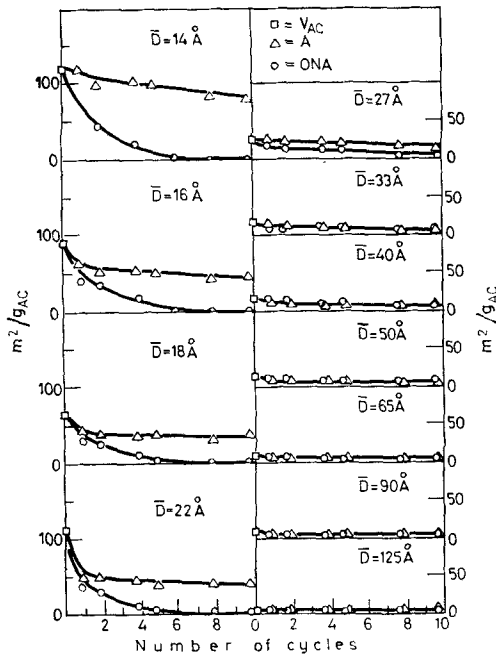


Fig. 5. Progressive single pore surface variations

of residues on AC are to be expected from these compounds under the investigated conditions, the build-up of which is measured by the area between the \bar{C}_{ads} and \bar{C}_{des} curves in Fig. 3. According to data by Balice [5] in a similar, non-destructive investigation of chemically regenerated AC, however, once the smaller pores ($<30 \text{ \AA}$) are filled up with adsorbate residue, a quite constant adsorptivity (30–70% of the initial value, depending on the solvent employed) should be maintained almost unlimitedly.

A stoichiometric regeneration efficiency is effectively reached after a few preliminary cycles with aniline-loaded AC, with complete adsorbate desorption thereafter. Once such a steady-state situation has been attained, an overall adsorptivity decay of about 50% is measured, a figure which favourably compares with similar results (about 5–7% decay per cycle) [6] occurring during thermal AC regeneration under standard conditions, where a much higher energy consumption must be paid for.

It should be noted, however, that even after the mass balance has been attained (i.e. 100% desorption of adsorbate), the adsorption capacity still continues to decrease (see aniline). Apart from incomplete adsorbate desorption, therefore, a major reason for performance deterioration under these conditions should be related to AC surface physico-chemical modifications, which, through melting of inner pores, smoothing of angles and corners, and reduction of oxygen-containing groups [7], lower the overall adsorptivity of AC.

In order to confirm this, a direct inspection of progressive surface modifications has been carried out through the determination of total and single pore surfaces.

As shown by Figs 4 and 5, indeed, an impressive loss of overall surface occurs in the first cycles, which can be essentially related to disappearance of smaller pores (14–30 \AA), due either to irreversible obstruction by pyrolytic fragments or/and surface levelling-out by local melting under the investigated conditions. Furthermore, such initial microporosity consumption is more pronounced with nitro adsorbates, where local combustion around adsorption sites is likely to occur. If a less direct NO_2 energy utilization can be reasonably expected in larger pores, this could help to explain the progressive lowering of exo-peaks in nitro compounds.

Our data agree with the overall micro to macroporosity shift during the regeneration cycle, with an accompanying net 40% decrease in adsorption capacity reported by Ford [8]. Lower losses should be expected if a properly oxidizing atmosphere, i.e. with oxygen and/or ozone as shown by Osanai [9] and Hernandez [10], is used under these conditions.

Conclusions

Cyclic performances of AC loaded with aniline, *o*-nitroaniline or *o*-nitrophenol, thermally regenerated at relatively low temperatures (up to 450°) in nitrogen atmosphere, seem quite comparable with those obtained when the costly, more

energy-consuming conventional regeneration (i.e. drying, baking and oxidation in a controlled atmosphere up to 950°) is applied, with adsorptivity losses around 5–7% per cycle. Present data thus suggest the possibility of a cheaper thermal regeneration technique, where a standard, high-temperature treatment is routinely scheduled after a number of milder thermal treatments.

Further researches are planned to optimize thermal ranges for other adsorbates in an oxygenated atmosphere.

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Thanks are due to Mr. L. Pace for skilful contribution to the experimental work.

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RÉSUMÉ — Le charbon actif en granules, chargé d'aniline, d'*o*-nitroaniline et d'*o*-nitrophénol, régénéré à une température relativement faible (450° dans une atmosphère d'azote) montre des pertes de rendement d'adsorption cyclique (environ 5 p.c. par cycle) comparables à celles qui ont lieu lors de la régénération thermique standard (950° en atmosphère contrôlée). On a déterminé la constitution des adsorbats et les modifications relatives de surface.

ZUSAMMENFASSUNG — Mit Anilin, *o*-Nitroanilin und *o*-Nitrophenol beladene, bei relativ niedriger Temperatur (450° in N₂-Atmosphäre) regenerierte granuliert Aktivkohle, zeigt zyklische Verluste der Adsorptionsleistung (etwa 5% je Zyklus), welche mit den bei thermischer Standard-Regenerierung (950° in gesteuerter Atmosphäre) vorkommenden vergleichbar sind. Der Aufbau der Adsorbate und die damit verbundenen Oberflächenänderungen wurden bestimmt.

Резюме — Гранулированный активированный уголь, наполненный анализом, *o*-нитроанилином, и *o*-нитрофенолом был регенерирован при относительно низкой температуре — 450° в атмосфере азота. Установлено, что при этом потери циклических адсорбционных характеристик (около 5% за один цикл) были аналогичны полученным со стандартной термической регенерацией — 950° в контролируемой атмосфере. Определены встроенные молекулы адсорбата и поверхностные модификации.