

LOW-TEMPERATURE REGENERATION OF ACTIVATED CARBON II. Kinetic evaluation of consecutive *o*-NO₂-phenol thermodesorptions

G. Baldassarre and V. Amicarelli

ISTITUTO DI CHIMICA APPLICATA, FACOLTÀ DI INGEGNERIA, UNIVERSITÀ DI BARI,
200 VIA RE DAVID, 70125 BARI, ITALY

(Received August 8, 1984)

Activated granular carbon samples, routinely equilibrated with synthetic aqueous solutions of *o*-NO₂-phenol, were regenerated by heating up to 500 °C in a dynamic N₂ atmosphere. Kinetic evaluation of five subsequent thermodesorption cycles was accomplished by two different non-isothermal computation methods. Quantitative estimation of adsorbent-adsorbate interactions was carried out by means of the thermal coefficient of the massive adsorbate release.

A mild thermal treatment (500°), instead of the more drastic industrial one (1000°), was performed before submitting one granular activated carbon (GAC) sample to the next batch-adsorption test in the cyclic heating-readsorption procedure previously performed with different aromatic nitro derivatives [1]. The adsorbent material underwent surface area modification and an adsorption capacity decrease, the values of which were then utilized in assessing the progressive decay of the GAC performance. At the same time, a meaningful modification of the thermodesorption pattern was found from a qualitative inspection of thermoanalytical curves recorded for consecutive heating treatments [1]. Quantitative characterization of thermodesorption curves was also carried out by non-isothermal kinetic analysis. With reference to this, for a once-used GAC sample, a substantial physical adsorption was demonstrated, together with an activation energy sensitive to the chemical structure of the adsorbed pollutant [2, 3].

This work is devoted to the kinetic evaluation of thermodesorption curves recorded for a consecutively recycled GAC sample equilibrated with aqueous *o*-NO₂-phenol solution.

Experimental

Filtrisorb 400 (from Calgon Corp., Pittsburgh, Pa.) was the tested GAC. Aqueous reagent grade *o*-NO₂-phenol solutions (300 ppm) were used for the batch-adsorption test at a solid/liquid ratio of 1 g/l. The thermogravimetric analysis of exhausted GAC

samples was performed with a TA1 Mettler thermoanalyzer at a constant heating rate of 6 deg/min in a dynamic N₂ atmosphere (5 l/h). Other experimental details are described elsewhere [1].

Results and discussion

The left side of Table 1 shows a portion of the TG curves and their derivatives (DTG) for a five-times recycled GAC sample. As pointed out elsewhere, the massive adsorbate release must be associated with this thermogravimetric step [4].

Depending on the mathematics adopted to solve problems arising from the non-isothermal utilization of the Arrhenius law, different computation methods can easily be carried out, allowing characterization of the above curves according to the fundamental kinetic equation

$$\frac{d\alpha}{dT} = \frac{A}{a} e^{-\frac{E}{RT}} f(\alpha) \quad (1)$$

where the designation recommended by ICTA is used [5].

The most suitable form of $f(\alpha)$ can be achieved with the Chen–Fong procedure [6] by testing the five functions of conversion degree which are considered able to describe almost all thermal transformations. Other computation methods, in contrast, utilize only the most simple form of $f(\alpha)$, i.e. $(1 - \alpha)^n$. Among the latter, the Zsakó nomogram method [7], besides kinetic parameters, provides a special one, ∇ , whose value indicates whether a simple or complex process is described by the investigated thermogravimetric step.

Both methods were utilized in this kinetic analysis.

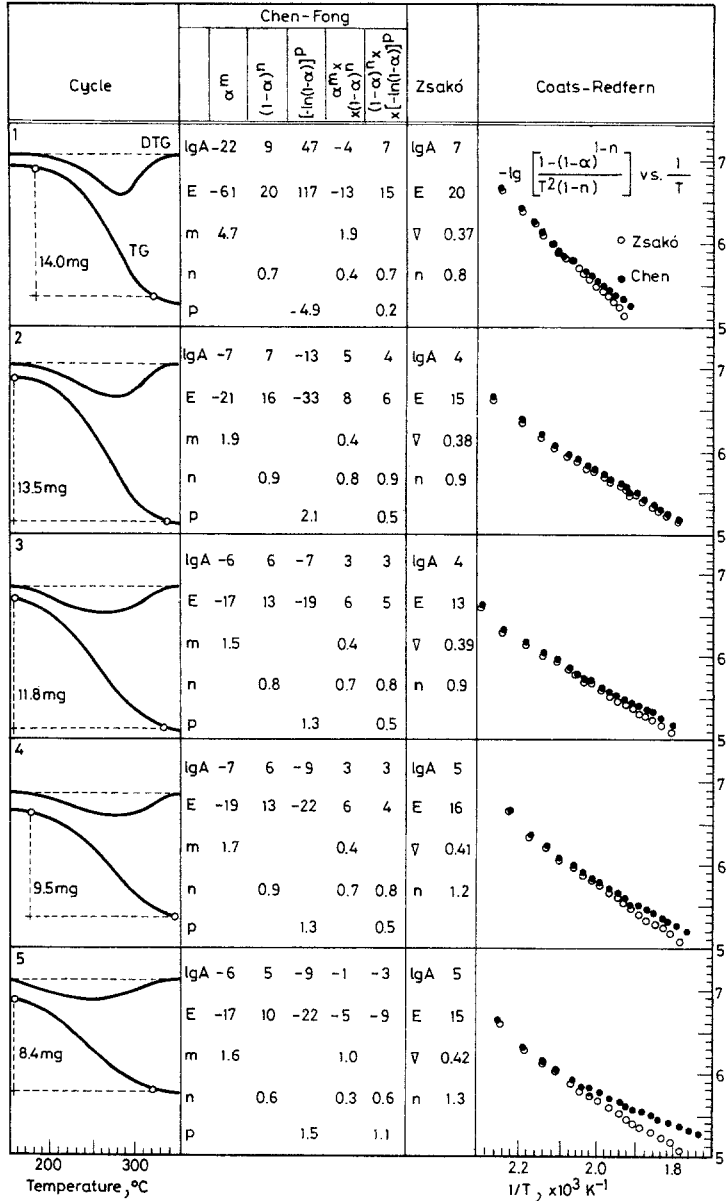
From the numerical results summarized in the middle of Table 1, the essentially positive E value invariably appears only when $(1 - \alpha)^n$ is the form of $f(\alpha)$ tested by the Chen–Fong procedure, so that the other tested functions of the conversion degree cannot be used to compare all thermodesorption runs.

For that kinetic law, on the other hand, comparable kinetic results are almost always given by the two computation methods. Moreover, Zsakó's procedure never yields a meaningful process complexity through parameter ∇ , the value of which sometimes barely exceeds the limit value of 0.4, under the adopted experimental conditions.

To compare the goodness of the results from the two procedures, a Coats–Redfern [8] "graphical check", which would give an almost linear plot when the best solution of Eq. (1) is found, was finally used.

From the right side of Table 1, better linearization is obtained when Zsakó's results are used to plot the appropriate function of the "true" kinetic law vs. the reciprocal absolute temperature. Zsakó's nomogram method, which requires that only three TG–T pairs need to be evaluated graphically, can therefore be adopted advantageously if a not very detailed kinetic law is to be found.

Table 1



It is clear from the kinetic results that the thermal cleaning of an exhausted adsorbent surface is a phase-boundary controlled process, whose thermal coefficient E (kcal/mol), i.e. the activation energy, diminishes as the cycle continues.

This is in good agreement with the progressive modification of the overall energy consumption involved in the adsorbate release, as previously elucidated from DTA curves [1].

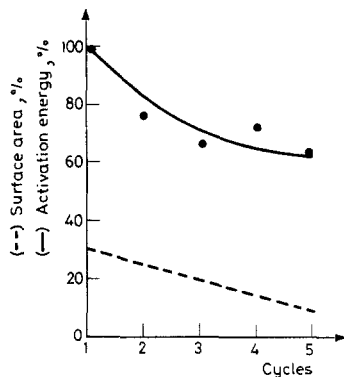


Fig. 1

Proper mechanistic considerations could therefore be obtained from kinetic exponent, n . In accordance with Gorbachev [9] in ranging from < 1 to > 1 (cf. Zsakó's results in Table 1), this parameter confirms that the desorption of volatile products coming from the depths of the GAC grain replaces the thermal destruction of the carbonaceous microporous system [1] as the controlling mechanism when the cycles follow one another.

Figure 1 illustrates the trend of the thermodesorption activation energy, whose relative decrease reaches about 40% in the fifth thermal treatment.

The same Figure also shows the well-established trend of the GAC total surface area [1], as measured after the corresponding cycle number.

Due to the lack of proper physical meaning of the non-homogeneous kinetic parameters, together with the expected influence from the use of normalized TG values in performing kinetic analysis of partially overlapping thermoanalytical effects [10], unfounded conclusions relating the easier thermal release of adsorbed pollutant to the surface area decrease of the adsorbent material could be argued. Further investigation is therefore planned to clarify the fitness of the kinetic parameters, and mainly the activation energy, to describe the consecutive variations occurring in the adsorbent-adsorbate interactions.

Conclusions

Under the adopted experimental conditions, massive *o*-NO₂-phenol thermodesorption, evaluated kinetically by two different computation methods, appears to be a phase-boundary controlled process.

Of these computation methods, Zsakó's nomogram procedure can conveniently be used because of its few graphical requirements.

The *E* values found indicate that physical adsorption interactions must be broken in order to obtain the thermal release of adsorbed pollutant.

Further investigations must be performed to clarify the influence of both experimental and computation procedures on the measured activation energy values, whose progressive variations agree well with our previous DTA results [1].

Useful implications result from a kinetic evaluation of the thermodesorption curves. From an applied point of view, for instance, a quantitative characterization of thermodesorption patterns from such information allows a useful adjustment of an operative baking procedure, the influence of which is to be found when implications concerning pollution control and energy-saving stem from both gaseous and solid-phase characteristics.

References

- 1 V. Amicarelli, G. Baldassarre and L. Liberti, *J. Thermal Anal.*, 18 (1980) 155.
- 2 V. Amicarelli, G. Baldassarre and L. Liberti, *Proc. VI ICTA, Bayreuth, 1980*, p. 433.
- 3 G. Baldassarre, in F. Sandrolini (Ed.), *Proc. 1st Nat. Meet. ASMI, Pitagora Pubs., Bologna, 1983*, p. 625.
- 4 V. Amicarelli, G. Baldassarre and L. Liberti, *Thermochim. Acta*, 30 (1979) 255.
- 5 R. C. Mackenzie, *J. Thermal Anal.*, 21 (1981) 173.
- 6 D. T. Y. Chen and Kai Wing Lai, *J. Thermal Anal.*, 20 (1981) 233.
- 7 J. Zsakó, *J. Thermal Anal.*, 15 (1979) 369.
- 8 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 9 V. M. Gorbachev, *J. Thermal Anal.*, 26 (1983) 319.
- 10 S. Boy and K. Böhme, *Thermochim. Acta*, 75 (1984) 263.

Zusammenfassung — Routinemäßig mit synthetischen wässrigen Lösungen von *o*-Nitrophenol äquilibrierte, granuliert Aktivkohle-Proben wurden durch Aufheizen auf 500 °C in einer dynamischen N₂-Atmosphäre regeneriert. Fünf aufeinanderfolgende Thermodesorptionszyklen wurden nach zwei verschiedenen nicht-isothermen Berechnungsmethoden kinetisch ausgewertet. Die quantitative Bestimmung der Adsorbent-Adsorbat-Wechselwirkungen wurde mittels der thermischen Koeffizienten der massiven Adsorbatdesorption ausgeführt.

Резюме — Образцы гранулированного активированного углерода, обычно находящиеся в равновесии с водными растворами *o*-нитрофенола, были регенерированы нагреванием их до 500 °C в динамической атмосфере азота. Кинетическая оценка пяти последовательных термодесорбционных циклов была проведена двумя различными неизотермическими расчетными методами. Количественное определение взаимодействия типа адсорбент—адсорбат осуществлено с помощью термического коэффициента разъединения массивного адсорбата.