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

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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 °C) instead of the more drastic industrial one (1000 °C) 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, in 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

Filtrasorb 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

\[ \frac{d\alpha}{dT} = \frac{A}{a} e^{-\frac{E}{RT} f(\alpha)} \]  

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, \( \nabla \), 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 \( \nabla \), 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.

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