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OPTIMAL ADSORBENTS FOR THE EXTRACTION OF FOOD INGREDIENTS: SEARCH AND CHARACTERIZATION

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ABSTRACT

The isolation and/or purification of many food ingredients proceeds via adsorption processes. We describe the search for and characterization of adsorbents especially useful for the destraction of caffeine from green coffee beans.

INTRODUCTION

Extraction processes are widely used in the food or pharmaceutical industries for the removal or isolation of ingredients. In many cases the natural substances extracted are in the main goal and the residues are discarded, in other cases the removal of certain ingredient(s) may be necessary for the improvement of the natural product. The decaffeination of coffee is one of the few cases where the residue (the decaffeinated coffee) and the extracted ingredients (caffeine and possibly other purines, coffee wax) find their market (ref. 1).

For many decades caffeine has been extracted from green coffee beans by organic solvents (CH_2Cl_2, ClH_2C-CH_2Cl, esters) or water. To avoid residues of potentially hazardous solvents, in the last few years a new decaffeination process using liquid or supercritical CO_2 has been developed and put into service (ref. 2). In the hitherto most practicable variant of the CO_2-process the caffeine is transferred from steamed green coffee beans to an adsorbent from which it is then recovered by desorption (this has recently also been called a destraction process). The present paper describes part of our search for and characterization of optimal adsorbents for this destraction process.

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ADDITIONAL AND NON-THERMAL INVESTIGATIONS

Samples of a great number of technical adsorbents were ordered from their manufacturers. These adsorbents fall into the following main classes

- activated charcoals
- molecular sieves
- silica gels
- bentonites
- organic resins.

Before beginning with the adsorption and desorption measurements a number of additional tests was performed with the adsorbents (ref. 3).

Stability against moisture: The bentonites and the activated silica gels were not stable against moisture and were ruled out from further consideration.

Abrasive stability: Samples, separated from adhering powdery material, were weighed into small circular boxes. These were rotated at constant speed for a predetermined time, sieved (0.38 mm mesh) and the residue weighed again.

Hardness: In a special apparatus individual grains of the adsorbents were exposed to a slowly increasing force and the minimum force to break the grain was determined.

Specific surface area: These were determined according to the BET-method as well in a simplified way (Ströhlein AREAmeter II) (ref. 4) as in some cases with the Sorptomatic 1800 (Carlo Erba Strumentatione).

Porosity: The Porosimeter 200 (Carlo Erba Strumentatione) was used to determine the porosity and pore size distribution of the adsorbents by mercury pressure porosimetry for pores with $r > 370$ nm. The distribution of the smaller pores was determined with the Sorptomatic 1800.

From the results of the non-thermal investigations briefly described we concluded that activated charcoals were the most promising for our objective and the following will be devoted to these.

ADSORPTION ISOTHERMS

Since desorption experiments by TG showed no significant differences whether the adsorbents were charged from CO_2 or from H_2O solutions, adsorption was performed from the latter because of greater ease.

Samples of 1 g of activated charcoals (air dried at 110 °C for 24 h) were weighed into 100 cm^3 flasks. Desired volumes of caffeine solution of known concentration and water were added. The flasks were stoppered and kept in a thermostat for extended periods. All concentrations were determined spectrophotometrically (Shimadzu UV-240) after suitable dilution. For 3 samples the solution concentration was determined every day (Fig. 1).

About 90 % of adsorption took place within 4 days, but complete equilibrium was only attained after about 25 days.

Thereafter the adsorption isotherms for various activated charcoals were determined, allowing all solutions to be in contact for 25 days at 20 °C. Fig. 2 shows the results for 5 different charcoals. As may be seen from Fig. 3 for 2 typical samples the data are well represented by the LANGMUIR adsorption isotherm in its form

$$\frac{c}{q} = \frac{1}{bq_m} + \frac{c}{q_m} \quad , \qquad (1)$$

where c = solution concentration in g caffeine / kg H_2O

q = amount of substance adsorbed in g caffeine / g adsorbent

q_m= maximum of q, obtained from the slope of eq. (1)

b = a constant.

The FREUNDLICH equation was found to be less useful. For 3 activated charcoals adsorption measurements were also performed at 40 °C, the results are shown in Fig. 4. As expected, the degree of adsorption decreased from 20 ° to 40 °C. The isosteric adsorption enthalpy at q = 0.5 g caffeine / g charcoal was determined to

$\Delta_{ads}H° = - 44.3$ kJ mol^{-1} (charcoal No. 1)

$\Delta_{ads}H° = - 68.9$ kJ mol^{-1} (charcoal No.11).

DESORPTION CHARACTERISTICS

The desorption characteristics were obtained by simultaneous thermogravimetry and thermal analysis (Stanton Redcroft STA 780). With

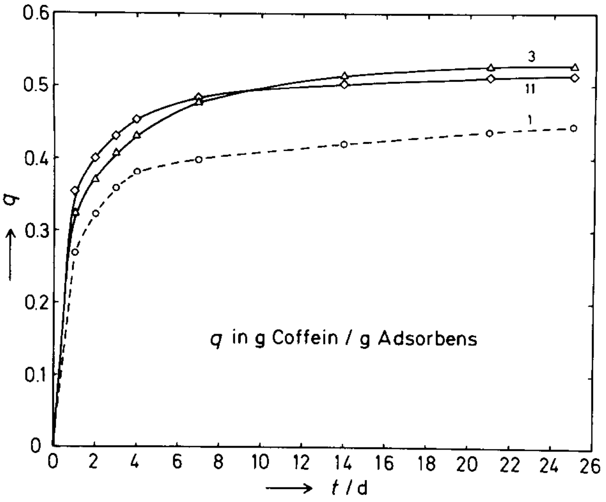

Fig. 1. Amount of caffeine adsorbed by 3 activated charcoals from aqueous solution as a function of time.

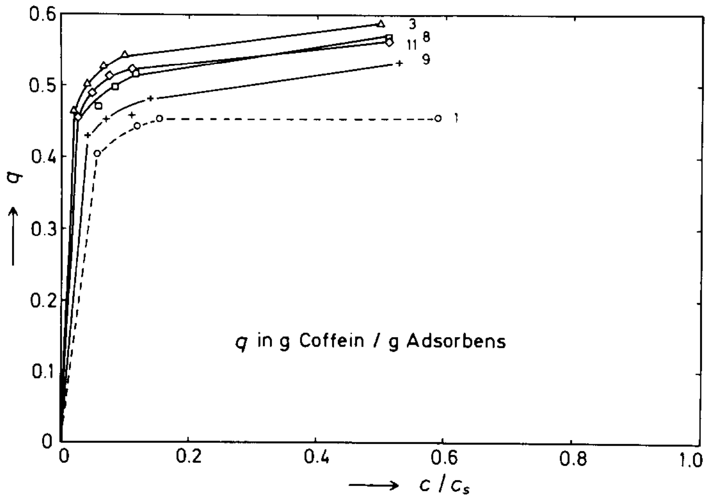

Fig. 2. Adsorption isotherms of caffeine for 5 activated charcoals at 20 °C. c_s is the saturation concentration.

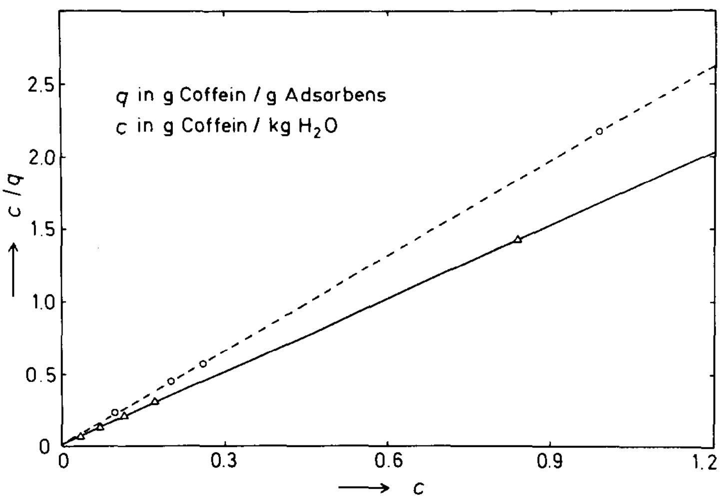

Fig. 3. LANGMUIR plot, eq. (1), for two of the data sets of Fig. 2.

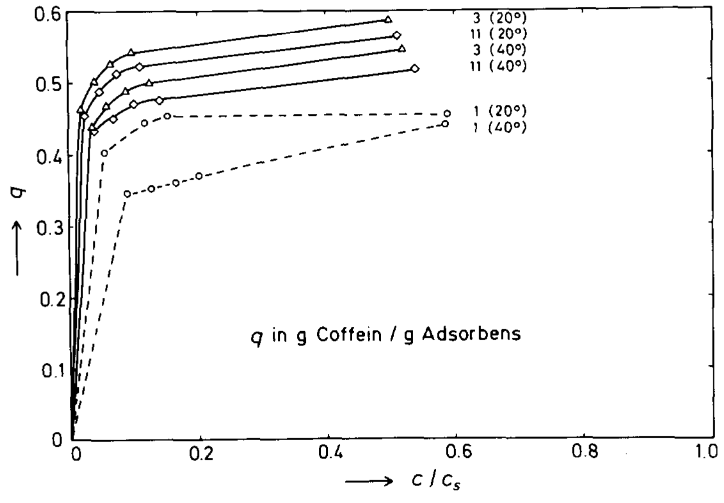

Fig. 4. Adsorption isotherms of caffeine for 3 activated charcoals at 20 ° and 40 °C. c_s is the saturation concentration.

the microprocessor balance control unit 100 % weight loss was set directly on the recorder full scale. Purified nitrogen at a flow rate of 88.7 cm^3 min^{-1} was used for all samples. The heating rate was 10 K min^{-1}.

The results for desorption for 2 samples of activated charcoals are shown in Fig. 5. Activated charcoals are hydrophobic, the water adsorbed is thus easily removed. A one-step weight loss occurs in the region 250 ... 520 °C corresponding to the desorption of caffeine. Table 1 gives the temperatures for peak onset and end for the same charcoals the adsorption isotherms of which are shown in Fig. 2. Data given are the mean of 10...15 determinations with individual pellets of each sample.

The interpretation of the DTA curve is difficult except for the desorption peak of water. The material desorbed from the different charcoal samples (mainly caffeine) was collected within the thermobalance and purity analysis was performed by computer assisted thermal analysis (Heraeus TA 500). Samples of 3 mg in aluminium crucibles were run at 5 K min^{-1}. The data are also given in Table 1.

THERMAL DECOMPOSITION OF CAFFEINE

As may be seen from Fig. 5 (exothermal DTA signal for temperatures above ca. 250 °C) and from the data in Table 1 partial decomposition of caffeine takes place at higher temperatures. The thermal stability of caffeine was therefore investigated in independent experiments. Samples of caffeine with an initial purity of 99.94 mol-% (melting point 236.0 ± 0.2 °C, ref. 5) were placed in hermetically sealed glass vials with and without the presence of activated charcoal. The vials were then kept at preset temperatures for 1 h, quenched, opened and several milligrams of substance weighed into aluminium crucibles. The results of the subsequent purity analysis are shown for pure caffeine and for caffeine in the presence of charcoal No. 1 in Fig. 6. At temperatures below 300 °C the stability of caffeine is remarkably high for a heterocyclic organic compound and charcoal has little effect. At higher temperatures, however, thermal decomposition becomes more pronounced and a catalytic effect of charcoal may be seen.

In assuming that thermal decomposition proceeds according to a scheme

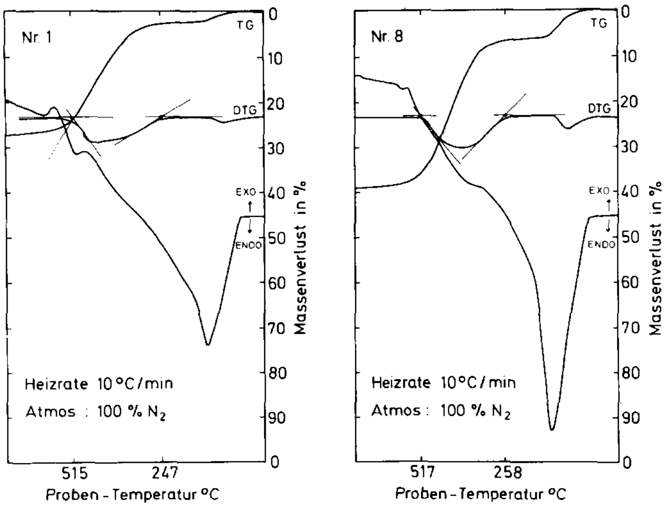

Fig. 5. Simultaneous TG, DTG and DTA curves for the desorption of caffeine from 2 activated charcoals. Flow gas is purified nitrogen at 88.7 cm^3 min^{-1}.

TABLE 1

Temperatures (in °C) for the onset and end of caffeine desorption of several activated charcoals and purity of the recovered caffeine (in mol-%)

No.	1	3	8	9	11
onset	250±7	246±11	257±7	260±5	252±11
end	508±6	519±12	513±7	514±9	518±9
purity	(72.7)	94.7	88.2	91.9	89.5

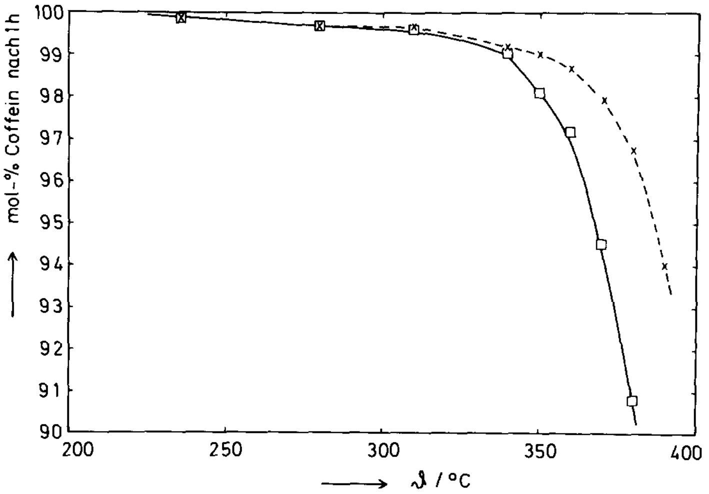

Fig. 6. Remaining purity of caffeine after the sample had been maintained for 1 h at preset temperatures as a function of these temperatures.
Broken line: caffeine alone; full line: caffeine in the presence of charcoal No. 1

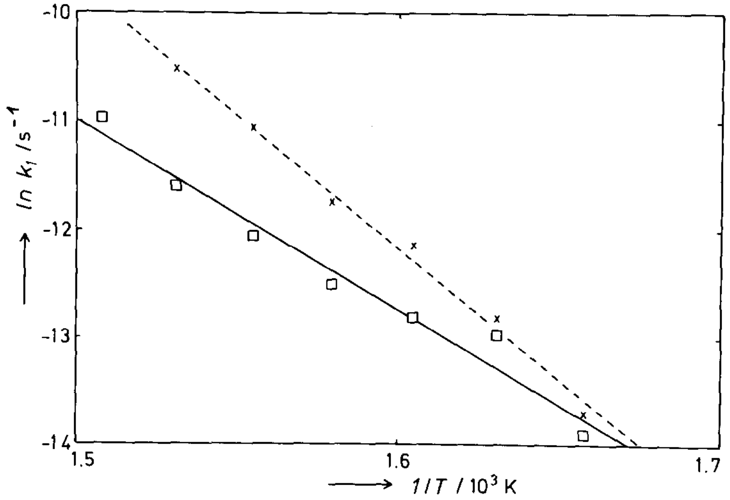

Fig. 7. Data of Fig. 6, evaluated according to a first order rate equation for k_1, in an ARRHENIUS-plot.

$$\text{caffeine} \longrightarrow \text{caffeine}^{*} \xrightarrow{k_1} \text{products} \qquad (2)$$

and a first order rate law

$$\ln (1-\alpha) = - k_1 \cdot t, \qquad (3)$$

where $(1-\alpha)$ is the fraction not decomposed, the rate constants k_1 have been calculated for the experiments shown in Fig. 6 and are reproduced as an ARRHENIUS-plot in Fig. 7.
The data thus determined compare rather well with the purity of material collected during the adsorption studies, indicating a high recovery of caffeine.

CLOSING REMARKS

A survey and characterization of adsorbents suitable for coffee decaffeination has been undertaken. Further studies will be devoted to the decomposition of caffeine during desorption and its correlation with the ash constituents of charcoals of different origin, inter alia by dispersive X-ray spectroscopy in the scanning electron microscope.

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