- This work was supported by CNR, Rome, in the framework of 'Progetto Finalizzato Chimica Fine e Secondaria'. Amico, V., Oriente, G., Piattelli, M., Tringali, C., Fattorusso, E.,
- Magno, S., and Mayol, L., Tetrahedron Lett. 1978, 3593.
- De Napoli, L., Fattorusso, E., Magno, S., and Mayol, L., Experientia 37 (1981) 1132.
- Blackman, A.J., and Wells, R.J., Tetrahedron Lett. 1978, 3063.
- Sun, H. H., and Fenical, W., Tetrahedron Lett. 1979, 685.

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Increase in micropore volume of N-containing activated carbon treated with methylol melamine urea solution

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Summary. The micropore volume of N-containing activated carbon was increased and the average radius of supermicropore was extended by treatment with methylol melamine urea solution.

20°C

(30°C)

(40°C)

500

400

The theory of volume filling of micropores (TVFM)² is applied for describing the physical adsorption of gas in micropores. The adsorption for micropores (radius < 5-6 Å) and supermicropores $(5-6 < \text{radius} < 15-16 \text{ Å} \text{ according to TVFM is expressed by the two-term equation}^3)$,

 $a\!=\!W_{01}/\mu*\,exp\big[\!-\!(A/\beta\,E_{01})^2\big]\!+\!W_{02}/\mu*\,exp\big[\!-\!(A/\beta\,E_{02})^2\big],$ where a is the amount adsorbed; $\mu *$ is the molar volume of an adsorbate; W_{01} and W_{02} are the micropore and the supermicropore volumes, respectively; A is the decrease of free energy of adsorption; E₀₁ and E₀₂ designate the characteristic energies of adsorption in micropores and supermicropores, respectively; and β is the similarity coefficient. In the previous paper⁴ it was demonstrated that the N-con-

taining activated carbon (N-CAC) prepared with methylol melamine urea (MMU) solution had the highest adsorption capacity for hydrogen sulfide at pressures up to about 400 Torr among the 20 kinds of N-CACs. N-CAC would be of great value for a large scale utilization because of the effects of its molecular sieving nature⁵ and its surface polar nature⁵. The present investigation was undertaken to describe the difference in porous structure between the raw activated carbon and the N-CAC prepared with MMU solution on the basis of the results of application of the

200

150

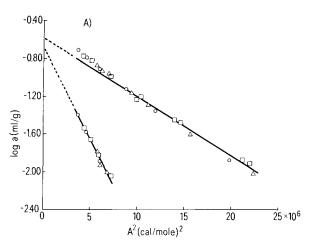
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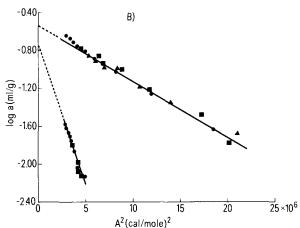
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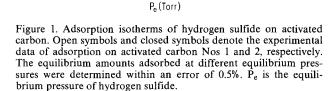
Amount of H₂S adsorbed(mg/g)

two-term equation to the experimental isotherms of hydrogen sulfide on them.

Materials and methods. The purity of hydrogen sulfide gas was indicated to be 99.9%. The physical properties of raw activated carbon (No.1) and N-CAC prepared with MMU







200

300

Figure 2. Application of the Dubinin-Radushkevich equation and the two-term equation to the experimental adsorption isotherms of hydrogen sulfide. A Activated carbon No.1; B activated carbon No.2; a, the amount of hydrogen sulfide adsorbed (ml/g); A, the decrease of free energy of adsorption.

Parameters of the two-term equation, structural constant, inertia radius, and characteristic size of micropores and supermicropores

Activated carbon No.	Micropores					Supermicropores				
	W ₀₁ (ml/g)	E ₀₁ (cal/mole)	B_1 (10^{-6} K^{-2})	R _{il} (Å)	(Å)	W ₀₂ (ml/g)	E ₀₂ (cal/mole)	$^{\circ}B_{2}$ (10^{-6} K^{-2})	R _{i2} (Å)	(Å)
1	0,2642	6737	0.46	5.35	4.69	0.2108	3815	1.44	9.44	8.29
2	0.2923	6921	0.44	5.21	4.57	0.1780	3121	2.15	11.54	10.13

solution (No.2) are as follows: specific surface area by N₂ gas, 949.6, 892.8 m²/g; pore volume, 0.5186, 0.5039 ml/g; true specific gravity, 2.16, 2.18 g/ml; element analysis, H: 0.62%, C: 96.69%, N: 0.87%; H: 0.38%; C:87.82%. N: 4.31%; pH of an aqueous dispersion, 6.5, 6.7. The preparation of N-CAC with 25% (w/v) MMU solution and the procedures for adsorption were described in previous papers⁴

Results and discussion. The adsorption isotherms at 3 different temperatures (fig. 1) showed that the amounts adsorbed on No.2 were larger than those on No.1 over the whole range up to 400 Torr. The Dubinin-Radushkevich (D-R) equation²

$$a = W_0/\mu^* \exp[-B(T/\beta)^2 \log^2(p_s/p)]$$

and the two-term equation were applied to the adsorption isotherms (fig. 2), where B is the structural constant, ps/p is the reciprocal number of the relative pressure, and T is the absolute temperature. The fact that the D-R plots showed a deviation from linearity at the ranges of $A^2 < 7 \times 10^6$ (No. 1) and $A^2 < 5 \times 10^6$ (No. 2) seems to indicate that these activated carbons possess heterogeneous pores, that is, micropores and supermicropores with a flattened shape as suggested by Huber et al.⁷, Izotova and Dubinin⁸, and Perret and Stoeck li^9 . The micropore volume (W_{01}) and the supermicropore volume (W_{02}) were estimated by extrapolation of the intercept to $A^2 = O$ of the upper line and the lower line, respectively, obtained by the least-squares method (fig. 2). E_{01} , B_1 , E_{02} , and B_2 were calculated from the slopes of the straight lines in figure 2. Increase in the micropore volume and decrease in the supermicropore volume of No.2 as compared to those of No.1 (table) were produced by treatment with MMU solution. The inertia radius R_i of a flat-shaped pore is expressed by $R_i = \sqrt{62B \times 10^6}$. The relationship between the inertia radii (R_i) of micropores and supermicropores and their characteristic sizes (x) is expressed by the equation³ $x = 0.878 R_i$. The characteristic size expresses the linear dimension which is of importance for the properties of micropores, and it is an average value of radii which correspond to the characteristic points of the adsorption isotherm³. The results that No.2 was almost equal in x₁ to No.1 and that No.2 was longer than No.1 by 1.84 Å in x₂ indicate that only the average radius of supermicropores was extended by treatment with MMU solution. It may be suggested that an increase of about 11% in micropore volume of No.2 results not from an extension of micropore radius but from a numerical increase of micropores with the same radius as that of No. 1.

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- Dubinin, M. M., Prog. Surf. Membrane Sci. 9 (1975) 1.
- Dubinin, M.M., in: Characterisation of porous solids, pp. 1-12. Eds S.J. Gregg, K.S.W. Sing, and H.F. Stoeckli. Society of Chemical Industry, London 1979.
- Tanada, S., Boki, K., Sakaguchi, K., Kitakouji, M., Matsumoto, K., and Yamada, Y., Chem. pharm. Bull. 29 (1981) 1736.
- Tanada, S., and Boki, K., unpublished data. Boki, K., and Tanada, S., Chem. pharm. Bull. 28 (1980) 1270.
- Huber, U., Stoeckli, F., and Houriet, J.Ph., J. Colloid Interface Sci. 67 (1978) 195.
- Izotova, T.I., and Dubinin, M.M., Zh. fiz. Khim. 39 (1965) 2796.
- Perret, E.A., and Stoeckli, H.F., Helv. chim. Acta 58 (1975) 2318.

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Enhanced inhibitory effect of UV on cell-cycle progression in cultures of lymphocytes from malnourished children

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Summary. Lymphocytes from malnourished children subjected to UV-irradiation were found to have a diminished entry into the proliferation pool and an increased cell-cycle duration in phytohaemagglutinin (PHA) treated cultures.

Protein energy malnutrition (PEM) is a disease due to inadequacy of proteins or calories in the diet and is known to cause a number of functional changes in children². At the cellular level the disease is characterized by a prolongation of the cell-cycle duration and a diminished blast transformation and DNA synthesis in lymphocyte cultures treated with PHA^{3,4}. Studies in our laboratory have been directed at understanding the possible presence of an increased 'spontaneous' and induced mutagenic environment in cells from children with severe PEM. We have recently reported that in lymphocytes from malnourished children UV induces more chromosome aberrations than it does in those from normal children controls³. In the present study, the inhibitory effect of UV on cell-cycle progression in PHA treated cultures of lymphocytes from malnourished children is reported.

Materials and methods. Six children suffering from severe PEM, diagnosed as having either kwashiorkor or kwashiorkor-marasmus, and 5 normal healthy children were investigated. The clinical and biochemical characteristics of symp-