RETENTION OF 2,4-DICHLOROPHENOXIACETIC ACID BY AN ACTIVATED CARBON

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According to some workers (1) there are some functional groups in active carbons which are very similar to those existing in the organic components of soil; as it is well known these organic components are in some way related to the degradation of many herbicides (2). Taking in account the above considerations we have studied the retention of 2,4-Dichlorofenoxiacetic acid (2,4-D) in aqueous solution by a granular activated carbon (supplied by Merck) with a particle size of 1,5 mm. We have studied the kinetics of the retention process and at the same time, the adsorption isotherms of such herbicide. The active carbon used has been characterized by determining its oxygen content, surface area (by $N_2$ adsorption at 77K) and pore size distribution.

The kinetic study has been carried out at 10, 20, 30, 40 and 50ºC using solutions of different initial concentrations of 2,4D and a constant amount of adsorbent for each temperature. From the plots $-\frac{dc}{dt} = f(t)$ (Fig. 1) the initial velocities of retention have been calculated, and the order of the retention process and the specific velocities have been calculated from the plots of $\log(-\frac{dc}{dt} = f(\log c)$ (Fig. 2). According to Eyring (3) the changes in enthalpy and entropy for the formation of the activated species have been calculated from the plot of $\log \frac{k}{T} = f(\frac{1}{T})$ (Fig. 3) giving values of $\Delta H^{+} = 6.7$ Kcal $mol^{-1}$ and $\Delta S^{+} = 45.5$ cal/ºmol. The change in free energy and the equilibrium constant have been calculated from the above values at each temperature.

The retention isotherms of 2,4-D at 20 and 50ºC (Fig. 4) have been obtained; they are of the L-3 type of Giles's clasification (4). For $C/C_o$ values greater than 0.5 the retention is taking place in multilayer. On the other hand, the isotherms follow the Langmuir equation (Fig. 5) up to $C < 8 \times 10^{-4}$ M (equivalent to $C/C_o < 0.50$). From these plots, the values of Xm and b have been calculated. The values of Xm are:

$$Xm_{(20ºC)} = 2.69 \times 10^{-3} \text{ mole g}^{-1}$$
$$Xm_{(50ºC)} = 2.19 \times 10^{-3} \text{ mole g}^{-1}$$

The surface accesible to 2.4-D has been calculated from these data, assuming that the molecule is retained perpendicularly to the solid surface. Since in these conditions the cross-sectional area of the molecule is 30 $Å^2$, the values of the surfaces are

$$S_{(20ºC)} = 486 \text{ m}^2 \text{ g}^{-1}$$
$$S_{(50ºC)} = 396 \text{ m}^2 \text{ g}^{-1}$$

The values of the constant b are:

$$b_{(20ºC)} = 6.45 \times 10^3 \text{ l} \times \text{mole}^{-1}$$
$$b_{(50ºC)} = 6.65 \times 10^3 \text{ l} \times \text{mole}^{-1}$$

and they indicate that although the retention process is almost enterely physical, there is some contribution of chemisorption.

Finally, the differential heats and entropies of retention have also been calculated (Fig. 6 and Fig. 7). The $\Delta \bar{H}$ values range from 0 to 3 Kcal $mole^{-1}$ and this seems to confirm that the retention is a physical process.

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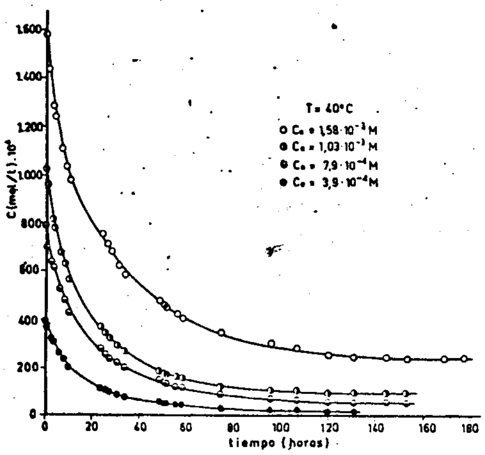


Fig. 1

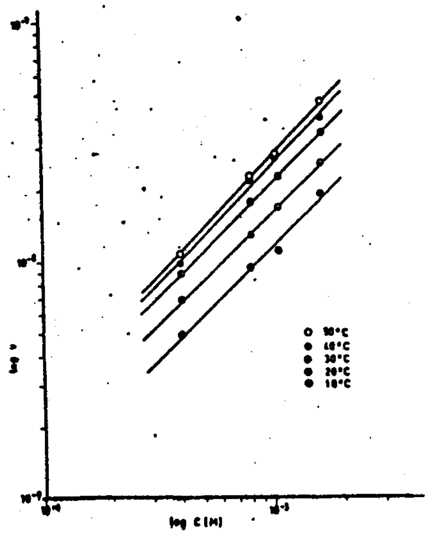

Fig. 2

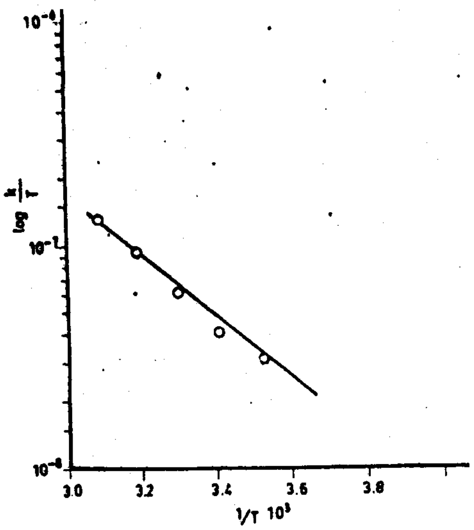


Fig. 3

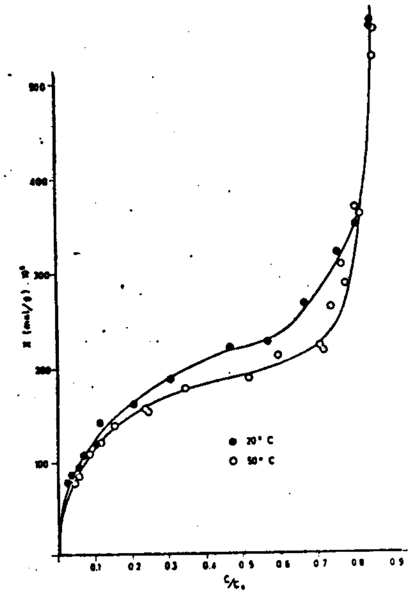


Fig. 4

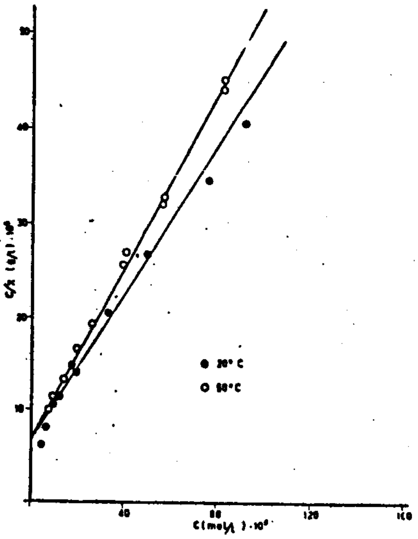

Fig. 5

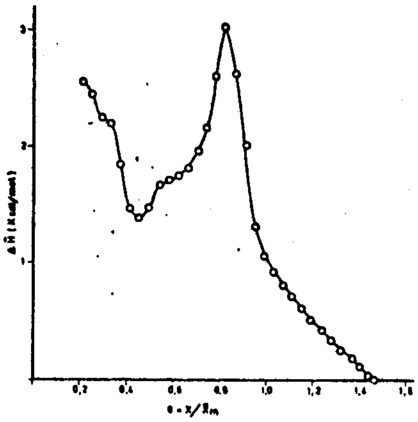

Fig. 6

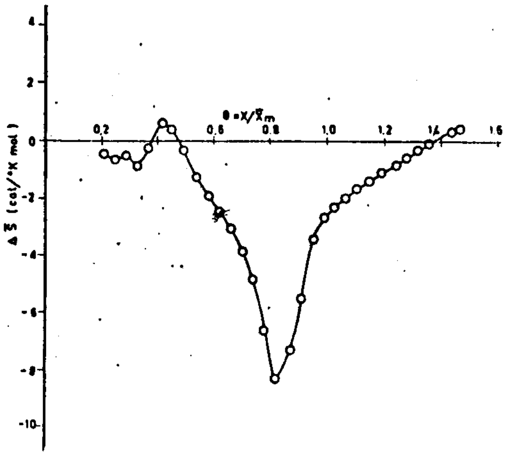


Fig. 7