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Adsorption and Desorption of Linuron by Activated Charcoals

Marinella Bosetto, Paola Arfaioli, and Paolo Fusi

Department of Soil Science and Plant Nutrition, Florence University—Study Center for Soil Colloids, C.N.R., Florence, Piazzale delle Cascine, 28 - 50144 Florence, Italy

The use of activated charcoals to eliminate phytotoxic residues of herbicides in soil has been well documented.

The use of these products, although limited by economic factors as consequence of the high rates required to obtain satisfactory results, has been very effective in removing herbicide residues (Andersen, 1968; Coffey and Warren, 1969; Mallegni, 1975; Fusi et al., 1977). The herbicide adsorption by activated charcoals changes with the carbon type, and it is, generally, higher than that exibited by natural soil adsorbents, soil-like materials and wood powders (Weber et al., 1965; Jordan and Smith, 1971; Toth and Milham, 1975).

This paper reports on the adsorption and desorption of the Linuron herbicide [3-(3,4 dichlorophenyl)-1-methoxy-1-methylurea] on two activated charcoals.

MATERIALS AND METHODS

Linuron (99% of purity) was supplied by Riedel-de-Haen. The product has the following characteristics: mp = 93-94 °C; mw = 249.1; molecular surface area = 68.8 $Å^2$ $molecule^{-1}$ (Bailey and White, 1965); water solubility at 25°C = 75 ppm.

The adsorbent materials used were two activated charcoals: GRO-SAFE (American Norit Company) and NORIT W 52 (Norit, N.V.), both amorphous to X-rays. Their properties are reported in Table 1.

Adsorption isotherms were obtained by addition of 50 mL of aqueous Linuron solution (concentration ranging from

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Send reprint requests to Marinella Bosetto at the above address.

0 to 20 μg mL^{-1})to activated charcoals (5 mg). The samples (in duplicate) were thermostatized at 5°, 25° and 40 °C under intermittent shaking for 15 h, time widely sufficient to reach the equilibrium.

Table 1. Properties of the activated charcoals.

Charcoals	pH(*) in H_2O	C.E.C. meq/100g	C %	H %	N %	O %	Residue at 900 °C %	Surface area (m^2/g)
GRO-SAFE	8.8	5.0	65.0	0.78	0.45	10.2	23.5	559
NORIT W52	10.4	2.5	89.6	0.36	0.37	4.1	6.7	608

(*) Charcoal:water = 1:50

Preliminary cinetic measurements showed that the equilibrium was reached in less than 10 h. After rapid filtering under pressure through Whatman filter n. 42, the equilibrium concentration of Linuron was determined by U.V. spectrophotometry at 248 nm, using a Perkin Elmer Lambda 3B Spectrophotometer.

Desorption experiments (in duplicate) were carried out as follows: after adsorption the equilibrium solution was removed and replaced with 20 mL of water. The samples were equilibrated under shaking for 15 h at 25 °C. After removing the supernatant for analysis another aliquot of 20 mL of water was added. This procedure was repeated 8 times.

RESULTS AND DISCUSSION

The results concerning the adsorption isotherms of Linuron on activated charcoals (Gro-Safe and Norit) are reported in Figure 1. The vertical line of the isotherms shows an high adsorption value at lower concentrations. The isotherms are of H/2 class described by Giles et al. (1960) showing, as observed for Atrazine (Fusi et al., 1977), a so high affinity of Linuron for the two adsorbents that it was impossible to find measurable solute quantities in solution at low concentrations. The adsorption capacity of Norit charcoal appeared always higher than Gro-Safe one. This behaviour can be ascribed to the higher surface area of Norit charcoal.

For high concentrations the isotherms fit the Langmuir equation:

$$\frac{Ce}{Cs} = \frac{1}{ab} + \frac{1}{b} \cdot Ce$$

where Ce is the equilibrium solute concentration

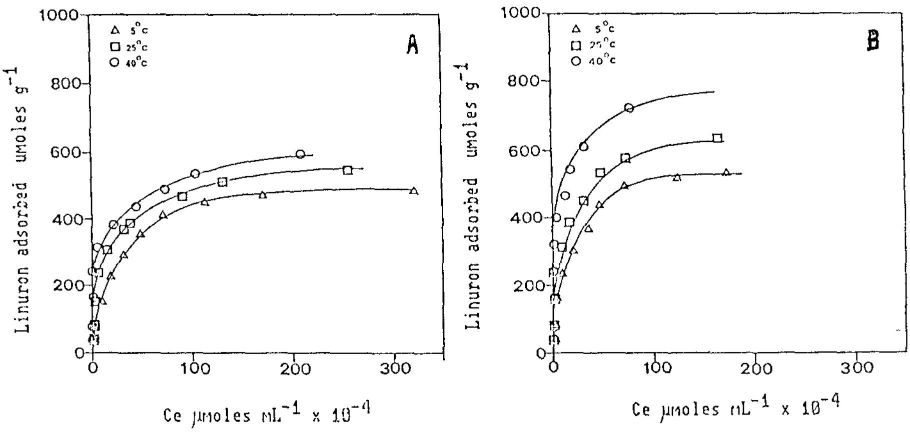

Figure 1. Adsorption isotherms of Linuron by Gro-Safe (A) and Norit (B) at 5°, 25° and 40°C.

in solution (µmoles mL^{-1}); Cs is the amount of solute adsorbed for unit mass of adsorbent (µmoles g^{-1}); "a" is an "affinity" parameter and "b" is a "capacity" parameter (i.e. "b" is the value of Cs when all sites on the surface are occuped). A plot of Ce/Cs against Ce will give a straight line (Figure 2) whose slope allows to calculate the capacity parameter and y-intercept (with the slope value), the affinity parameter.

Table 2. "a" and "b" values (on molar basis) of Langmuir isotherm.

	a		b	
T°C	Gro-Safe	Norit	Gro-Safe	Norit
5	460	619	518	581
25	770	770	567	683
40	718	1470	621	779

These values (Table 2) further confirm the higher adsorption power of Norit charcoal in comparison to Gro-Safe.

The recovery of the herbicide by washing with distilled water at 25°C is only possible when the amount of Linuron adsorbed on Norit is higher than about 200 µmoles g^{-1} (in Figure 3 is only reported the desorption isotherm related to the last two points of the adsorption isotherm). Linuron desorption from Gro-Safe at 25°C shows a similar behaviour.

The adsorption process from solution and the adsorbate

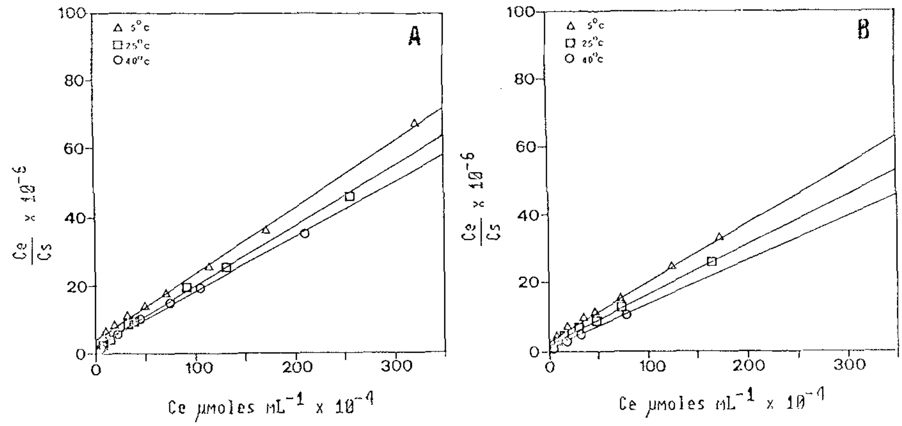

Figure 2. Langmuir adsorption isotherms of Linuron by Gro-Safe (A) and Norit (B) at 5°, 25° and 40°C

solubility are both affected by temperature: however, solubility and adsorption are anthagonistic phenomena and the adsorption will be higher when the solubility is lower. If the adsorbate solubility increases with temperature, the adsorption decreases as the adsorption is generally an exothermic phenomenon. If the solubility decreases with increasing of temperature the solubility process would be exothermic and therefore the adsorption will decrease or increase with the temperature according to the process quantitatively prevalent (under the same entropic factor). As the Linuron solubility increases with temperature, a lower adsorption should be expected at 40 °C than at 5 °C because of both the exothermicity of the adsorption process and the effect of solubility. On the contrary we have a higher adsorption at 40°C than at 5°C. This means that the overall process is endothermic whereas adsorption is an exothermic phenomenon. Therefore, we must admit that an adsorption coupled to a process of opposite sign (+) to the normal sign of adsorption heat (-) would take place.

The adsorption heat (entalpy) was determined using the Clausius-Clapeyron equation:

$$d \ln Ce/dt = \Delta H/RT^2 \qquad [1]$$

The indefinite integral form of eq. [1] is:

$$\ln Ce = -\Delta H/RT + K \qquad [2]$$

and the definite integral form is:

$$\ln Ce_1/Ce_2 = -\Delta H/R \ (T_1-T_2) \qquad [3]$$

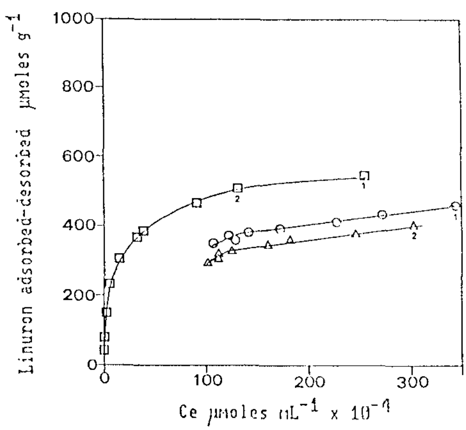

Figure 3. Adsorption (□) - Desorption(○ , △) isotherms for Linuron on Norit in water at 25°C.

where Ce_1 and Ce_2 are the equilibrium concentration at T_1 and T_2 and ΔH is constant in the range $T_1 - T_2$.

Table 3 gives the ΔH values according to equations[2] and [3].

The adsorption heats vary between 4111 and 13569 cal $mole^{-1}$ for Gro-Safe, and between 8016 and 11208 cal $mole^{-1}$ for Norit (Table 3). In both cases ΔH is higher the lower is the amount of herbicide adsorbed. It is considered that the adsorption heat varies between 20000 and 100000 cal $mole^{-1}$ for a chemical adsorption and it is about 5000 cal $mole^{-1}$ for a physical adsorption (Glasstone, 1960). This is a negative value, but we find the total heat positive, because in our

Table 3. ΔH values of Linuron adsorbed on charcoals.

Linuron adsorbed ($\mu g\ g^{-1}$)	Norit ΔH (a) (cal $mole^{-1}$)	Norit ΔH (b) (cal $mole^{-1}$)	Gro-Safe ΔH (a) (cal $mole^{-1}$)	Gro-Safe ΔH (b) (cal $mole^{-1}$)
$130x10^3$	8016	8200	-	-
$120x10^3$	7837	8017	-	-
$110x10^3$	8025	8210	4111	4208
$100x10^3$	9295	9509	4491	4603
$90x10^3$	9918	10146	5688	5819
$80x10^3$	10957	11208	7673	7849
$70x10^3$	-	-	13266	13569

(a) Calculated according to eq. [2].
(b) Calculated according to eq. [3].

case the adsorption is an endothermic process. The processes which probably compensate the negative value of the adsorption heat are the breaking off of solvent molecules from the adsorbent surface and the diffusion of solute to the adsorbent surface. These phenomena are essentially endothermic and their contribution is generally small, but in our case sufficient to exceed that due only to the adsorption, which is exothermic.

Therefore, the ΔH values relative to adsorption only will be smaller as the total ΔH ones. However our results need to be examined more closely in order to explain also the type of binding between irreversibly adsorbed Linuron and the charcoals.

The averages of the ΔH values vs. amounts of Linuron adsorbed are reported in Figure 4. The curves tend to an approximately constant ΔH, and therefore we can assume the formation of a monomolecular film at a particular value of adsorbed Linuron (100×10^3 $\mu g\ g^{-1}$) on Gro-Safe, which has a surface area of 559 $m^2\ g^{-1}$:

$$\frac{559\ m^2\ g^{-1}}{68.8 \times 10^{-20}\ m^2\ molecule^{-1}} = 8.12 \times 10^{20}\ molecules\ g^{-1}$$

are necessary to form a monolayer,the Linuron molecular surface area being 68.8×10^{-20} $m^2\ molecule^{-1}$. On the other hand, 100×10^3 $\mu g\ g^{-1}$ of Linuron adsorbed correspond to 4.01×10^{-4} moles g^{-1}, i.e 2.41×10^{20} molecules g^{-1}. Therefore, this value indicates the formation of an almost monomolecular film. The calculation carried out for other points of the curve gives the following values: $110 \times 10^3 \mu g\ g^{-1}$ correspond to 2.65×10^{20} molecules g^{-1}, 120×10^3 $\mu g\ g^{-1}$ to 2.90×10^{20} molecules g^{-1}, 130×10^3 $\mu g\ g^{-1}$ to 3.14×10^{20} molecules g^{-1}.

For Norit which have a surface area of 608 $m^2\ g^{-1}$

$$\frac{608\ m^2\ g^{-1}}{68.8 \times 10^{-20}\ m^2\ molecule^{-1}} = 8.84 \times 10^{20}\ molecules\ g^{-1}$$

are necessary to form a monolayer. On the other hand 110×10^3 $\mu g\ g^{-1}$ of Linuron adsorbed correspond to 4.40×10^{-4} moles g^{-1}, i.e. 2.65×10^{20} molecules g^{-1}. This value also indicates the formation of an almost monomolecular film, as we have observed for Gro-Safe.

Therefore, for Norit and Gro-Safe, we are always below, even if by not much, the theoretical amount necessary for a monomolecular film (8.84×10^{20} and 8.12×10^{20} molecules g^{-1} for Norit and Gro-Safe respectively); however, we must consider the heterogeneity of the

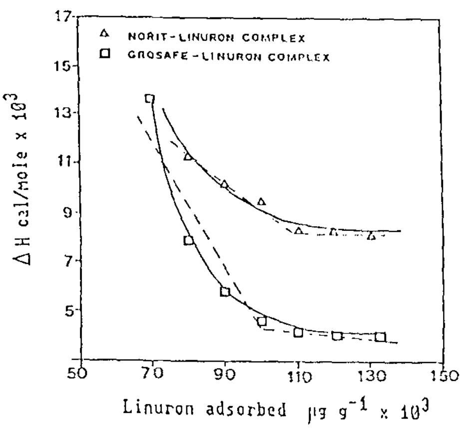

Figure 4. Amount of Linuron adsorbed on charcoals vs. ΔH values.

activated carbons and therefore we can regard the active centres of charcoals entirely saturated by Linuron.

These results evidence the effectiveness of the two activated carbons (particularly Norit) in controlling and eliminating Linuron residues.

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