A KINETIC STUDY OF PESTICIDE SORPTION ON VARIOUS MEDITERRANEAN SOILS

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Introduction

Adsorption of pesticides on soils is a time-dependent process governed by the difference between the amount currently adsorbed and the amount that would be adsorbed if the system was in equilibrium. Therefore, kinetic studies are needed to evaluate the equilibrium time and the mechanisms involved. In this work we have dealt with kinetic aspects of pesticide adsorption on agricultural soils with contrasting properties

Materials and Methods

Table 1. Soil properties

	SV	RM1	RM3
Soil use	Irrigated crops	Rainfed crops	Olive orchards
Soil type (FAO/UNESCO)	Calcaric fluvisol	Chromic vertisol	Calcic cambisol
Sand (%)	31	10	19
Silt (%)	58	39	50
Clay (%)	11	51	31
Cation exchange capacity (meq_z/100g)	8.4	18.3	12.3
Water holding capacity (%)	24	14	28
$CaCO_3$ (%)	24.9	42.1	58.7
pH	8.5	7.9	8.1
OC (%)	0.92	0.61	0.79
Electrical conductivity (µS/cm)	1034	416	251
Bulk density (g/cm³)	1.32	1.48	1.62

Adsorption kinetics setup (triplicate)

5g soil/20 mL distilled water

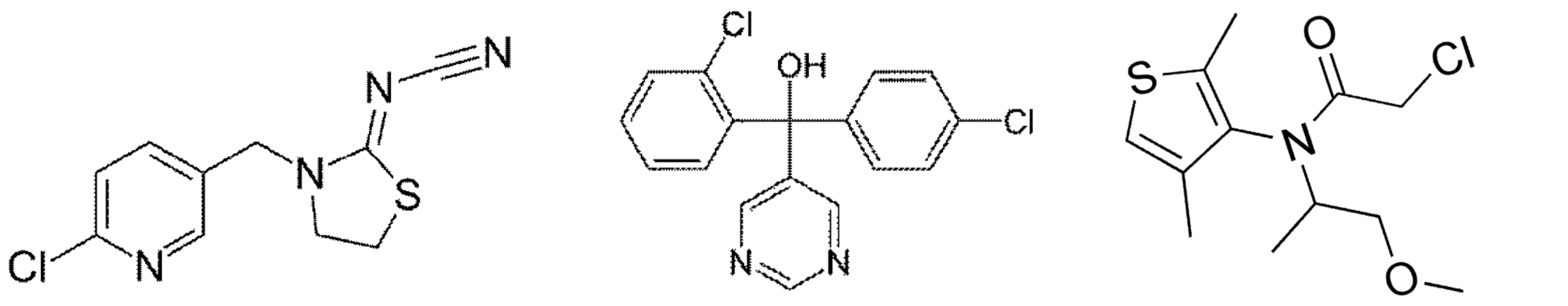
Pesticide concentration 2 µg mL^{-1}

Shaking at 20ºC up to 24h

Centrifugation at 3000 rpm

$$X = \frac{V}{m}(C_0 - C_e)$$

X (µg g⁻¹): soil adsorbed concentration
V (mL): volume
m (g): soil mass
C_0 (µg mL^{-1}): initial solution concentration
C_e (µg mL^{-1}): concentration at equilibrium in solution (HPLC-DAD)



Thiacloprid (THC)
Class: neonicotinoid insecticide
Mol. weight (g mol^{-1}): 252.7
Water sol. (mg L^{-1}): 184 (20 ºC)
Log k_{ow}: 1.26

Fenarimol (FEN)
Class: pyrimidine fungicide
Mol. weight (g mol^{-1}): 331.2
Water sol. (mg L^{-1}): 13.7 (25 ºC)
Log k_{ow}: 3.69

Dimethenamid (DIM)
Class: chloroacetamide herbicide
Mol. weight (g mol^{-1}): 275.8
Water sol. (mg L^{-1}): 1200 (25 ºC)
Log k_{ow}: 2.15

Figure 1. Pesticide structure and properties

Kinetic models

Intraparticle Diffusion (IPD) Model

$X_t = C + K_{int}\, t^{1/2}$

C (µg g⁻¹): constant related to the extent of the boundary layer thickness
K_{int} (µg g^{-1} $min^{1/2}$): IPD rate constant

The initial adsorption factor R_i (dimensionless) is defined as:

$R_i = (K_{int}\, t_{ref}^{1/2} / X_{ref}) = 1 – (C / X_{ref})$

$X_{ref} = K_{int}\, t_{ref}^{1/2} + C$

t_{ref} (min): longest time in adsorption process
X_{ref} (µg g^{-1}): adsorbed amount at t = t_{ref}

Pseudo Second Order (PSO) Model

$t/X_t = (1/K_{PSO} X^2_{max}) + (t/X_{max})$

K_{PSO} (g $µg^{-1}$ min^{-1}): PSO kinetic rate constant
X_{max}, X_t (µg g^{-1}): adsorbed concentration at equilibrium and at time t

Elovich Equation

$X_t = \ln(\alpha\beta)/\beta + \ln(t)/\beta$

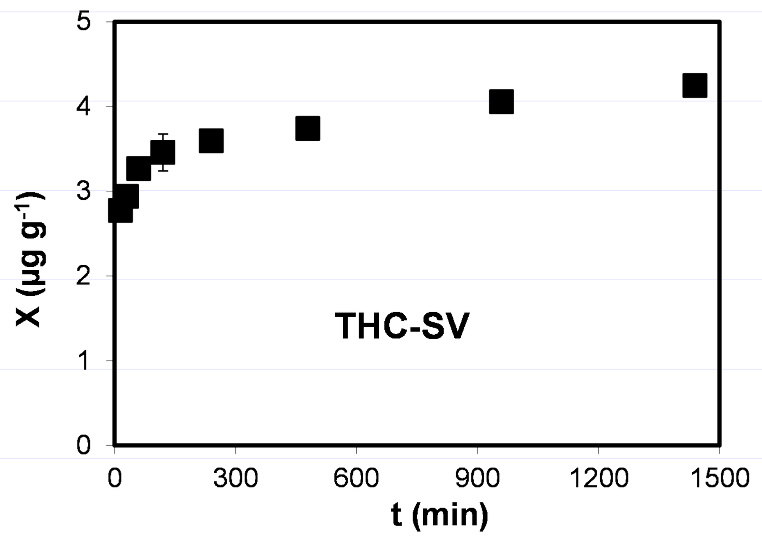
α (µg g^{-1} min^{-1}): initial adsorption rate
β (g $µg^{-1}$): extent of surface coverage

References

- PLAZINSKI W., RUDZINSKI W. & PLAZINSKA A. (2009). Theoretical models of sorption kinetics including a surface reaction mechanism: A review. Adv. Colloid Interface Sci., 152, 2-13.
- WU F.C., TSENG R.L. & JUANG R.S. (2009). Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. Chem. Eng. J., 153, 1-8.

Results and Discussion

Kinetic curves indicated that adsorption equilibrium was achieved within 24 h. Adsorption capacity of the soils was ranged as FEN > THC > DIM, according to pesticide properties (Figure 1)



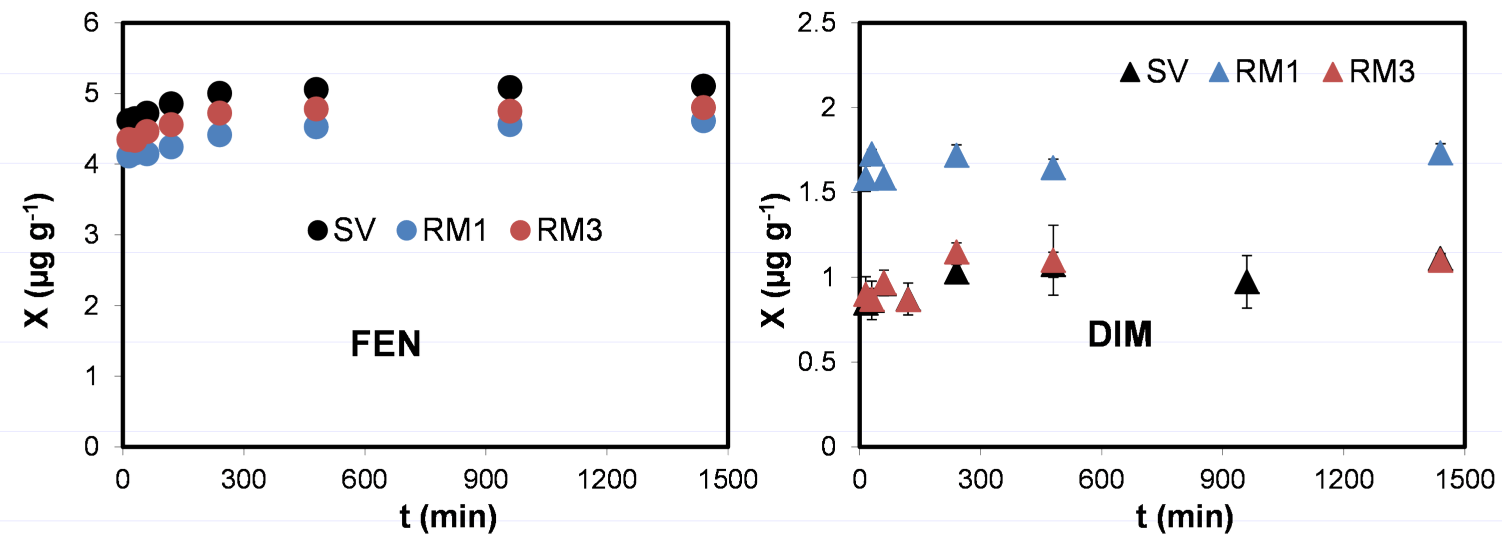


Figure 2. Kinetic curves for pesticide adsorption on soils

			PSO		
Soil	**Pest.**	Exp. X_{max}	X_{max}	K (x10³)	R^2
SV	THC	4.24	4.25	8.39	0.998**
	DIM	1.11	1.08	57.7	0.994**
	FEN	5.10	5.11	43.9	1**
RM1	DIM	1.73	1.73	100.3	1**
	FEN	4.61	4.62	29.98	1**
RM3	DIM	1.15	1.11	106.3	0.999**
	FEN	4.80	4.80	50.5	1**

PSO was the model that best described experimental data

Predicted X_{max} values agreed with the experimental ones

Adsorption rate constants (K_{PSO}) dependent on soil properties

		Elovich		
Soil	**Pest.**	α	β	R^2
SV	THC	157	3.2	0.987**
	DIM	58369	19.7	0.693*
	FEN	2.3 10^{14}	8.2	0.956**
RM1	DIM	3.3 10^{30}	47.4	0.268#
	FEN	2.6 10^{12}	8.2	0.941**
RM3	DIM	8310	16.8	0.617*
	FEN	2.5 10^{14}	8.8	0.925**

Elovich equation also described pesticide kinetics, but low R^2 for DIM

This equation could neglect simultaneous desorption due to high DIM water solubility (Figure 1) (Plazinski et al., 2009)

Values of α and β confirmed the higher FEN affinity for soil particles

		IPD			
Soil	**Pest.**	K_{int}	C	R_i	R^2
SV	THC	0.04	2.85	0.34	0.923**
	DIM	0.006	0.86	0.22	0.623*
	FEN	0.015	4.64	0.11	0.818**
RM1	DIM				
	FEN	0.016	4.08	0.13	0.906**
RM3	DIM				
	FEN	0.014	4.36	0.11	0.773**

*P < 0.05; **P < 0.01; #not significant (P > 0.05)

IPD successful, except for DIM, only fitted in SV soil

R_i between 0.11 and 0.34 and positive C ⇨ strong contribution of initial adsorption (Wu et al., 2009) (Figure 2)

IPD more relevant for THC (higher R_i), followed by DIM and FEN, for which adsorption occurs mainly in the initial rapid stage (≈ 90%)

Conclusions

- The PSO model shows that different mechanisms are involved depending on pesticide and soil properties
- Elovich and IPD models suggest that pesticide retention occurs rapidly in the initial stage, especially for the most hydrophobic FEN. Slow diffusion into the soil macropores and micropores was more pronounced for THC
- A different behaviour was observed for DIM adsorption on the clayey RM1 soil
- The use of different models sheds more light on the mechanisms governing the adsorption of organic contaminants on soils

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