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Alkaline hydrolysis of vinclozolin: Effect of humic acids aggregates in water

J. Morales[a,*], A. Cid[b], J.C. Mejuto[a]

[a] Department of Physical Chemistry, Faculty of Sciences, University of Vigo, 32004 Ourense, Spain
[b] Chemistry Department, REQUIMTE-CQFB, Faculty of Science and Technology, New University of Lisbon, 2829-51-6 Monte da Caparica, Portugal

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ABSTRACT

The influence of natural organic substances as humate colloidal aggregates in water solutions upon the chemical stability of vinclozolin has been investigated in basic media. A large inhibition (9 times-fold) has been observed and it has been rationalized in terms of a micellar pseudophase model. The observed behaviour could increase significantly the half-life of this fungicide. Moreover, these experimental results have been compared with the corresponding ones of other substances in these natural colloidal aggregates.

1. Introduction

Vinclozolin (V) is a dicarboxamide non-systemic pesticide (Scheme 1) used to control fungal diseases, blights, rots and moulds in vineyards (grapes), fruits (strawberries, raspberries and kiwi), vegetables (snap beans, lettuce and onions) or different types of ornamentals [1–5]. It may also be used on turf grass for golf courses [6]. Being highly effective against common fungi caused by *Botrytis* spp., *Sclerotinia* spp. or *Monilinia* spp. [7–9]. It is well known that this fungicide is moderately persistent in soil [10] and it is only partially broken down by soil microorganisms [11–13]. Vinclozolin may degrade [14] to 3′,5′-dichloro-2-hydroxy-2-methylbut-3-enanilide (see Scheme 1A) or 2-[(3,5-dichlorophenyl)-carbamoyl]oxy-2-methyl-3-butenoic acid (see Scheme 1B). Both reactions will continue to degrade to a third degradation product, 3,5-dichloroaniline (see Scheme 1C). In water, it can be degraded by photolysis and/or hydrolysis processes, which are favoured under neutral or basic conditions [15]. The acute median lethal dose (LD_{50}) for V is greater than 15,000 mg kg^{-1} in rats [10].

Humic substances, and more specifically humate colloidal aggregates (HCAs), represent a large portion of organic matter in natural environments and soils [16,17]. In fact, these organic colloids include highly decomposed organic matter generally more known as humus. Their nature as colloids and their behaviour in solution is quite similar to the micellar aggregates [18–20]. Their ability to absorb or adsorb different types of pollutants, both organic and inorganic, made reconsider the use of these substances from a chemical point of view, since traditionally they were considered carriers. The adsorption properties and the respective compartmentalization of different substrates by humic substances cause changes in the chemical reactivity when a reaction occurs in the presence of these kind of colloidal aggregates [21]. Therefore, to understand the role that humate aggregates currently have in environmental processes, it requires the knowledge of their role from a chemical kinetic view [22] because they can act as solvents, and toxic reagents scavengers or natural catalysers. Furthermore, it has been considered that the primary route of elimination of organic xenobiotics such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides or other substances is related to the microorganism activity found in soil, neglecting the essential importance of humus. However, the properties of these humate aggregates and their catalytic capacity can be assumed the need to consider other means of disposal [23–29].

New insights in the V reactivity, which is widely used in agriculture, on the basis of a pseudophase model, were carried out because the major composition of the organic matter in soils is HCAs [30] and, moreover these compounds are also present in some conditions in the natural waters [31]. Thus, the aim of the present work

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* Corresponding author. Tel.: +34 988 387031; fax: +34 988 387001.
E-mail addresses: morales@uvigo.es (J. Morales), acids@uvigo.es (A. Cid), xmejuto@uvigo.es (J.C. Mejuto).

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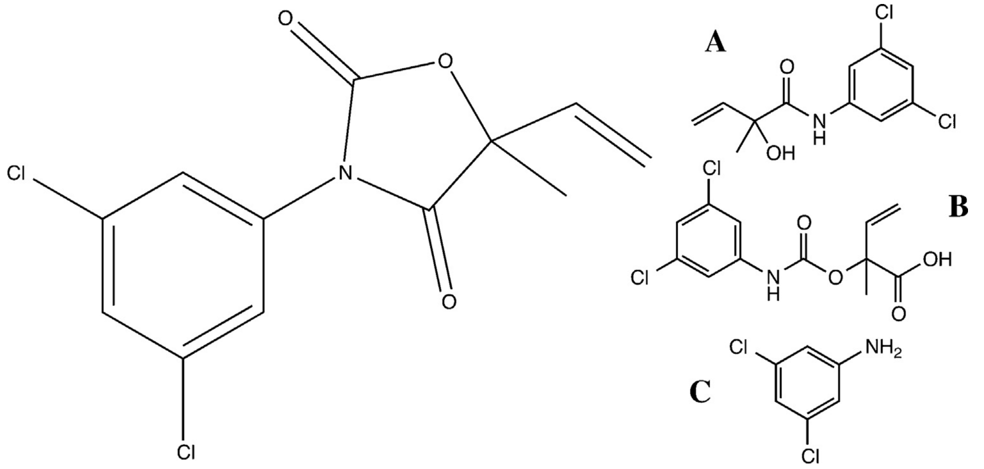

Scheme 1. Structural formula of vinclozolin and its three principal degradation products (A–C).

is to analyse the effect of HCAs "like-micelles" aggregates upon the V stability in order to evaluate if the presence of large amount of organic matter could modify the efficiency of V hydrolysis decomposition pathway.

2. Materials and methods

All reagents used in the present investigation were of the maximum commercially available purity, and none required further purification. HCAs used in this study were isolated from soil using the method described elsewhere [32]. 3-(3,5-Dichlorophenyl)-5-methyl-5-vinyloxazolidine-2,4-dione, better known as vinclozolin, was obtained from Sigma–Aldrich (Steinheim, Germany). Sodium hydroxide and acetonitrile were Panreac reagent (Barcelona, Spain). All aqueous solutions were prepared by weight using double-distilled water.

The kinetic tests were conducted under pseudo first-order conditions ($[V] \ll [OH^-]$). Reactions were monitored through the first-order basic hydrolysis of vinclozolin using a Varian Cary 50 Bio spectrophotometer with the observation cell thermostated at $(25.0 \pm 0.1)\,^\circ$C. When it was necessary, a rapid mixing stopped-flow unit supplied by Applied Photophysics was used. These spectra were carried out between 200 and 800 nm, and because HCAs absorb in the UV–vis region, the spectrum of HCAs in absence of reaction was used as blank. In each instance, it was observed that the final spectrum of the products of the reaction coincided with one obtained in pure water, guaranteeing that the presence of HCAs micelles would not alter the product of the reaction studied.

The basic hydrolysis of vinclozolin was monitored spectrophotometrically measuring the disappearance of the absorbance at its maximum wavelength, more specifically at 242 nm. As an example, Fig. 1 shows the increase in absorption caused by the V decomposition along in time in HCAs. Finally, nonlinear regressions were carried out using a commercial package called pro Fit 6.2 supplied by QuantumSoft in order to obtain the kinetic coefficients. The rate equation to measure the V disappearance is the following:

$$-\frac{d[V]}{dt} = k_W[V_t][OH_t^-] = k_{obs}[V_t] \qquad (1)$$

where [V] is the concentration of vinclozolin pesticide and k_W and k_{obs} are the bimolecular rate and the pseudo-first rate constants, respectively, for the basic hydrolysis of vinclozolin.

Integrating Eq. (1) and expressing the concentration in terms of absorbance, Eq. (2) can be obtained being A_t, A_0 and A_∞ the absorbance at times zero, t, and infinity, respectively.

$$A_t = A_0 \exp(-k_{obs}t) + A_\infty(1 - \exp(-k_{obs}t)) \qquad (2)$$

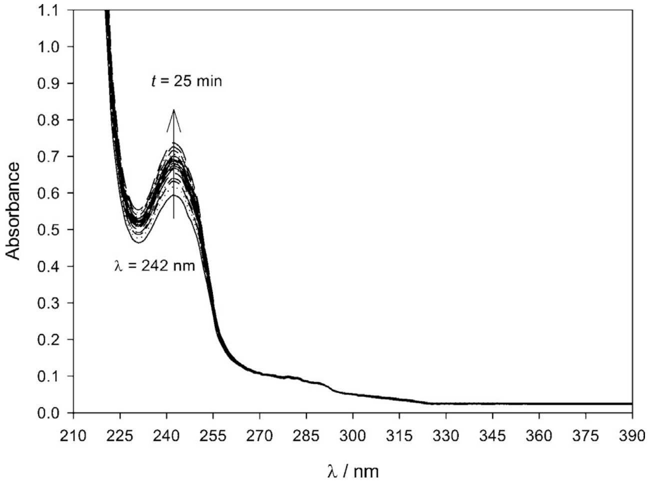

Fig. 1. Spectrograms showing the basic hydrolysis of vinclozolin in humate colloidal aggregates. $[HCAs] = 6.67\ mg\,L^{-1}$; $[V] = 5 \times 10^{-5}$ M; $[OH^-] = 2 \times 10^{-4}$ M; $T = 25\,^\circ$C; $\lambda = 242$ nm.

As an example, in Supplementary information, Fig. S1 shows a typical kinetic run for the basic hydrolysis of vinclozolin as well as the fitting of the experimental data to Eq. (2). Thus, k_{obs} values can be calculated. Fig. 2 shows the influence of $[OH^-]$ on k_{obs} in pure water and in HCAs, respectively. As can be observed a linear dependence between the pseudo-first order rate constant and $[OH^-]$ was obtained.

The influence of HCAs upon the basic hydrolysis of vinclozolin has been analysed in the present manuscript. Pseudo-first order conditions (see Supplementary information: Figs. S2 and S3) were kept in all experiments where the V concentration was kept in all of experiments and equal to 5.0×10^{-5} M. This concentration was chosen to optimize the change in absorbance with time during the kinetic process. Sodium hydroxide concentrations were chosen to obtain a suitable half-life time to monitor the reaction. HCAs concentration was varied between 0 and $0.08\ g\,L^{-1}$.

3. Results

Recent studies in our research group [33–36] showed that the presence of micellar aggregates could significantly modify the kinetic processes of some pesticide degradations used in agriculture.