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Stability study of Iprodione in alkaline media in the presence of humic acids

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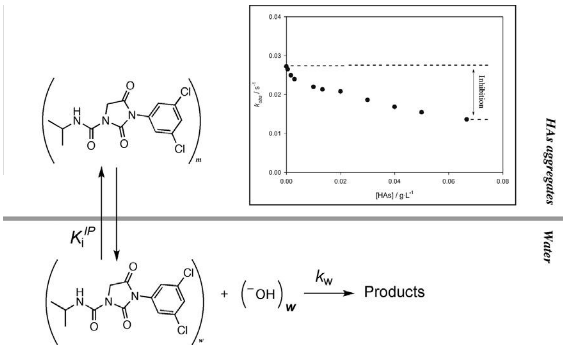
HIGHLIGHTS

- Influence of humic acids on the stability of Iprodione was investigated.
- The catalytic activity of these natural colloidal aggregates in mentioned reaction was studied.
- Inhibitory effects for this pesticide were observed in the presence of these humic substances.
- These behaviors were rationalized in terms of the micellar pseudophase model.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of humic aggregates in water solution upon the chemical stability of Iprodione has been investigated under basic conditions. Taking into account that an important part of soils are colloids, the possibility of its presence implies that soil composition and its structure will play an important role in the stability of this pesticide. A kinetic model was applied to this system and the kinetic coefficients were obtained. An inhibition upon the alkaline hydrolysis of Iprodione (2-fold) was observed and it was rationalized in terms of the micellar pseudophase model. These results have been compared with the corresponding ones in the same natural colloidal aggregates in the presence of other pesticides.

1. Introduction

The behavior of humic substances (HSs) in solution presents certain similarities with other colloidal aggregates (Guetzloff and Rice, 1994; Conte and Piccolo, 1999a). This similarity in physical properties suggests that the organic material is dissolved in natural waters and could be a chemical nanoreactor (Anderson et al., 1995; Conte and Piccolo, 1999b; Vogel et al., 1999). The ability to concentrate and compartmentalize nanoreactors reagents and their specific properties of polarity or microviscosity can play an

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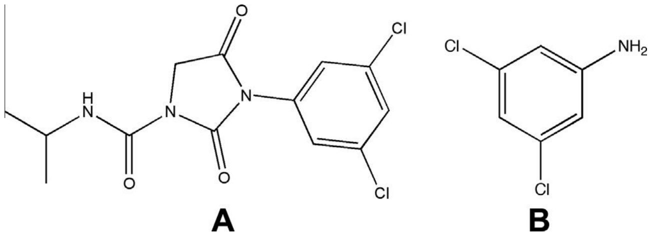
important role in various chemical processes which occur in the environment and provide a natural route of elimination of xenobiotic organic substrates environmental interest, such as pesticides whose degradation has been demonstrated the effect of the presence of different colloidal aggregates (Arias et al., 2005; Astray et al., 2011a; Morales et al., 2012a) or in supramolecular systems (Morales et al., 2012b) in previous studies and therefore the goal of this research.

It is well known that humic substances represent a large portion of organic matter in natural environments and soils (Kinniburgh et al., 1996). In fact, this group represent more than 85% of the total pool of soil organic matter (Foth and Turk, 1972). These compounds are anionic polyelectrolytes with a molecular weight between 2 and 400 kDa (Steelink, 2002). These humic substances are able to form complexes with organic and inorganic substrates (Davies et al., 1998; Gu et al., 2011). In solution, these portions of organic matter can form complexes with environmental pollutants like heavy metals or persistent organic xenobiotics (Kungolos et al., 2006; Bednar et al., 2007; Buffle et al., 2007; Liu et al., 2011; Xi et al., 2012). It has been considered that the primary route of elimination of organic xenobiotics such as pesticides, Polychlorinated Biphenyls (PCBs), Polycyclic aromatic hydrocarbons (PAHs) and other substances is related to the microbial activity found in the soil, neglecting the role played by the humic substances, but the properties of humic acids (HAs) and catalytic capacity can be assumed the need to consider other means of disposal (Moza et al., 1995; Yang et al., 2001; Singh et al., 2009).

In the literature, there are some studies reported the influence of humic substances on the hydrolysis (the major transformation pathway for numerous of pesticides or pharmaceuticals in the environment) of agricultural xenobiotics (Kamiya et al., 1992; Lei et al., 2001), other pollutants (Perdue and Wolfe, 1982; Liu et al., 2012) and diverse hydrophobic compounds (Sabadie, 1997; Georgi et al., 2007, 2008) showing a high association for these compounds by the HSs micellar aggregates.

On the other hand, the imidazole fungicide, Iprodione (Scheme 1A), is widely used in agriculture as a contact pesticide with plenty of adverse effects. Its use has been increased in recent years due to the fact it is effective on different crops (fruits, vegetables, ornamental trees, scrubs and on lawns) affected by *Botrytis bunch rot*, *Brown rot*, *Botrytis allii*, *Sclerotinia sclerotiorum*, *Penicillium expansum*, *Monilinia fructigena*, *Rhizoctonia solani*, *Alternaria solani* and other many fungal diseases in plants (Rosenberger and Meyer, 1981; Osorio et al., 1994; Stepanovic et al., 2009; Hamada et al., 2011; Angioni et al., 2012). It inhibits the germination of the fungal spores and consequently it blocks the growth of the fungal mycelium.

It is highly toxic to crustaceans, moderately toxic to fish and slightly toxic to birds, but not toxic to bees or plants. It inhibits the protein kinase interfering with the intracellular signals that control many cellular functions. Since this pesticide is moderately persistent in soil with a half-life time of 7–60 d depending on the environmental conditions (Carmona et al., 2001). In plants, it is quickly degraded once adsorbed by the roots with the formation of 3,5-dichloroaniline (Scheme 1B) as the main metabolite (Athiel et al., 1995; Lindh et al., 2007). This metabolite generated is highly nephrotoxic (Lo et al., 1990) and carcinogenic. In water, it decomposes quicker under aerobic conditions than anaerobic. Here we were prompted this issue, analyzing experimental observed rate constants in terms of kinetic models. This model allows us to obtain the kinetic coefficients of the catalytic process.



Scheme 1. Chemical structure of the main metabolite (B) from the degradation of Iprodione (A).

The kinetic coefficients were obtained in order to determine and model the kinetic behavior in colloidal suspensions. These experiments also carried out because the major part of the organic matter present in soils is humic substances, and also because they are present in some conditions in the natural waters. The aim of this work is to analyze the effect of humic acids, one of these humic substances, "like-micelles" aggregates upon the stability of Iprodione (IP) to evaluate if the presence of large amount of organic matter can modify the efficiency of hydrolysis IP decomposition pathway.

2. Materials and methods

2.1. Reagents

All reagents were of the maximum commercially available purity and none required further purification. 3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide (Iprodione) was obtained from Sigma–Aldrich (Steinheim, Germany). Sodium hydroxide and acetonitrile were Panreac reagents (Barcelona, Spain). All aqueous solutions were prepared by weight using double-distilled water. HAs used in the present study were isolated from soil using the method described elsewhere (Methods of Soil Analysis, 1999). The composition of these HAs used was determined by CNH elemental analysis using a Fisons EA-1108 elemental analyzer.

2.2. Kinetic measurements and data analysis

Reactions were monitored through the first-order basic hydrolysis of IP using a Varian Cary 50 Bio spectrophotometer with the observation cell thermostated at 25.0 ± 0.1 °C. All kinetic tests were conducted under pseudo first-order conditions ($[\mathrm{IP}] \ll [\mathrm{OH}^-]$). In each instance, it was observed that the final spectrum of the product of the reaction coincided with one obtained in pure water, guaranteeing that the presence of HSs micelles would not alter the product of the reaction.

To monitor the alkaline hydrolysis, the reactions were measured at 248 nm and because HAs absorb in the UV–vis region, the spectrum of HAs in absence of reaction was used as blank. As an example, Fig. 1 shows the increase in absorption caused by the decomposition of IP and the products formation along in time in humic substances aggregates. Nonlinear regression was carried out using a commercial package Profit 6.2 supplied by QuantumSoft.

The rate equation to measure the disappearance of IP is the following:

$$v = -\frac{d[\mathrm{IP}]}{dt} = k_w[\mathrm{IP}]_t[\mathrm{OH}^-]_t = k_{\mathrm{obs}}[\mathrm{IP}]_t = k_{\mathrm{obs}}([\mathrm{IP}]_0 - [\mathrm{products}]) \quad (1)$$

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

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.

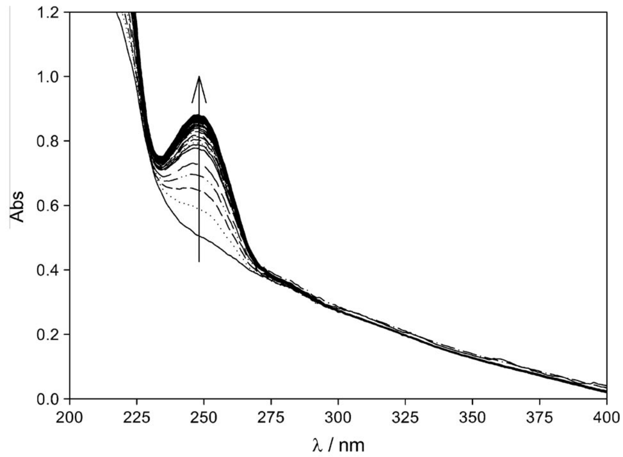


Fig. 1. Spectrograms showing the basic hydrolysis of Iprodione in HSs colloidal aggregates. [HAs] = 0.02 g L^{-1}; [IP] = 5 × 10^{-5} M; [OH^-] = 4.2 × 10^{-4} M; T = 25 °C; λ = 248 nm.

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

As an example, in Supplementary Information, Fig. S1 shows a typical kinetic run for the basic hydrolysis of IP in the presence of HAs as well as the fitting of the experimental data to Eq. (2) and therefore, k_{obs} values can be calculated.

Fig. 2 shows the influence of [OH^-] on k_{obs} in water pure and in HAs concentration respectively. As can be observed a linear dependence between the pseudo-first order rate constant and [OH^-] was obtained. The intercept in these linear regressions is due to the consumption of hydroxyl ions by the humic acids. To minimize the possible consumption of NaOH by the humic substances, for each concentration of humic acid the influence of NaOH concentration on the basic hydrolysis of IP was investigated to obtain the apparent rate constant (k_{app}).

3. Results and discussion

The basic hydrolysis of IP has been analyzed in the presence of HSs micellar aggregates. Pseudo-first order conditions were kept in all experiments where IP concentration was kept in all of experiments and equal to 5.0 × 10^{-5} M, and sodium hydroxide concentration was varied between 0 and 3.33 × 10^{-3} M, respectively. IP concentration was chosen to optimize the change in absorbance with time during the kinetic process. NaOH concentrations were chosen to obtain a suitable half-life time to monitor the reaction. HAs concentration was varied between 0 and 67 mg L^{-1}.

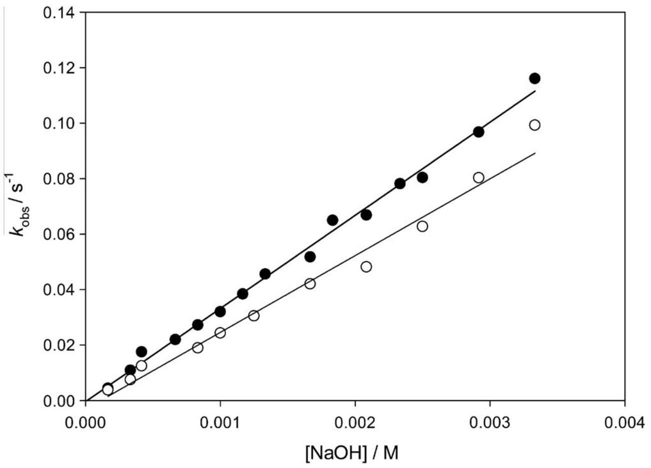


Fig. 2. Influence of the pseudo-first order rate constant, k_{obs}, on the basic hydrolysis of Iprodione in water pure (●) and in the presence of HAs (○). [HAs] = 0.013 g L^{-1}; [IP] = 5 × 10^{-5} M; T = 25 °C; λ = 248 nm.

An inhibition, 2-fold, was found in the IP degradation representing an increase of half-life time of this xenobiotic. This inhibition is due to the association of the humic substances to the IP. Taking into account that the HAs in water solution are micelle-like aggregates, these kinetic results have been rationalized in terms of micellar pseudophase model (Astray et al., 2011b,c).

In HAs dispersions the loci of a reaction could be located inside the HAs aggregate or in the bulk solvent. The nature of our HAs aggregates, like the interior of a micelle, formed by the hydrophobic portion of these humic acids is not fully well understood. The center of the HAs aggregates would be similar to liquid hydrocarbons, and then the water could penetrate the aggregates. Being this part of the hydrocarbon chains of HAs from the hydrophilic groups exposed to the water (Astray et al., 2010). So, the fact that a clear inhibition was observed increasing HAs concentration could involve that: (i) The hydrolysis rate in the dispersed phase is significantly slower than in the continuous phase (water). This decrease in the reactivity of the system must compensate a possible "concentration effect" of the reactants in the dispersed phase. (ii) The hydrolysis of IP is completely inhibited by the OH^- exclusion from the surface of the aggregate. The first point, the most likely, since knowing that the surface charge of HSs is negative, so simple electrostatic considerations allow us to postulate that the role played by the dispersed phase is to compartmentalize the reagents preventing the contact between IP and OH^-. This second point shown in the Scheme 2 would justify the kinetic results obtained. A third possibility would be given by the fact that the negatively charged groups on the surface of the dispersed phase (i.e.: phenolates among others) may act as nucleophiles on IP, having a new reaction pathway. However there is no kinetic evidence that involves this third way.

Hence, taking into account all these considerations, Scheme 2 shows the mechanism of the basic hydrolysis reaction of IP in terms of the two-pseudophase model formed by HAs micellar aggregates and water. K_i^{IP} and K_i^{OH} are the inclusion constants between micellar and water phases for the IP and hydroxyl ions, respectively, and k_m and k_w the basic hydrolysis rate constants in the micellar phase and water phase. Due to the electrostatic considerations the hydroxyl ions concentration in the micellar pseudophase must be very low owing to the anionic character of the micellar head group and therefore the reaction rate contribution of micellar reaction pathway is negligible. According to this pseudophase model, where $[IP]_{total} = [IP]_w + [IP]_m$, and $K_i^{IP} = [IP]_m/([IP]_w[HAs])$ and $[OH^-]_{total} = [OH^-]_w + [OH^-]_m \approx [OH^-]_w$, the following rate equation can be obtained:

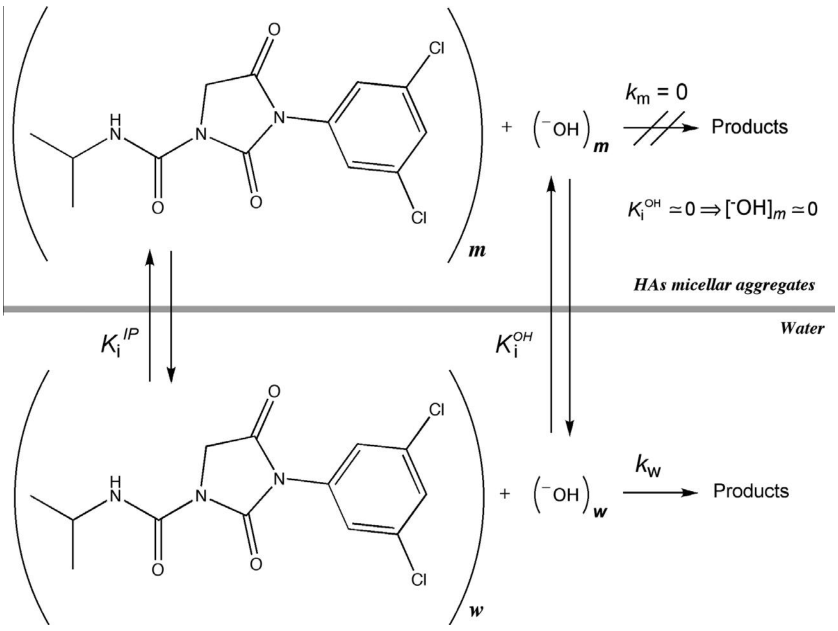
$$\begin{aligned} v &= -\frac{d[IP]}{dt} = k_w[IP]_w[OH^-]_w + k_m[IP]_m[OH^-]_m \\ &= k_w[IP]_w[OH^-]_{total} = \frac{k_w[OH^-]_{total}}{1 + K_i^{IP}[HAs]}[IP]_{total} \end{aligned} \tag{3}$$

Comparing Eq. (3) with Eq. (1) k_{obs} can be deduced as Eq. (4):

$$k_{obs} = \frac{k_w[OH^-]_{total}}{1 + K_i^{IP}[HAs]} = k_{app}[OH^-]_{total} \tag{4}$$

where k_{app} is the apparent rate constant obtained from fitting the experimental data.

As we can see in Supplementary Fig. 2 and Table 1, the value of the pseudo-first order rate constant (k_{obs}) and the apparent bimolecular rate constant (k_{app}) respectively, decrease on increasing the



Scheme 2. Pseudophase model upon the basic hydrolysis of Iprodione in humic aggregates.

Table 1
Influence of [HAs] upon the apparent bimolecular rate constant for the basic hydrolysis of Iprodione in the presence of humic acids. [IP] = 5 × 10^{-5} M; [OH^-] = 8.33 × 10^{-4} M; T = 25 °C; λ = 248 nm.

10^3 [HAs]/g L^{-1}	k_{app}/M^{-1} s^{-1}
0	32.61
0.50	31.75
1.67	29.90
3.00	28.73
10.00	26.34
13.34	25.54
20.00	24.94
30.00	22.32
40.00	20.18
50.00	18.50
66.67	16.30

HAs concentration. Hence, the presence of these HSs inhibits the basic hydrolysis of IP.

$$\frac{k_w}{k_{app}} = 1 + K_i^{IP}[\mathrm{HAs}] \qquad (5)$$

Moreover, the values of the inclusion constants for IP as well as the rate constants in pure water (k_2) were obtained by a non-linear fitting of Eq. (5) to the experimental results and are shown in the Table 2.

In order to determine the activation parameters of the system, we have evaluated the influence of the temperature on the rate constant in the basic hydrolysis of IP. For these experimental serials, it was carried out keeping the sodium hydroxide and IP concentration, respectively equal to [OH^-] = 5.00 × 10^{-4} M and [IP] = 8.33 × 10^{-5} M, and varying the temperature between T = 15 °C and T = 30 °C. These experimental data have been fitted to the Arrhenius equation, Eq. (6). The settings of the experimental data to these equations have been satisfactory (R > 0.99).

$$k = A \cdot e^{-\frac{E_a}{RT}} \qquad (6)$$

The Eq. (6) can be readily linearized which were adjusted experimental data. Thus, a value of 68.40 kJ mol^{-1} was found for the activation energy. Table 3 shows the values of the rate constants obtained for each temperature tested.

So as to confirm the pseudophase model in these microheterogeneous media, the apparent rate constants were theoretically calculated for the IP. Fig. 3 shows the good correlation between the experimental results with those calculated from Eq. (4). These results help us to understand the role of organic matter in soils upon the stability and persistence of the pesticide investigated in this work.

As quote above, these kinetic results imply a large increase of IP half-life time, due to the effect of the total inhibition inside the HSs aggregates. As we can see, the pseudophase model predicts satisfactorily the kinetic behavior of this xenobiotic in humic aggregates. This model represents a useful tool for a quantitative analysis of these kinetic measurements.

As can be observed in Table 2, the inclusion constant of IP calculated in humic acids is relatively higher than other reactions studied by us in other pesticides (Morales et al., 2012c), and

Table 2
Inclusion constants and second order rate constants for the basic hydrolysis of Iprodione and other pesticides in HSs colloidal aggregates. K_i^P is equivalent to K_i^{CF}, K_i^{3KCF}, K_i^{3HCF} and K_i^{IP} for the respective pesticides.

Pesticide	Effect	K_i^P (L g^{-1})	k_w (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})
Carbofuran	No effect	–	1.10 ± 0.10	1.16
3-keto-Carbofuran	Inhibition	5 ± 1	190 ± 10	210
3-Hydroxy-carbofuran	Inhibition	10 ± 1	3.10 ± 0.10	2.80
Iprodione	Inhibition	14 ± 1	31.30 ± 0.10	33.6

Table 3
Values of the activation parameters at different temperatures according to the Arrhenius equation in basic media. [IP] = 8.33 × 10^{-5} M; [OH^-] = 5.00 × 10^{-4} M; λ = 248 nm.

T/°C	k/s^{-1} M^{-1}	T^{-1}/k^{-1}	ln$k$
15	7.80 × 10^{-3}	3.47 × 10^{-3}	−4.854
20	1.04 × 10^{-2}	3.41 × 10^{-3}	−4.566
25	1.65 × 10^{-2}	3.35 × 10^{-3}	−4.104
30	3.23 × 10^{-2}	3.30 × 10^{-3}	−3.433

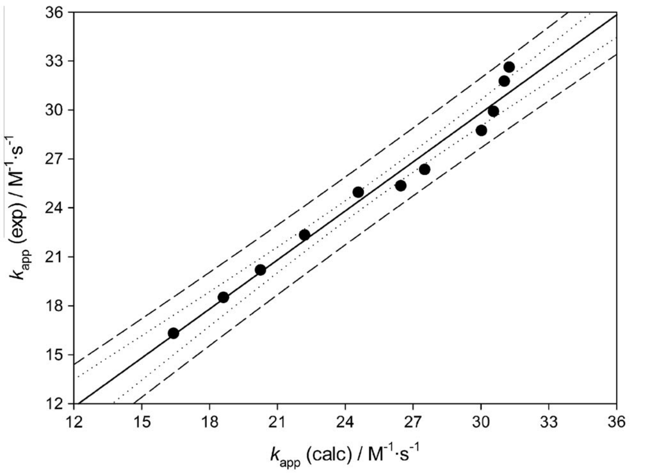


Fig. 3. Experimental rate constant, k_{app} (exp), and calculated rate constant, k_{app} (calc), for the basic hydrolysis of Iprodione in the presence of humic substances colloidal aggregates. Dotted and short dashed lines represent the 95% confidence band and the 95% prediction band, respectively.

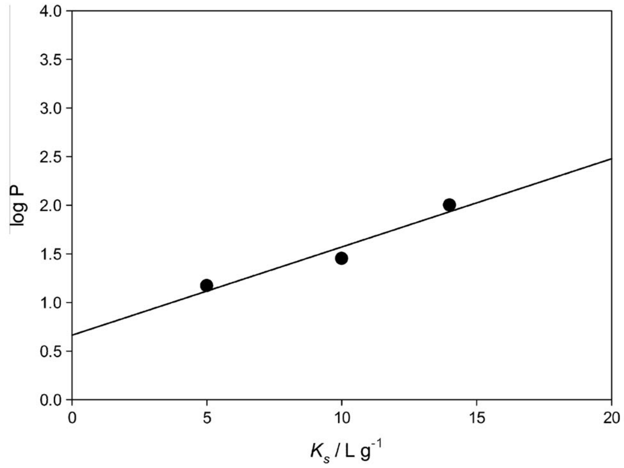


Fig. 4. Inclusion constants for different pesticides in HSs aggregates as a function of log P coefficient.

probably could be explained in terms of hydrogen bonding of IP with the phenolate and carboxylate groups in the interface of the HSs micellar aggregates. Finally, according to the results observed in Fig. 4 and comparing these experimental data we could affirm that hydrophobicity of the HAs core is the main force of interaction between these natural colloidal aggregates and the pesticide studied.

4. Conclusions

Natural colloidal aggregates were used to provide new insights in the reactivity of pesticides IP, which is widely used as fungicide in agriculture, on the basis of a pseudophase model. Due to the toxicology and high stability of this compounds in soils, finding of new catalytic elimination pathways, is an important issue. HAs are colloid dispersions in water, and their influence on chemical reactivity can be rationalized considering that this humic substance type are micelle-like colloids. In this way, it should be noted that their presence of in restricted media implies an inhibition of the basic hydrolysis of IP (2-fold) in the presence of humic acids. This inhibition also represents an increase of half-life time of IP of approximately 100%.

Finally this behavior has been compared with the corresponding one in the same natural colloidal aggregates in the presence of other substances with different behavior according electrostatic and hydrophilic/hydrophobic considerations. As quote above, the binding constant of IP calculated in these humic substances is relatively higher than other pesticides studied previously in our research group. Differences in inhibition behavior between the carbofuran family of pesticides and Iprodione would be attributed to their differences in hydrophobicity and, hence, differences in their penetrability inside HAs aggregate core. This fact is definitely probed attending the linear relationship observed between binding constant of different xenobiotics and their hydrophobicity measured in terms of logP value.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.04.020.

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