Prometrine – Humic Acids Interactions Studied at a Water/1,2-Dichloroethane Interface

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Received: June 13, 2009
Accepted: September 29, 2009

Abstract

The interaction of the herbicide prometrine (PROM) with humic acids (HA) in water was analyzed at a pH range between 2.00 to 10.00. For this purpose the transfer current of protons facilitated by PROM across a water/1,2-dichloroethane interface was employed to quantify PROM concentration in absence or in presence of HA. When humic acids were added in increasing amounts to the solution containing PROM, a gradual decrease in current values was observed, evidencing the retention of PROM by HA. This effect was more important at high pH values. From the results it is concluded that the adsorption of PROM is dependent on the pH and HA concentration. At high pH values the herbicide is strongly retained by HA, revealing a strong interaction probably due to the possibility of PROM (neutral species) to access to hydrophobic regions of AH, where van der Waals interactions prevail. The amount of PROM bounded to HA was calculated by subtracting peak current values in presence and in absence of HA and the adsorption isotherm was plotted. The concave or S type curves obtained, indicative of a process with high resistance to adsorption at low concentrations, was fitted with Freundlich isotherm.

Keywords: Liquid/liquid interfaces, Triazines, Humic acids, Herbicides adsorption, Prometrine, Interfaces

DOI: 10.1002/elan.200900302

1. Introduction

Herbicides are applied as pre- and post-emergent weed control agents to improve crop yields. S-triazines (1,3,5-triazines) are an important group of herbicides which are able to incorporate into weed and inhibit photosynthesis enzymes.

The use of agricultural chemicals requires knowledge of their stability and transformation in the environment as well as their influence on micro-organisms. Triazine herbicides are stable in the soil for 3 – 12 months and they, as well as some of their degradation products, are used by water and soil microbes as a source of energy (alkyl fragments) and nitrogen (amine fragments) [1]. In the last years, the environmental pollution by pesticides has become in a serious problem especially in marine ecosystem. Due to their heavy use in agriculture and to their persistence, many of the compounds are present in surface and ground waters, and have to be considered a potential risk for marine life as well as for drinking water quality [2]. Environmental Protection Agency (EPA) has included triazines and their degradation products as a group of the Contaminant Candidate List (CCL). For this reason, in many countries of Europe and North America the permitted level of these pesticides in water is very low (in order of 0.1 $\mu g\ L^{-1}$).

Development of new sensitive and selective analytical techniques for the determination of s-triazine herbicides and their metabolites in the environment as well as the recognition of their interactions with different elements, especially with heavy metals cations or organic molecules present in soils, are important problems in modern s-triazine chemistry. The study of complex formation or adsorption behavior between herbicides and organic molecules, as humic acids (HA) contained in soils, is an important topic because it determines pesticide mobility, bioavailability and effectiveness. Under environmental conditions, s-triazines are usually degraded to compounds with better water solubility. Indeed, the most important physicochemical properties of these pesticides and their degradations products are the solubility in water and the capacity to be retained by the organic matter of the soil [3, 4].

Humic acids are macromolecules with a relative weight higher than 30000 Da and a chemical structure consisting in aromatic rings bonded, with large alkyl groups (Fig. 1a) and possessing carboxylic and other functional groups such as phenol, alcohol, carbonyl, ether, ester, amide and amine. These species behave as negatively charged polyelectrolyte in aqueous solution at pH values higher than pKa or as hydrophobic molecules in the uncharged form, in acidic medium [5 – 7].

Humic acids are widely distributed in soils and, under natural conditions, they have been found as colloid suspension in water forming a large part of the dissolved carbon. Organic pollutants, such as pesticides, can exist in dissolved

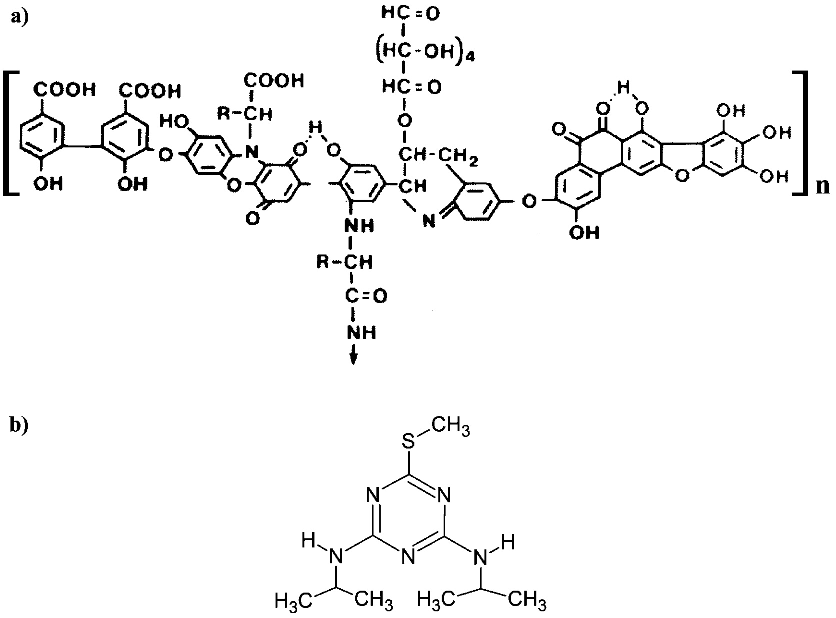


Fig. 1. Chemical structures of: a) Humic acids (HA), b) Prometrine (PROM).

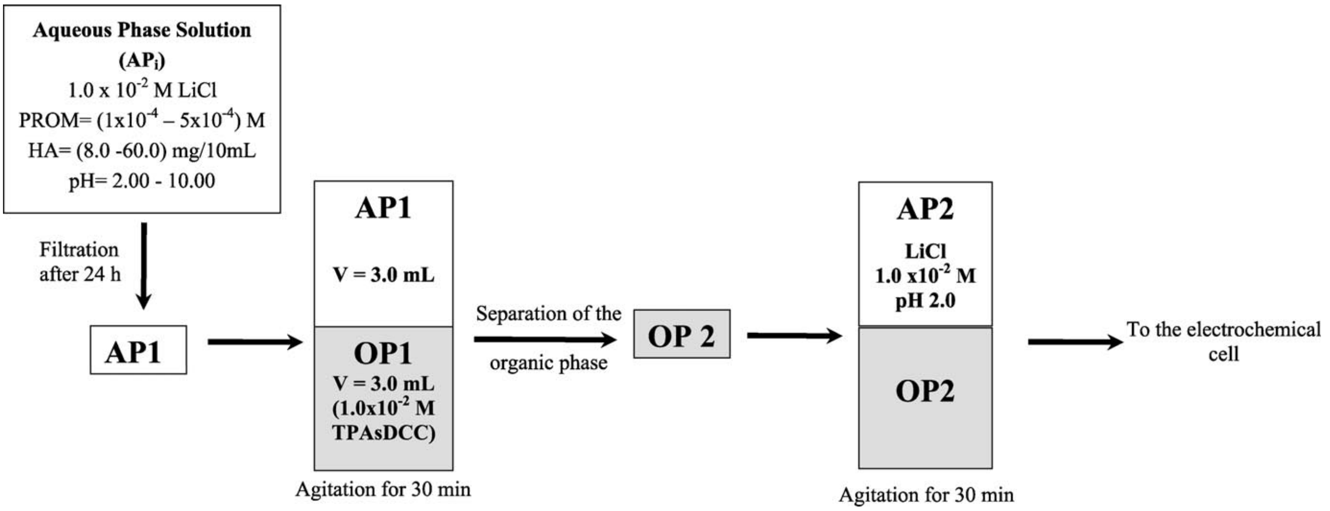
state or in association with the colloidal phase, or adsorbed by the soil. The driving forces of this adsorption involve electrostatic interactions, hydrogen bond, charge transfer, acceptor–donor mechanisms, van der Waals forces and hydrophobic interactions [8]. These mechanisms operate simultaneously and their competition determines the retention of pesticides in soil and aquatic systems. Adsorption of the pollutant is strongly influenced by the properties of the solute and the composition of soil organic matter. For this reason, the characteristics of soils affect the herbicide adsorption, transport and degradation processes and, in consequence, the fate of herbicides in the environment. The knowledge of the interactions between herbicides and humic acids are relevant not only as an approach to the study of herbicides behavior in the environment but also in the aspects regarding to their quantification especially in the sampling and processing of soil and water.

Voltammetry at liquid/liquid interfaces has proven to be a valuable tool to elucidate complexes formation, and to obtain thermodynamic and kinetic data of ion transfer [9–23].

In a previous paper [24], the transfer of three s-triazine herbicides, atrazine, propazine and prometrine, across the water/1,2-dichloroethane interface was investigated using cyclic voltammetry. A facilitated proton transfer mechanism from the aqueous to organic phase was demonstrated by the analysis of positive peak potential and peak current as a function of pH. It was shown that the determination of 2.5×10^{-5} M – 5.0×10^{-4} M concentration of herbicides in aqueous phase is possible under the experimental conditions employed. Moreover, to improve the detection limit for the quantification of prometrine (PROM, Figure 1b), a combined procedure consisting in a previous preconcentration stage, followed by SWV at a water/1, 2-dichloroethane interface was carried out [25]. The preconcentration of the analyte in the organic phase was possible due to its high solubility and partition coefficient ($\log P = 3.34$) in this solvent. On another hand, with the purpose of contributing to the knowledge of the interaction between PROM and inorganic components of soils, we have studied the complex formation of Al(III) cation with the herbicide PROM at the water/1,2-dichloroethane interface [26].

Several authors have studied and characterized the interaction between humic acids and cations present in soils, employing electrochemical systems [27–30]. Moreover, the anion binding to other polyions, such as protamine, has been studied by cyclic voltammetry at a polarized liquid–liquid interface [31], showing evidences of the formation of an ion pair, between protamine and the organic anion, at the aqueous side of the interface. The results were explained using the Frumkin isotherm, while the conductivity of the aqueous solutions could be interpreted with the Manning–Oosawa counterions condensation approach.

The aim of the present paper is to apply cyclic voltammetry at a 1,2-dichloroethane interface to study the interaction between PROM and humic acids, analyzing the effect of pH. The analysis is based on the changes produced by the presence of humic acids on the voltammetric current corresponding to proton transfer facilitated by PROM. As mentioned above, the carboxylic groups present in the HA molecule can dissociate to generate negatively charged species with apparent pKa values between 3.54 and 5.30. On the other hand, the amide and amine groups can undergo protonation reactions leading to positively charged molecules. The dissociation degree of these groups, at a given pH value, determines the surface charge of humic acids. In the same way, pH values determine the ionization of herbicides with acidic–basic properties as triazines [32]. Previous studies demonstrated that the main driving force involved in the interaction between triazines



Scheme 1. Experimental procedure employed to quantify PROM not bounded to HA.

and humic or fulvic acids, at low pH values, is hydrogen bond [5, 7], while hydrophobic interaction prevails in basic medium.

2. Experimental

The voltammetric experiments were performed in a four–electrode system using a conventional glass cell of 0.18 cm^2 interfacial area. Two platinum wires were used as counter-electrodes and the reference electrodes were Ag/AgCl. The reference electrode in contact with the organic solution was immersed in an aqueous solution of 1.0×10^{-2} M tetraphenyl arsonium chloride (TPAsCl) (Sigma).

The base electrolyte solutions were 1.0×10^{-2} M LiCl (Merck p.a.) in ultrapure water (MilliQ RiOs 16, Millipore) and 1.0×10^{-2} M tetraphenyl arsonium dicarbollyl cobaltate (TPhAsDCC) in 1,2-dichloroethane (DCE, Dorwil p.a.). TPhAsDCC was prepared by metathesis of tetraphenylarsonium chloride (TPhAsCl, Sigma) and cesium dicarbollyl cobaltate (CsDCC, Lachema p.a.). The precipitate was recrystallized from a water: acetone mixture and then dried in an oven at 30 °C for two days.

Prometrine (PROM), from Riedel-de-Haen, was used without further purification while Humic Acid (HA), obtained from Fluka was washed, previous to its use, to remove traces of heavy metals and ash.

PROM, at concentration values within the range $1.0 \times 10^{-4} - 5.0 \times 10^{-4}$ M, and HA, at concentrations 8.0, 10.0, 12.0, 14.0 and 60.0 mg/10.00 mL, were added to the aqueous phase (Initial Aqueous Phase, AP_i). The pH of AP_i was adjusted at the following values: 2.00, 5.50, 6.50, 7.50 and 10.00, by addition of HCl (Merck p.a.) and LiOH (Merck p.a.). In this way, the pH value determines not only the charge of HA but also, the existence of PROM or $HPROM^+$ species in the solution. The charge of both, PROM and HA is one of the main important factors determining the interaction between these species. The aqueous solutions were prepared 24 hours before using them to ensure the complete interaction between PROM and HA under each experimental condition. After this time, the solutions were filtrated, with 0.45 μm Millipore membranes, to separate the solid fraction of AH and aliquots of 3.00 mL of the supernatant liquid (Aqueous Phase 1, AP1) were agitated with 3.00 mL of organic base solution (Organic Phase 1, OP1) during 30 minutes, to favor the partition of free PROM to the organic phase. Finally, the organic phase resulting from agitation (Organic Phase 2, OP2), containing the whole amount of free PROM present in AP1, was separated and put in contact with a fresh aqueous base solution, pH 2.00 (Aqueous Phase 2, AP2). The electrochemical cell was filled with OP2 and AP2 previously equilibrated by agitation. The voltammetric peak currents are proportional to free PROM concentration in OP2, so, they can be used to calculate the concentration of PROM bound to HA in AP1 subtracting the free PROM concentration to the initial value. Scheme 1 summarizes the experimental procedure described above.

Cyclic voltammetry was performed using a four–electrode potentiostat, which automatically eliminates the IR drop by means of a periodic current–interruption technique [33]. A Hi-Teck Instruments waveform–generator and a 10 bit Computer Boards acquisition card connected to a personal computer were also employed.

The potentials values E reported are the applied potentials which include $\Delta^{\circ}_{w}\phi^{\circ}_{TPA+} = -0.364$ V for the transfer of the reference cation, $TPhAs^+$.

3. Results and Discussion

Figure 2 shows the voltammetric response obtained for the system AP2/OP2 when AP_i contained PROM, dissolved at 5.0×10^{-4} M concentration, in absence or presence of 12.0 mg HA/10.00 mL and 14.0 mg HA/10.00 mL at pH 6.50. Voltammogram plotted in solid line corresponds to the first condition (absence of HA) and the transfer process responsible for the current peaks is the electrochemical H^+ transfer facilitated by PROM as it was demonstrated in a previous paper [24]. Due to the high partition coefficient of PROM (log $P = 3.34$), the partition equilibrium favors the access of these molecules to the organic phase where they act as proton carrier according to the following mechanism:

$$\mathrm{PROM_{(w)}} \rightleftharpoons \mathrm{PROM_{(o)}} \tag{1}$$

$$\mathrm{H^+_{(w)}} + \mathrm{PROM_{(o)}} \rightleftharpoons \mathrm{HPROM^+_{(o)}} \tag{2}$$

When HA is present (dotted and dashed lines), no changes in peak potential but a decrease in peak current can be observed. This change becomes more important while HA increases. This is a clear evidence that a fraction of PROM adsorbs at HA according to:

$$\mathrm{PROM_{(w)}} + \mathrm{HA_{(s)}} \rightleftharpoons \mathrm{PROM\text{-}HA_{(ads)}} \tag{3}$$

this adsorbed form of PROM prevails in the initial aqueous phase, associated to HA, and it does not partition to OP2, leading to a decrease in proton transfer current. It is possible to calculate the fraction of PROM adsorbed at HA from the decrease in current values, as follow:

$$I_P^0 - I_P^{HA} = 0.44634\ \mathrm{zFA}(zF\ v\ D^0_{PROM}/RT)^{1/2} \times (c^0_{PROM} - c^{HA}_{PROM}) \tag{4}$$

$$V_{APi}(c^0_{PROM} - c^{HA}_{PROM})\ MW_{PROM} = mg^{ADS}_{PROM} \tag{5}$$

where I_P^0 and I_P^{HA} are the peak currents due to electrochemical H^+ transfer facilitated by PROM in absence and in presence of HA respectively, D^0_{PROM} is the diffusion coefficient of PROM in the organic phase (OP2), c^{HA}_{PROM} and c^0_{PROM} are the equilibrium concentration of free PROM in the organic phase (OP2) when AP_i contained or not HA respectively, V_{AP} is the AP_i total volume (mL) in which the HA and PROM were put in contact, MW_{PROM} is the PROM molar weight, mg^{ADS}_{PROM} is the total mass of PROM retained by the HA, while z, F, A, R and T have the usual meanings.

Taking into account the PROM retention by HA, the effect of changing the pH value in AP_i was analyzed. Figure 3 shows the *i*/*E* profiles obtained for the system AP2/OP2 when AP_i contained 5.0×10^{-4} M PROM, and 14.0 mg HA/10.00 mL at different pH values in the range between 2.00 and 10.00. As it can be noticed, a decrease in peak current values is observed as the pH increases. This behavior is indicating that PROM retention in aqueous phase by the HA is favored at high pH values. Figure 4 summarizes the variation of I_p as a function of the HA concentration and the pH of AP_i. A general decrease in I_p values, and therefore an enhancement in the fraction of PROM associated to HA, is observed as HA concentration increases, in the whole pH range studied. Nevertheless, this decrease is more pronounced at high pH values indicating a stronger interaction between PROM and HA under these conditions. It is important to remark that the fraction of neutral species of PROM (not protonated form) as well as the fraction of negatively charged HA increase with the increase of pH. As mentioned in the introduction, two driving forces have been proposed for the interaction between several *s*-triazines and humic or fulvic acids [5, 7]: at low pH values hydrogen bond interactions predominate, while at high pH values hydrophobic associations are more important. The results shown in figure 4 indicate that the hydrophobic interactions lead to greater retention of the herbicide by HA, compared to hydrogen bond interactions. These hydrophobic interactions lead to the adsorption of the herbicide at HA. The possibility of ion–pair formation is disregarded considering that the herbicide is present as neutral species at high pH values. This behavior can be explained taking into account that the autoaggregation of HA molecules is favored in acidic solutions blocking their binding sites [5]. This aggregation is enhanced in presence of ionic salts (as it is the case of LiCl in the present experimental conditions) [34].

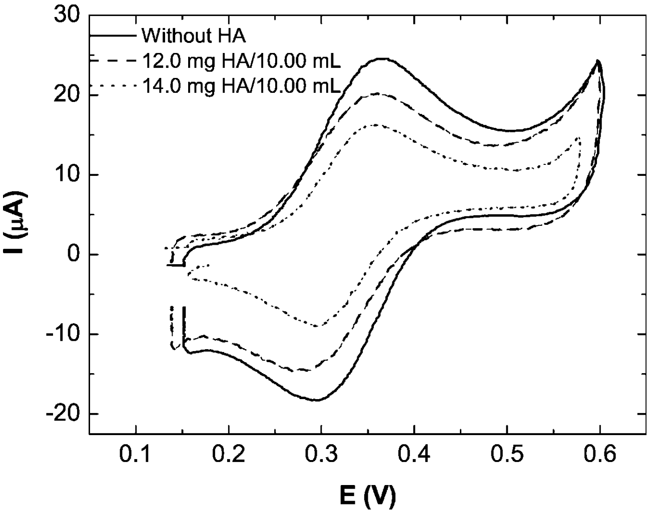


Fig. 2. *i*/*E* profiles corresponding to the system AP2/OP2 (see Scheme 1). AP_i: 1.0×10^{-2} M LiCl + 5.0×10^{-4} M PROM + (—) 0 mg HA, (----) 12.0 mg HA/10.00 mL or (·····) 14.0 mg HA/10.00 mL. pH 6.50. $v = 0.050$ Vs^{-1}.

The behavior above described leads us to study and quantify the adsorption of PROM on HA at pH 10.00. With this aim, the variations in the concentration of free PROM, proportional to current peak, at several PROM and HA concentrations in AP_i were analyzed. The results are shown in Figure 5. As it can be noted within the whole range of PROM concentration analyzed, the peak current decreases with the concentration of HA up to a value of $c_{HA} = 14.0$ mg/10.00 mL, after which there is no change in the current values. This is a clear evidence that the adsorption sites available at this c_{HA} value are enough to achieve the adsorption equilibrium.

The adsorption processes are mainly characterized by adsorption–desorption isotherms, which are graphic representations relating the concentration of the herbicide in solution with the amount adsorbed on the solid phase, according to the equilibrium in Equation 3. One of the

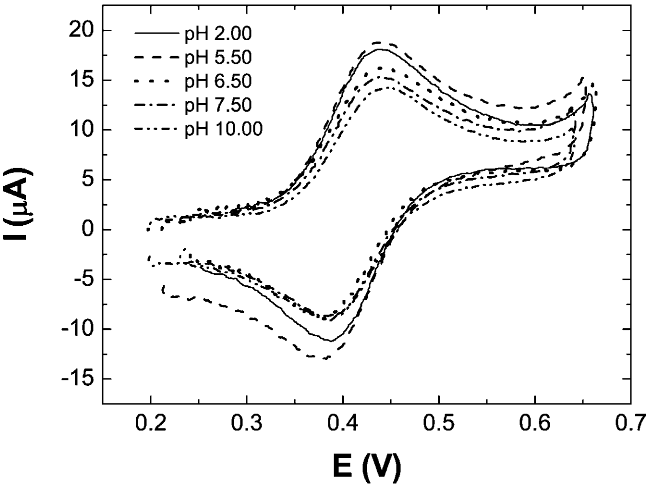


Fig. 3. i/E profiles corresponding to the system AP2/OP2 (see Scheme 1). AP_i: 1.0×10^{-2} M LiCl + 5.0×10^{-4} M PROM + 14.0 mg HA/10.00 mL. pH (—) 2.00, (----) 5.50, (·····) 6.50, (·······) 7.50, (-·····-) 10.00. $v = 0.050$ Vs^{-1}.

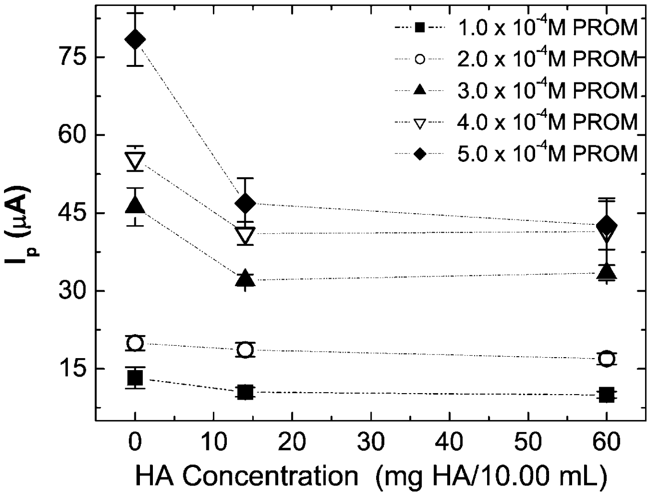


Fig. 5. Plot of I_p values for the system AP2/OP2 (Scheme 1) as a function of HA amount in AP_i for different PROM concentrations at pH 10.00. AP_i: 1.0×10^{-2} M LiCl + x mg HA/10.00 mL + PROM= (■) 1.0×10^{-4} M, (○) 2.0×10^{-4} M, (▲) 3.0×10^{-4} M, (▽) 4.0×10^{-4} M, (◆) 5.0×10^{-4} M. $v = 0.050$ Vs^{-1}.

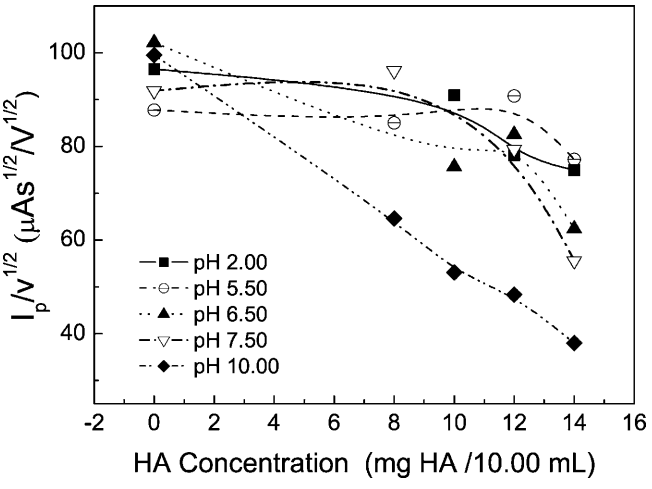


Fig. 4. I_p vs. $v^{1/2}$ variation with HA concentration for different AP_i pH values. AP_i: 1.0×10^{-2} M LiCl + 5.0×10^{-4} M PROM + x mg HA/10.00 mL. pH (■) 2.00, (○) 5.50, (▲) 6.50, (▽) 7.50, (◆) 10.00.

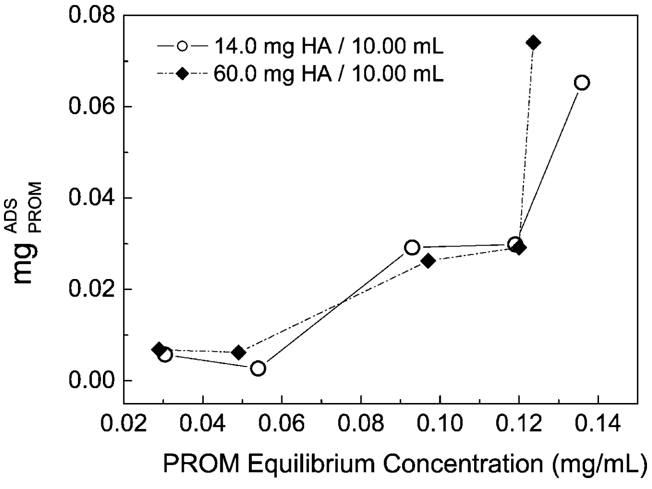


Fig. 6. Adsorption isotherm of PROM for two different HA concentrations. AP_i: 1.0×10^{-2} M LiCl + x M PROM + (○) 14.0 mg HA/10.00 mL or (◆) 60.0 mg HA/10.00 mL, pH 10.00. mg^{ADS}_{PROM} was calculated from Equation 5.

simplest mathematical functions to describe adsorption isotherms is the Freundlich equation [35]:

$$mg^{ADS}_{PROM} = K_f \, (c^{APi}_{PROM})^{1/n} \tag{6}$$

where mg^{ADS}_{PROM} has the same meaning as in the Equation 5, c^{APi}_{PROM} is the concentration of free PROM in AP_i, while K_f and n are empirical parameters representing the adsorption capacity and the affinity of PROM for HA, respectively. When the parameter n is equal to unity, Equation 6 becomes to the Langmuir isotherm and linear relationships are obtained. Figure 6 shows the variation of mg^{ADS}_{PROM}, calculated according Equation 5, with c^{APi}_{PROM} calculated from I_P^{HA}, defined in Equation 4, for two different concentrations of HA. A not linear relation is observed, so the experimental data were fitted with the logarithmic form of Freundlich isotherm:

$$\log mg^{ADS}_{PROM} = \log K_f + \frac{1}{n} \log c^{APi}_{PROM} \tag{7}$$

thus, K_f and n values were obtained from the intercept and the slope of a $\log mg^{ADS}_{PROM}$ vs. $\log c^{APi}_{PROM}$ plot (not shown). These values, as well as regression coefficients are shown in Table 1:

The $1/n$ values higher than 1 are indicatives of concave or S type isotherms which are typical for processes with high resistance to adsorption at low concentrations.

Table 1. K_f, $1/n$ and R values obtained from linear regression of Equation 7.

HA concentration	K_f	$1/n$	R
14 mg/10 mL	1.621	1.802	0.8464
60 mg/10 mL	0.937	1.489	0.9002

4. Conclusions

In the present paper the analysis of the current corresponding to proton transfer facilitated by PROM in absence and in presence of HA allows us to analyze the retention of PROM in aqueous phase, produced by adsorption at HA molecules, and to gain insight into the interactions between adsorbates.

From the results it can be concluded that the adsorption of PROM is dependent on the pH and HA concentration. At high pH values the herbicide is strongly retained by HA, revealing a strong interaction probably due to the possibility of PROM (neutral species) to access to hydrophobic regions of HA, where van der Waals interactions prevail. On the contrary, at low pH values hydrogen bond interactions can take place, nevertheless, these experimental conditions produce the aggregation of HA macromolecules decreasing the possibility of interaction with PROM by blocking of specific union sites. This aggregation can be enhanced by the presence of LiCl in the aqueous phase.

The concave or S type adsorption isotherms obtained are indicative of a process with high resistance to adsorption at low concentrations. The K_f values determined in this paper are similar to those obtained employing other methodologies [35].

The results obtained in this paper contribute to the knowledge of interactions between herbicides and the organic components of soils, which in turn affect the persistence and transport of these pollutants in the environment.

5. Acknowledgements

Financial support from Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET) and Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba (SECyT) is gratefully acknowledged. A. V. Juarez and J. S. Riva wish to thank CONICET for the fellowship awared.

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