



Effect of pH, anions and cations on the dissolution kinetics of humic acid particles

Maximiliano Brigante^{a,*}, Graciela Zanini^{a,b}, Marcelo Avena^a

^a INQUISUR, Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

^b CERZOS (CONICET-UNS), Departamento de Agronomía, Universidad Nacional del Sur, Bahía Blanca, Argentina

ARTICLE INFO

Article history:

Received 30 June 2008

Received in revised form 19 February 2009

Accepted 1 April 2009

Available online 8 April 2009

Keywords:

Solid humic acid

Humic acid–water interface

Hydrophobic associations

Electrostatic interactions

Metal complexes

Dissolution rate

ABSTRACT

The dissolution kinetics of solid humic acid (HA) particles under different conditions is reported and analyzed. The dissolution rate at pH 4 and 5 is very slow and several years may take to achieve equilibration. The rate is strongly increased by increasing pH, and at pH 11 complete dissolution is achieved in 30 min. The dissolution rate is also markedly increased by the presence of monocarboxylic acids and anionic herbicides such as glyphosate and 2,4-D. On the contrary, the rate is decreased by inorganic divalent cations (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}). The divalent cation paraquat has a dual behavior, decreasing the dissolution rate at pH >7 but increasing it at pH <7. Simple modeling assuming a surface-controlled dissolution kinetics can reproduce reasonably well the effects of anions and cations. The different ions seem to affect the dissolution rate by modifying intermolecular forces between HA molecules located at the surface of the particles.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Humic substances (HS), such as humic acids (HA), fulvic acids (FA), etc., are very active in binding ions, mineral surfaces and organic molecules, and thus they are very important to soil structure, soil fertility and transport of pollutants in natural waters. They usually participate in dynamic processes where their constituent molecules interact with metal ions mainly through electrostatic forces and complexation reactions, with surfaces through adsorption reactions, with organic molecules through hydrophobic bonding and hydrogen bonds (H-bonds), and among themselves through aggregation or association processes. The first two types of processes have been the subject of extensive research [1–3]. Although the third and fourth cases were less investigated, there also exists information about them [4–6].

HS, and especially HA, have been regarded for a long time as polymeric molecules or polyelectrolytes having a relatively high molecular mass. For the case of HA, for example, molecular masses of several tens of thousands Da or even higher molecular masses have been reported. In the last years, however, a new concept has emerged in which HS are regarded as supramolecular associations of many relatively small and chemically diverse organic molecules that are kept together by different kind of interactions. Many evidences for this new concept of HS structure were given by Piccolo [7,8] and were summarized by Sutton and Sposito [9].

Even though the structure of HS may be still a controversial topic, there is a general consensus in that HS molecules (either large polymeric molecules or small individual moieties) are able to form supramolecular structures or aggregates under certain conditions and to disaggregate under other conditions. Indeed, HA aggregates have been detected by many techniques such as light scattering, turbidimetry, fluorescence spectroscopy, fluorescence correlation spectroscopy [10], etc. The formation of aggregates is usually favored by decreasing the solution pH because of protonation of functional groups (mainly carboxylate and phenolate), leading to a decreased electrostatic repulsion among the molecules and to the formation of intermolecular H-bonds. The aggregation is so favored at low pH that formation of large aggregates or solid HA particles occurs at pH around 2, property that is used to operationally define the HA fraction of HS. Aggregation is also promoted by the presence of cations [11], via charge neutralization and cation bridge formation. On the other hand, disruption of aggregates or disaggregation takes place by increasing the pH of the solution [10] and by several other factors. Piccolo et al. [12,13], for example, indicated that simple organic acids such as monocarboxylic and dicarboxylic acids can penetrate the aggregates and separate them into smaller associations.

Since HS can form supramolecular structures, characterization of these materials should focus now on intermolecular interactions and factors that promote aggregation or disaggregation. Our approach here is to contribute to these important topics by performing dissolution kinetic experiments of solid HA particles, which were isolated, purified and dried according to the IHSS (International Humic Substances Society). Such kind of particles can be

* Corresponding author. Tel.: +54 291 4595101x3593.

E-mail address: brigante@uns.edu.ar (M. Brigante).

regarded as a large and rather pure aggregate of HA molecules, which are held together by different interaction forces such as H-bonds, π -bonds, van der Waals forces and hydrophobic interactions. If some metal ions, such as Fe(III) and Al(III) impurities, are within the particles, additional electrostatic interactions and coordinative bonds between the cations and functional groups of HA molecules should be also present. By immersing these particles in a dissolving aqueous solution, the attractive interaction forces are weakened or overcome by some repulsive forces and then dissolution, i.e., passage of HA constituting molecules to the solution bulk, takes place. The evaluation of factors that favor dissolution will give good insights into the factors that favor disaggregation, and could also give insight into the strength of the attractive or repulsive interaction forces among HA molecules. In addition, understanding the dissolution behavior of HA is also important in daily laboratory experiments with humics, since most of the studied HA samples are HA solutions prepared by dissolving dried and purified samples.

The aim of this article is to obtain information on the mechanism of HA dissolution by analyzing the effects of pH and several ions and molecules on the dissolution rate of HA particles in aqueous media.

2. Materials and methods

The HA sample used in this work was taken from an andisol (Boqueixon, A Coruña, Spain) and, as stated above, purified according to the IHSS procedures. The solid sample was formed by particles of different shapes and sizes, whose average size was 250 μm [14]. X-ray diffraction analyses (not shown here) showed that the particles were amorphous. The elemental composition of the sample is N (4.86%), C (52.57%), H (5.06%), O (34.77%) and S (0.33%), and contained some Fe (1.65%) and Al (0.76%) impurities. Solid state ^{13}C nuclear magnetic resonance, as obtained with a Bruker AMX 300 spectrophotometer, indicates that the studied sample contains 29% of alkyl C (0–45 ppm), 38% of O-alkyl C (45–110 ppm), 19% of aromatic and phenolic C (110–160 ppm), 11% of carboxyl C (160–190 ppm) and 3% of carbonyl C (190–240 ppm) [15]. More information about the general characteristics of this humic acid can be found elsewhere [16].

The methodology employed in the dissolution kinetic experiments is very similar to that employed and thoroughly described in earlier publications [14]. Briefly, the experiments were performed in a cylindrical, temperature-controlled ($25.0 \pm 0.2^\circ\text{C}$) reaction vessel covered with a glass cap. Fifty milliliters of an aqueous 10^{-3} M KCl solution with or without the addition of a dissolving agent were placed in the reaction vessel. This solution was constantly stirred (450 rpm) and purged with N_2 , and its pH was adjusted to the desired value with KOH and/or HCl solutions. The dissolution experiment was started by adding a known weight (around 8 mg) of solid HA to the mentioned solution. At different reaction times, a 5 mL aliquot was withdrawn, the particles were separated from the supernatant either by sedimentation or centrifugation [14] and the supernatant was immediately analyzed to quantify the concentration of dissolved HA. After the quantification (see below), that took around 30 s, the supernatant and the HA particles were reintroduced into the reaction vessel. This procedure (aliquot withdrawal, separation, quantification of HA and reintroduction of the aliquot into the reaction vessel) was repeated during several hours in order to achieve complete dissolution of the sample or to gather enough data points. The pH was checked periodically and kept constant by adding minute volumes of concentrated KOH or HCl solutions when necessary. In all experiments, the pH was measured with a Crison GLP 22 pH meter and a Crison 52-02 combined pH electrode. The dissolving agents that were added to the 10^{-3} M KCl solution were three different monocarboxylic (formic, acetic and propionic) acids, three herbicides (glyphosate, 2,4-dichlorophenoxyacetic acid (2,4-

D) and paraquat), and four divalent metal chlorides, MCl_2 , where M represents Mg, Ca, Sr, or Ba. Analytical grade chemicals were used in all experiments.

Quantification of dissolved HA was performed by UV–Vis spectroscopy, using an Agilent 8453 UV–VIS diode array spectrophotometer equipped with a Hellma 1 cm quartz cell. The supernatant of the withdrawn aliquot was placed into the cell and the spectrum was recorded in the 300–900 nm wavelength range. The concentration of HA, c_{HA} , in the supernatant was then estimated from the absorbance at 400 nm. Calibration curves at the working pH were constructed with several HA solutions having concentrations that ranged between 2 mg L^{-1} and 200 mg L^{-1} . A uniform absorption coefficient was assumed for the different dissolved fractions, which gives rather accurate concentration values [14].

The dissolution kinetics of the studied HA was evaluated by plotting the degree of progress of the dissolution reaction, α , as a function of time, t . α is defined as

$$\alpha = \frac{c_{\text{HA}}}{c_{\text{T}}} \quad (1)$$

where c_{HA} is the HA concentration in the supernatant and c_{T} is the total concentration of HA that would be present in the supernatant after complete dissolution of the solid. The magnitude of c_{T} was calculated from the initial weight of HA and the volume of KCl solution used in the dissolution run. The values $\alpha = 0$ and $\alpha = 1$ mean respectively that 0% and 100% of the solid has been dissolved. A plot α vs. t will be called dissolution curve.

3. Results and discussion

3.1. Effect of pH on the dissolution rate

In Fig. 1 several dissolution curves of the studied HA are shown. Fig. 1a show the curves obtained at different pH values between 4 and 11 [14]. The dissolution rate is strongly dependent on the pH, being relatively high at pH 11 and becoming lower by decreasing the pH. At pH 11, for example, complete dissolution took place in around 30 min, whereas at pH 4 even after 6 h of reaction only 5–6% of dissolution could be achieved. The dissolution rate, R , is defined as $R = d\alpha/dt$ and was estimated from the maximum slopes of the dissolution curves. Examples of these slopes are given by the straight lines drawn in the figure. R is almost 400 times larger at pH 11 than at pH 4, demonstrating the very strong effect of pH on the dissolution behavior of HA. The dissolution curves indicate that complete dissolution was obtained at pH 9 or higher, but not at pH 8.5 or lower. Weng et al. [17] and Kipton et al. [18] have shown that the solubility of HA decreases by decreasing the pH. Therefore, it may be possible that dissolution is slow and incomplete at low pH because solubility equilibrium is being reached at these low pH values, and thus some backward precipitation reaction is decreasing the net dissolution rate. Long-term experiments trying to approach solubility equilibrium from dissolution and precipitation allowed to discard this possibility [14]. This is exemplified in Fig. 1b, which shows the dissolution behavior of the HA at pH 4 during a 3-week period, compared with the precipitation–coagulation behavior of a sample whose pH was decreased to 4 after complete dissolution at pH 10. Dissolution at pH 4 increases monotonously in time and no signs of equilibration could be observed even after 3 weeks of reaction. Precipitation–coagulation, on the contrary, took place very quickly after decreasing the pH from 10 to 4. α decreased from 1 to 0.78 in less than 10 min and then remained at this last value during the 3 weeks of the experiment. The trends of the curves suggest that during dissolution the system was always far from solubility equilibrium. Therefore, the slow dissolution observed at low pH is because of the intrinsic slowness of the dissolution process and not

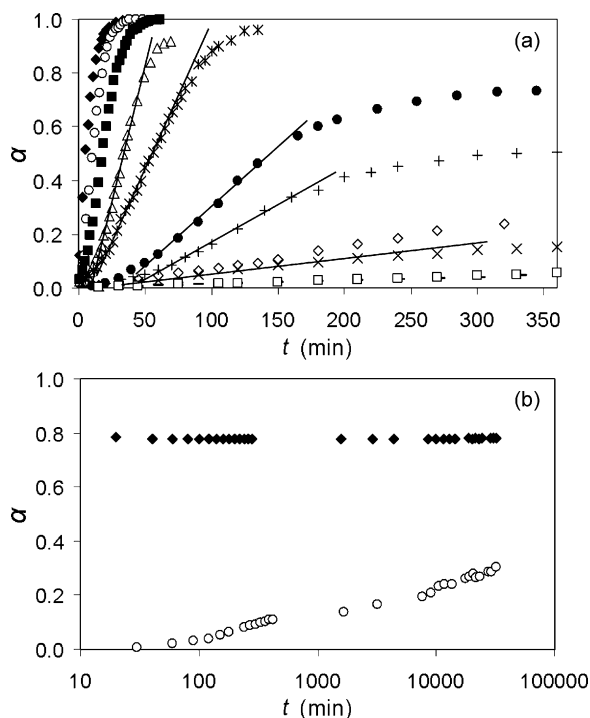


Fig. 1. Dissolution curves of the studied HA particles. (a) Effect of pH: solid diamonds, 11; open circles, 10.5; solid squares, 10; open triangles, 9.5; stars, 9; solid circles, 8.5; plus signs, 8; open diamonds, 7; crosses, 6; open squares, 5; dashes, 4. Some straight lines, whose slopes represent the dissolution rate are shown as examples. (b) Comparison of the dissolution curve (open circles) at pH 4 with the precipitation–coagulation curve (solid diamonds) of a sample whose pH was decreased to 4 after complete dissolution at pH 10.

because solubility equilibrium is being reached. Moreover, if linear shape is assumed for the dissolution curve in Fig. 1b and $\alpha = 0.78$ is taken as the “equilibrium” value, extrapolation of this curve suggests that more than 10 years are needed to reach equilibration during the dissolution experiment at pH 4. Although this may be a crude approximation, it gives the feeling of how slow a dissolution reaction can become at low pH.

Besides giving information on the dissolution behavior of solid HA particles, data such as those shown in Fig. 1 give also important practical information regarding manipulation of solid HA samples in laboratory experiments. Many studies such as proton binding to HA, metal ion binding to HA, HA adsorption and molecular mass determination are usually performed by using HA solutions that were obtained by “dissolving” solid HA particles purified according to the IHSS recommendations or other purification protocol. Placing the solid samples in neutral or acidic solution without a previous treatment at high pH may lead to incomplete dissolution and misinterpretation of the obtained results because a changing mix of dissolved and undissolved humics is obtained under these conditions.

The strong effects of pH on the dissolution rate of HA particles have been attributed to reactions and processes that take place at the surface of HA particles [14]. Surface HA molecules are interacting with molecules located at the surface and molecules located within the particle. When a particle is immersed in an aqueous solution, surface HA molecules become also in contact with water molecules and dissolved ions, and thus sorption–desorption reactions may take place at the surface. It is well known that HA and other HS molecules contain functional groups (mainly carboxylic and phenolic groups) that can deprotonate by increasing the pH of the aqueous solution. In the dissolved state, this deprotonation gives rise to the development and continuous increase of the nega-

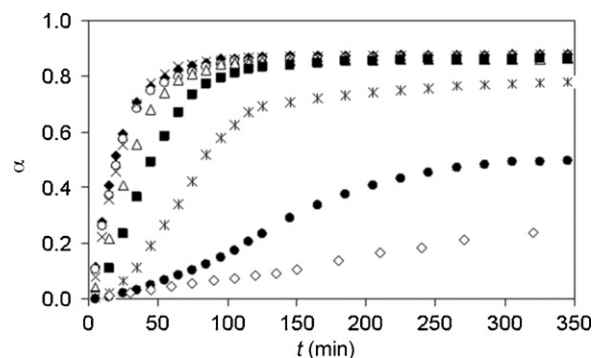


Fig. 2. Effect of propionate concentration on the dissolution curves of the studied HA at pH 7. Propionate concentrations: open diamonds, 0 M; solid circles, 3×10^{-4} M; stars, 1×10^{-3} M; solid squares, 3×10^{-3} M; open triangles, 6.5×10^{-3} M; crosses, 1×10^{-2} M; open circles, 2×10^{-2} M; solid diamonds, 3×10^{-2} M.

tive charge of the molecules as the pH increases up to values around 10 or 11 where most of the functional groups become deprotonated [19]. Similar reactions should take place in HA molecules located at the surface of a solid HA particle. These deprotonation reactions will, on one side, decrease the number of H-bonds that contribute to hold HA molecules together in the solid. On the other side, they will increase electrostatic repulsion among the molecules as a consequence of negative charge development. Both processes, which become more important as the pH is increased, contribute to leave surface molecules more susceptible to detachment and to increase the dissolution rate by increasing pH.

3.2. Effect of anions on the dissolution rate

Fig. 2 shows the effect of the presence of propionate on the dissolution curves of the studied HA. All the curves were obtained at constant pH 7 and at different concentrations of propionate. The dissolution is relatively slow in absence of propionate, but becomes faster as the propionate concentration increases. A very similar behavior was shown previously for the dissolution of the same HA in the presence of acetate at pH 7 [20]. Although not shown here, this kind of behavior is also shown by dissolution curves in the presence of a third monocarboxylate anion (formiate) and two anionic herbicides (2,4-D and glyphosate). The relatively strong effect of these anionic organic species on the dissolution rate can be better analyzed and compared by plotting the dissolution rate R as a function of the anions concentrations. This is done in Fig. 3a for monocarboxylates and in Fig. 3b for herbicides. For the case of carboxylates, R increases by increasing the anion concentration up to around 0.01 M, and then remains nearly constant and almost independent on the anion concentration. The capacity to increase the dissolution rate of propionate is only slightly higher than that of acetate but significantly higher than that of formiate. In the case of herbicides (Fig. 3b), the general shape of the curves is similar to that of monocarboxylates, showing a levelling off at high concentrations. Glyphosate is more active than 2,4-D in increasing the dissolution rate.

The increase in R in the presence of anionic species and the shape of the R vs. concentration curves can be rather well explained if a surface-controlled dissolution process is assumed. This kind of processes is common for dissolution of minerals in aqueous media, where there is at least one fast adsorption step followed by a slower and rate-determining release of molecules to the solution bulk [21–23]. In the case of dissolution of HA particles promoted by carboxylic or anionic herbicides, the fast sorption step is probably the attachment of these molecules to the surface of HA particles. This attachment leads to the formation of surface species that weaken the interactions between HA molecules at the surface of the par-

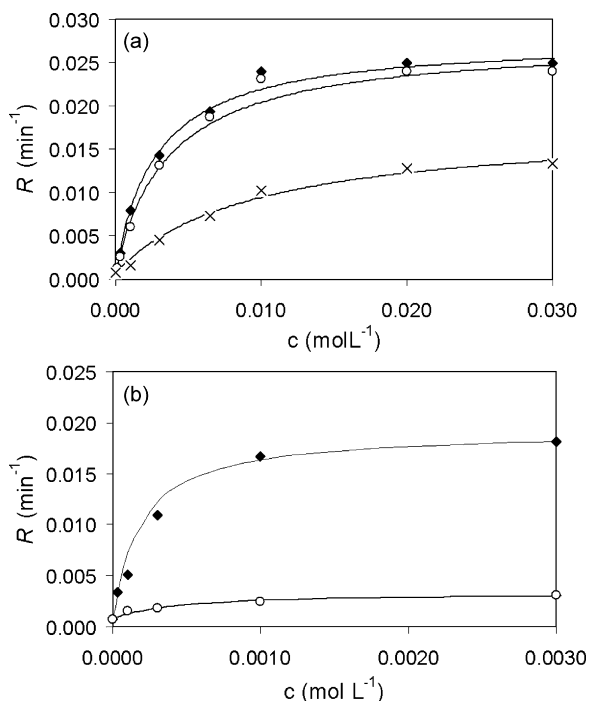


Fig. 3. Effect of the concentration of carboxylates and herbicides on the dissolution rate at pH 7. (a) Crosses, formiate; open circles, acetate; solid diamonds, propionate. (b) Solid diamonds, glyphosate; open circles, 2,4-D. Lines show predictions of Eq. (5) with parameters from Table 1.

ticles. The following and rate-determining step is the release of these surface molecules to the solution bulk. This release includes the breakage of attractive interactions induced by the presence of the sorbed molecules and the passage of HA molecules to solution. A simple model for a surface-controlled dissolution can be formulated to describe the results. The dissolution rate is expressed as

$$R = R_{\text{OH}} + R_{\text{L}}, \quad (2)$$

where R_{OH} is the rate promoted by deprotonation reactions and R_{L} is the rate promoted by anionic species or ligands. Eq. (2) is similar to that proposed by Furrer and Stumm [24] for surface-controlled dissolution kinetics of mineral particles. At constant pH R_{OH} is assumed to be constant and its value is directly the dissolution rate in absence of anionic species. In addition, since the adsorption step is assumed to be much faster than the detachment of HA molecules, R_{L} can be written in terms of the adsorbed anions concentration [L_{ads}]

$$R_{\text{L}} = k_{\text{L}}[L_{\text{ads}}] \quad (3)$$

where k_{L} is the rate constant of the rate-determining step [25]. [L_{ads}] can be then related to the anion concentration in solution through an adsorption isotherm. The Langmuir isotherm has been selected here as a first approximation:

$$[L_{\text{ads}}] = \frac{bK[L_{\text{sol}}]}{1 + K[L_{\text{sol}}]} \quad (4)$$

where b is the maximum concentration of anion that can be adsorbed at the surface, K is the Langmuir adsorption constant and [L_{sol}] is the anion concentration in solution. Combining Eqs. (2)–(4) the following expression that relates R and [L_{ads}] is obtained:

$$R = R_{\text{OH}} + \frac{k_{\text{L}}bK[L_{\text{sol}}]}{1 + K[L_{\text{sol}}]} \quad (5)$$

Plots according to Eq. (5) are shown by lines in Fig. 3a and b and compared to experimental points. Best fitting parameters are shown in Table 1. Unfortunately, the values of k_{L} and b cannot be

Table 1
Best-fit parameters for Eqs. (5) and (7).

pH	Dissolving ions	$k_{\text{L}}b$ (min ⁻¹)	log(K/L mol ⁻¹)	r^2
7.0	Formic acid	0.0171	2.0	0.99
7.0	Acetic acid	0.0269	2.4	0.99
7.0	Propionic acid	0.0270	2.6	1.00
7.0	2,4-D	0.0026	3.4	1.00
7.0	Glyphosate	0.0185	3.7	0.99
9.0	PQ ²⁺	–	3.3	0.97
9.0	Mg ²⁺	–	4.4	0.90
9.0	Ca ²⁺	–	4.5	0.95
9.0	Si ²⁺	–	4.4	0.92
9.0	Ba ²⁺	–	4.4	0.90

separately determined, thus only the values of K and the product $k_{\text{L}}b$ were estimated. Even though the formulated model is rather simple, it can fit reasonably well the dissolution behavior of HA.

A question arises here on how the studied anionic species bind surface molecules of HA particles and why this binding promotes dissolution. Piccolo et al. [8,12,13,26] have proposed that carboxylic acids (and carboxylates) can interact with HA molecules forming H-bonds between HA and carboxylics. Such interaction modifies the previously existing H-bonds between HA molecules and disrupts the hydrophobic forces. These authors concluded that carboxylics were able to penetrate HA aggregates and produce disaggregation. For the case of glyphosate, Piccolo and Celano [4] have reported by using infrared spectroscopy the formation of multiple H-bonds between the glyphosate phosphono-group and the oxygen groups of humic acid. As in the case of carboxylics, 2,4-D could also form H-bonds with HA molecules via its carboxylic group. Therefore, similar processes may take place at the surface of solid HA particles and induce dissolution, i.e., the investigated anions may bind surface HA molecules disrupting H-bonds and leaving the molecules susceptible for detachment.

According to Piccolo et al. [13], the extent of the interactions of carboxylic compounds having aliphatic chains of different lengths with HA molecules and the extent of conformational changes caused on HA aggregates depend on the hydrophobicity of the reactant compounds. The larger the number of carbon atoms in the aliphatic chain of the carboxylic, the greater is the affinity for the hydrophobic components of HA, and the greater is their capacity to alter the humic associations [13]. This is in line with the results found here, since according to K values in Table 1 the affinity of carboxylates for the HA surface increases in the order formiate < acetate < propionate.

Besides hydrophobic interaction, Brigante et al. [20] have suggested that carboxylate anions may also coordinate metal ions such as Fe(III) and Al(III) which are impurities of the HA sample. These cations surely act as bridges between adjacent molecules in the solid phase impeding their passage to solution. If carboxylates coordinate metal ions at the surface, some bonds that the metal ions establish with functional groups of HA molecules will be replaced by bonds with the reactant molecules favoring the dissolution. This seems also to be in agreement with the trends observed for the K values in Table 1, because the complexation constants of carboxylates with Fe(III) and Al(III) in solution increase slightly in the order formic < acetic < propionic [27]. This also explains why glyphosate, which is known to form very stable and strong complexes with metal ions [28,29] is so good in dissolving the HA. Although there is no data in the literature for complexation constants between 2,4-D and metal ions, Larrivee et al. [30] have reported using fluorescence spectroscopy the formation of an Al³⁺–2,4-D complex in aqueous solutions. This kind of complexation could also take place at the surface of the studied HA and thus dissolution could be also promoted by the presence of this herbicide.

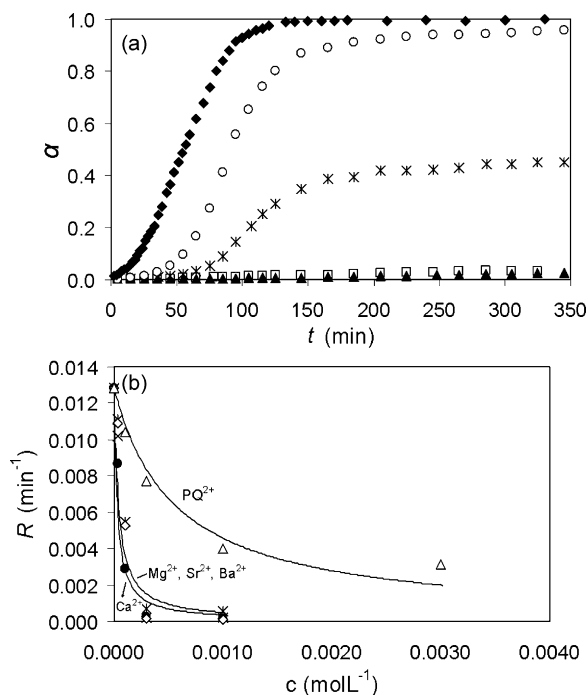


Fig. 4. Effects of divalent cations on the dissolution behavior of the studied HA at pH 9. (a) Dissolution curves at different Mg^{2+} concentrations: solid diamonds, 0 M; open circles, 3×10^{-5} M; stars, 1×10^{-4} M; open squares, 3×10^{-4} M; solid triangles, 1×10^{-3} M. (b) Effect of concentration on R : open triangles, PQ^{2+} ; stars, Mg^{2+} ; solid circles, Ca^{2+} ; crosses, Sr^{2+} ; open diamonds, Ba^{2+} . Lines show predictions of Eq. (7) with parameters from Table 1.

3.3. Effects of cations on the dissolution rate

Fig. 4 shows the effects of cations on the dissolution behavior of the studied HA. Fig. 4a shows the dissolution curves at constant pH 9 in the presence of varying concentrations of Mg^{2+} . Contrarily to the behavior shown for propionate and other anions, Mg^{2+} decreases the dissolution rate of the humic. A very similar behavior was shown previously for the dissolution of the same HA in the presence of Ca^{2+} [14]. Although not shown here, this kind of behavior is also observed in the presence of other divalent inorganic cations such as Sr^{2+} and Ba^{2+} and an organic cation, the herbicide paraquat (PQ^{2+}). Fig. 4b compares the effects of the five studied cations on the dissolution rate of HA. The inorganic cations have a stronger effect on the kinetics than PQ^{2+} .

Carboxylate and phenolate groups of HA are known to have a considerable affinity for divalent inorganic cations, which can bind to HA molecules in solution [1], or at the surface of solid HA particles [31,32]. Narine and Guy [33] have also demonstrated that PQ^{2+} can bind to humics in solution. Therefore, it seems that adsorption of these cations is the responsible for the decrease in the dissolution rates. The state of divalent cations at the surface of HA particles is not well known yet, but it may be speculated that adsorbed cations can (i) decrease the net negative charge of HA molecules decreasing the electrostatic repulsion between them, and (ii) act as bridges between functional groups of two adjacent molecules at the surface increasing the attractive forces between them. Both effects will end up with a decrease in the dissolution rate. Therefore, it may be assumed in a simple model of surface-controlled dissolution that cations adsorb according to the Langmuir equation inhibiting dissolution by blocking the fraction of the surface that contains adsorbed cations. This will cause a decrease in the dissolution rate because of the increase in cation adsorption. Cation adsorption is then assumed to be fast, and the detachment of HA molecules with

adsorbed cations is assumed to be completely blocked. The dissolution rate can be written as:

$$R = R_{OH}(1 - \theta) \quad (6)$$

$$R = R_{OH} \left(1 - \frac{K[C_{sol}]}{1 + K[C_{sol}]} \right) \quad (7)$$

where θ represents the fraction of the surface that is blocked by cations and $[C_{sol}]$ is the cation concentration in solution. Similar models have been proposed for the inhibition of mineral dissolution by metal cations [34]. It is clear that the model is very simple and that it has to be used just as a first approximation. More elaborated models should take into account surface heterogeneity, since cations should bind with different affinity to carboxylate groups and phenolate groups of HA. The binding of cations to two adjacent groups in order to act as bridging cations, and electrostatic effects could also be considered to improve the modeling. Predictions of Eq. (7) with parameters presented in Table 1 are shown together with experimental points in Fig. 4b. In spite of the simplicity of the model, it can predict reasonably well the general trends of the curves and the inhibitory effects of cations. All inorganic cations have very similar adsorption constants and no trend is observed by moving from Mg^{2+} to Ba^{2+} . Unfortunately, there are no data for binding constants of alkaline earth cations for the studied HA. There are, however, generic data published by Milne et al. [35] which show that these four cations have similar binding constants to humics, with no special trend, in agreement with the data found here. This is also in line with complexation constants of monocarboxylates (e.g. formate and acetate) with alkaline earth cations in solution, which are also similar [27]. Fig. 4b and Table 1 show that the inhibitory effect of PQ^{2+} is weaker than those of the inorganic cations. According to these results, the small inorganic cations seem to accommodate better between adjacent HA molecules at the surface of the particles than the larger PQ^{2+} ion, decreasing more effectively the dissolution rate.

3.4. Combined effect of ions and pH on the dissolution rate

Fig. 5 shows the effects of carboxylics and herbicides on the dissolution rate at different pH. Fig. 5a compares R vs. pH curves obtained by dissolving HA particles in absence and presence of 10^{-3} M solutions of carboxylics. Carboxylics strongly increase the rate at almost all investigated pH, except at pH >10 where the effects are very weak (or even absent). This weak effect may be due to the electrostatic repulsion between carboxylates and the highly charged HA molecules, which impedes significant adsorption. Fig. 5b, on the other hand, compares R vs. pH curves obtained by dissolving HA particles in absence and presence of 10^{-3} M solutions of herbicides. It must be said that 10^{-3} M divalent inorganic cations were very effective in decreasing the dissolution rate. They were so effective that at pH <9 no dissolution could be detected, and thus the data are not included in the figure. Glyphosate and 2,4-D behave as carboxylics, increasing significantly the dissolution rate at most investigated pH, except at pH >10 where the effects are weak. Paraquat, however, decreases the dissolution rate at high pH but increases it at pH <7. This herbicide is then having a dual effect, behaving as divalent inorganic cations do at high pH, but acting as anions do at pH <7. The effects at high pH can be well understood assuming that PQ^{2+} is blocking part of the surface upon adsorption. The effects at low pH are not clearly understood. The fact that the dissolution rate is modified by this herbicide strongly suggest that it interacts with the HA particle surface. However, the mechanism by which it weakens or disrupts attractive forces between humic molecules needs still to be investigated.

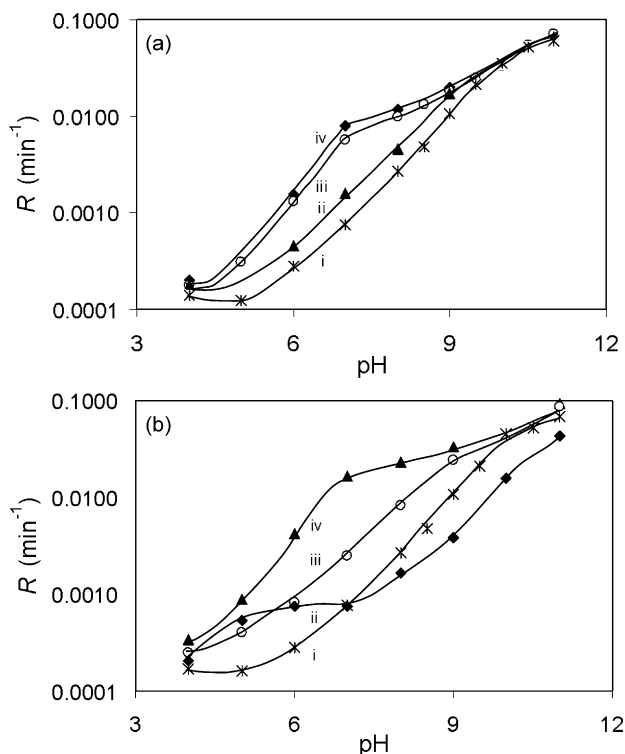


Fig. 5. Effect of pH on the dissolution rate of the studied HA in the presence of different substances. (a) i, 10^{-3} M KCl; ii, 10^{-3} M formic acid; iii, 10^{-3} M acetic acid; iv, 10^{-3} M propionic acid; (b) i, 10^{-3} M KCl; ii, paraquat; iii, 2,4-D; iv, glyphosate. In all cases where either carboxylics or herbicides are present, the solution also contains 10^{-3} M KCl.

4. Conclusions

HA particles can be regarded as large aggregates of HA molecules which are held together by different interaction forces. The study of their dissolution kinetics gives information on the factors that modify these interactions and on the dissolution mechanism.

The dissolution rate of HA particles is significantly affected by pH and the presence of monocarboxylic acids, herbicides, and metal ions. Simple modeling assuming a surface-controlled dissolution kinetics can reproduce reasonably well the effects of anions and cations. Surface protonation and cation adsorption reduce the dissolution rate apparently because they reduce electrostatic repulsion between surface molecules and because divalent cations also act as bridges between adjacent molecules. Anions, such as carboxylates and anionic herbicides increase the dissolution rate. They seem to adsorb at the HA particle surface disrupting H-bonds between HA molecules and also complexing with metal ion impurities in the solid phase.

The obtained data are useful to understand the factors that promote aggregation or disaggregation of HA constituent molecules. They are also helpful to establish the right dissolving conditions in experiments where HA solutions are prepared from purified and solid HA samples.

Acknowledgments

This work was financed by UNS, CONICET and ANPCYT. M. Brigante thanks CONICET for the fellowship granted. The authors thank F. Arce (University of Santiago de Compostela, Spain) and his research group, who kindly provided the HA sample. The authors are also very thankful for the friendship and the many good and constructive discussions with L.K. Koopal either in The Netherlands or Argentina.

References

- [1] D.G. Kinniburgh, W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti, M.J. Avena, Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency, *Colloids Surf. A: Physicochem. Eng. Aspects* 151 (1999) 147–166.
- [2] E. Tipping, C. Rey-Castro, S.E. Bryan, J. Hamilton Taylor, Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation, *Geochim. Cosmochim. Acta* 66 (2002) 3211–3224.
- [3] L. Weng, W.H. van Riemsdijk, L.K. Koopal, T. Hiemstra, Ligand and charge distribution (LCD) model for the description of fulvic acid adsorption to goethite, *J. Colloid Interface Sci.* 302 (2006) 442–457.
- [4] A. Piccolo, G. Celano, Hydrogen-bonding interactions between the herbicide glyphosate and water-soluble humic substances, *Environ. Toxicol. Chem.* 13 (1994) 1737–1741.
- [5] S. Chen, W.P. Inskeep, S.A. Williams, P.R. Callis, Complexation of 1-naphthol by humic and fulvic acids, *Soil Sci. Soc. Am. J.* 56 (1992) 67–73.
- [6] R. Baigorri, M. Fuentes, G. González-Gaitano, J.M. García-Mina, Analysis of molecular aggregation in humic substances in solution, *Colloid Surf. A: Physicochem. Eng. Aspects* 302 (2007) 301–306.
- [7] A. Piccolo, The supramolecular structure of humic substances, *Soil Sci.* 166 (2001) 810–832.
- [8] A. Piccolo, The supramolecular structure of humic substances: a novel understanding of humus chemistry and implications in soil science, *Adv. Agron.* 75 (2002) 57–134.
- [9] R. Sutton, G. Sposito, Molecular structure in soil humic substances: the new view, *Environ. Sci. Technol.* 39 (2005) 9009–9015.
- [10] M.J. Avena, K.J. Wilkinson, Disaggregation kinetics of a peat humic acid: mechanism and pH effects, *Environ. Sci. Technol.* 36 (2002) 5100–5105.
- [11] R.R. Engebretson, R. von Wandruszka, Kinetic aspects of cation enhanced aggregation in aqueous humic acids, *Environ. Sci. Technol.* 32 (1998) 488–493.
- [12] A. Piccolo, S. Nardi, G. Concheri, Micelle-like conformation of humic substances as revealed by size exclusion chromatography, *Chemosphere* 33 (1996) 595–602.
- [13] A. Piccolo, P. Conte, A. Cozzolino, Effects of mineral and monocarboxylic acids on the molecular association of dissolved humic substances, *Eur. J. Soil Sci.* 50 (1999) 687–694.
- [14] M. Brigante, G. Zanini, M. Avena, On the dissolution kinetics of humic acid particles. Effects of pH, temperature and Ca^{2+} concentration, *Colloid Surf. A: Physicochem. Eng. Aspects* 294 (2007) 64–70.
- [15] D. Gondar, R. Lopez, S. Fiol, J.M. Antelo, F. Arce, Characterization and acid–base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog, *Geoderma* 126 (2005) 367–374.
- [16] G.P. Zanini, M.J. Avena, S. Fiol, F. Arce, Effects of pH and electrolyte concentration on the binding between a humic acid and an oxazine dye, *Chemosphere* 63 (2006) 430–439.
- [17] L. Weng, E.J.M. Temminghoff, W.H. van Riemsdijk, Interpretation of humic acid coagulation and soluble soil organic matter using a calculated electrostatic potential, *Eur. J. Soil Sci.* 53 (2002) 575–587.
- [18] H. Kipton, J. Powell, R.M. Town, Solubility and fractionation of humic acid; effect of pH and ionic medium, *Anal. Chim. Acta* 267 (1992) 47–54.
- [19] C.J. Milne, D.G. Kinniburgh, E. Tipping, Generic NICA–Donnan model parameters for proton binding by humic substances, *Environ. Sci. Technol.* 35 (2001) 2049–2059.
- [20] M. Brigante, G. Zanini, M. Avena, On the dissolution kinetics of humic acid particles. Effects of monocarboxylic acids, *Chemosphere* 71 (2008) 2076–2081.
- [21] M.A. Blesa, A.D. Weisz, P.J. Morando, J.A. Salfity, G.E. Magaz, A.E. Regazzoni, The interaction of metal oxide surfaces with complexing agents dissolved in water, *Coord. Chem. Rev.* 196 (2000) 31–63.
- [22] W.H. Casey, The dissolution of mineral oxides, in: A. Hubbard (Ed.), *Encyclopedia of Surface and Colloid Science*, Marcel Dekker, New York, 2002, pp. 1486–1495.
- [23] W. Stumm, *Chemistry of Solid–Water Interface. Processes at the Mineral–Water and Particle–Water Interface in Natural Systems*, Wiley, New York, 1992.
- [24] G. Furrer, W. Stumm, The coordination chemistry of weathering. I. Dissolution kinetics of $\delta\text{-Al}_2\text{O}_3$ and BeO, *Geochim. Cosmochim. Acta* 50 (1986) 1847–1860.
- [25] D.L. Sparks, *Environmental Soil Chemistry*, Elsevier, New York, 2003.
- [26] A. Piccolo, P. Conte, A. Cozzolino, *Eur. J. Soil Sci.* 50 (1999) 687–694.
- [27] A.E. Martell, R.M. Smith, *Critical Stability Constants. Other Organic Ligands*, 3, Prentice Hall, New York, 1997.
- [28] T. Undabeytia, E. Morillo, C. Maqueda, FTIR study of glyphosate–copper complexes, *J. Agric. Food Chem.* 50 (2002) 1918–1921.
- [29] B.C. Barja, J. Herszage, M. dos Santos Afonso, Iron(III)–phosphonate complexes, *Polyhedron* 20 (2001) 1821–1830.
- [30] E.M. Larrivee, K.M. Elkins, S.E. Andrews, D.J. Nelson, Fluorescence characterization of the interaction of Al^{3+} and Pd^{2+} with Suwannee River fulvic acid in the absence and presence of the herbicide 2,4-dichlorophenoxyacetic acid, *J. Inorg. Biochem.* 97 (2003) 32–45.
- [31] E.A. Ghabbour, M. Shaker, A. El-Touky, I.M. Abid, G. Davies, Thermodynamics of metal cation binding by a solid soil-derived humic acid: binding of Fe(III), Pb(II), and Cu(II), *Chemosphere* 63 (2006) 477–483.

- [32] E.A. Ghabbour, M. Shaker, A. El-Toukhy, I.M. Abid, G. Davies, Thermodynamics of metal cation binding by a solid soil derived humic acid. 2. Binding of Mn(II), $\text{Co}(\text{NH}_3)_6\text{aq}^{3+}$ and Hg(II), *Chemosphere* 64 (2006) 826–833.
- [33] D.R. Narine, R.D. Guy, Binding of diquat and paraquat to humic acid in aquatic environments, *Soil Sci.* 133 (1982) 356–363.
- [34] G. Sposito, *The Surface Chemistry of Natural Particles*, Oxford University Press, New York, 2004.
- [35] C.J. Milne, D.G. Kinniburgh, W.H. van Riemsdijk, E. Tipping, Generic NICA-Donnan model parameters for metal-ion binding by humic substances, *Environ. Sci. Technol.* 37 (2003) 958–971.