



# Effect of humic acid on the adsorption/desorption behavior of glyphosate on goethite. Isotherms and kinetics



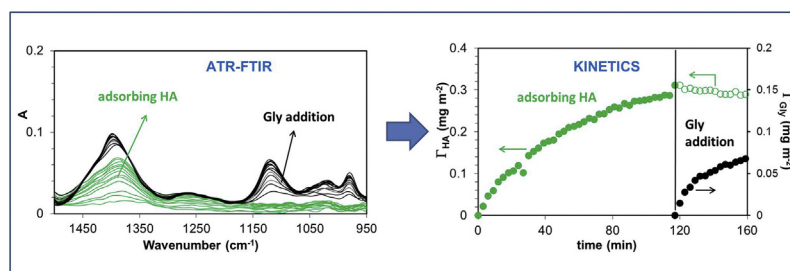
Jeison Manuel Arroyave, Carolina C. Waiman, Graciela P. Zanini, Marcelo J. Avena\*

INQUISUR, Department of Chemistry, Universidad Nacional del Sur, Av. Alem 1253, B8000CPB, Bahía Blanca, Argentina

## HIGHLIGHTS

- Attachment of glyphosate to goethite particles is inhibited by humic acid.
- Adsorbed humic acid decreases the adsorption rate of glyphosate.
- Humic acid in solution increases the desorption rate.
- Glyphosate desorbs by two parallel processes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The effects of humic acid (HA) on the adsorption/desorption of glyphosate (Gly) on goethite were investigated under pseudo equilibrium conditions by adsorption isotherms and under kinetic conditions by ATR-FTIR spectroscopy. Isotherms reveal that the attachment of Gly is almost completely inhibited by HA molecules. The opposite effect is not observed: HA adsorption is not affected by the presence of Gly. ATR-FTIR allowed the simultaneous detection of adsorbed HA and Gly during kinetic runs, revealing that HA at the surface decreases markedly the adsorption rate of Gly likely as a result of a decreased availability of sites for Gly adsorption and because of electrostatic repulsion. In addition, HA in solution increases the desorption rate of Gly. The rate law for Gly desorption could be determined giving important insights on the desorption mechanism. The herbicide is desorbed by two parallel processes: i) a direct detachment from the surface, which is first order in adsorbed Gly; and ii) a ligand exchange with HA molecules, which is first order in adsorbed Gly and first order in dissolved HA. Rate constants for both processes were quantified, leading to half-lives of 3.7 h for the first process, and 1.4 h for the second process in a 400 mg L<sup>-1</sup> HA solution. These data are important for modeling the dynamics of glyphosate in environmentally relevant systems, such as soils and surface waters.

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## 1. Introduction

Glyphosate (Gly) is a broad-spectrum organophosphorus

herbicide widely used in agriculture and horticulture (Aparicio et al., 2013; Yang et al., 2015). It is the most used herbicide in the world. Recently, the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) has classified Gly as probably carcinogenic to humans (Group 2A) because there is convincing evidence that it can cause cancer in laboratory animals (Guytona et al., 2015). It was also reported that it has some immunotoxic effects on fish (Ma and Li, 2015). Studying the

\* Corresponding author. INQUISUR, Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, B8000CPB, Bahía Blanca, Argentina.

E-mail address: [mavena@uns.edu.ar](mailto:mavena@uns.edu.ar) (M.J. Avena).

processes that affect the mobility and distribution of Gly in natural systems, such as soils and surface waters, is therefore of crucial importance to understand its behavior and fate in the environment.

The mobility of Gly in the environment is strongly influenced by adsorption/desorption processes on mineral surfaces, especially on hydrous ferric oxides surfaces, which bear high affinity for it. The adsorption of Gly on hydrous ferric oxides has been investigated in several studies (Barja and dos Santos Afonso, 2005; Gimsing and Borggaard, 2001, 2002) and takes place mainly by a ligand exchange mechanism, resulting in the formation of inner-sphere surface complexes, where the phosphonate group of Gly binds Fe(III) ions at the surface displacing coordinated water molecules and/or hydroxyl ions (Sheals et al., 2002). It is also well-known that the adsorption of Gly is affected by the presence of other adsorbing species, particularly those species that are also capable of forming complexes with Fe(III) ions at the surface. This is the case of phosphate, which is a good ligand and thus can displace Gly from adsorption sites by ligand exchange (Waiman et al., 2013). It should be also the case of humic substances, such as humic acids (HAs) or fulvic acids (FAs) (Tipping, 1994; Antelo et al., 2007; Fu and Quan, 2006; Weng et al., 2006), which have carboxylate groups in their structure, with the potential ability to affect Gly adsorption/desorption processes. The effects of phosphate on the adsorption behavior of Gly on metal oxides have been reported in several articles (Gimsing and Borggaard, 2001, 2002; Waiman et al., 2013). Conversely, the effects of humic substances were seldom investigated. In this respect, Day et al. (1997) informed that the natural organic matter obtained from a stream in Victoria, Australia, decreased the adsorption of Gly on goethite ( $\alpha$ -FeOOH), likely because of competition for surface sites and by electrostatic and perhaps steric shielding effects. This seems to be the only report in the literature regarding HA effects on Gly adsorption/desorption kinetics, and thus more information is still needed.

The aim of this paper is to study the effects of HA on the adsorption/desorption behavior of glyphosate on goethite. Adsorption isotherms in batch experiments are performed and adsorption/desorption kinetic studies using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) are reported. Emphasis is given in Gly desorption, aiming to investigate the influences of HA on its desorption rate, to assess a rate law for the desorption process, and to show the capabilities of ATR-FTIR to obtain kinetic information of environmentally relevant systems.

## 2. Experimental

### 2.1. Goethite and HA

Goethite particles were synthesized as described by Puccia et al. (2009), following the methodology proposed by Atkinson et al. (1967). A 5 M NaOH solution was added dropwise ( $10 \text{ mL min}^{-1}$ ) to a stirred 0.1 M  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  aqueous solution until the pH was 12.  $\text{N}_2$  was continuously bubbled in the reaction vessel during the NaOH addition to reduce  $\text{CO}_2$  contamination. The resulting suspension was aged at  $60^\circ\text{C}$  for 3 days in a capped teflon container in order to produce goethite crystallization. The suspension was then filtered and the solid particles were washed with  $\text{CO}_2$ -free water until the conductivity of the supernatant was lower than  $10 \mu\text{S cm}^{-1}$ . The washed solid was finally stored as a stock suspension at pH 4.5. It had a  $\text{N}_2$ -BET surface area of  $89.7 \text{ m}^2 \text{ g}^{-1}$ , a pore volume of  $0.36 \text{ cm}^3 \text{ g}^{-1}$  and a pore size of 16 nm. Its isoelectric point (IEP) was 8.6 in aqueous NaCl solutions.

The HA was extracted from an alfalfa-cultivated soil (INTA, Manfredi Experimental Station, Córdoba, Argentina) and purified according to the procedures recommended by the IHSS (International Humic Substances Society) (Swift, 1996). The HA sample has

an elemental composition of C (54.4%), H (4.0%), N (1.6%), and O (39.9%), and an ash content of 1.18%. More information about the general characteristics of this HA sample can be found elsewhere (Sola et al., 1988).

### 2.2. Gly and HA adsorption isotherms

Gly (pKa: <2, 2.12, 7.21 and 12.32) and HA adsorption isotherms were obtained by batch equilibration experiments. They were performed by adding 0.7 mL of the stock goethite suspension ( $9.63 \text{ g L}^{-1}$ ) to 15 mL polypropylene centrifuge tubes containing 10 mL of an aqueous solution of known concentration of Gly or HA. The background electrolyte was 0.1 M NaCl. The pH of these dispersions was adjusted to 7.0 and kept constant by adding a few microliters of either NaOH or HCl solutions. The tubes were shaken for 6 h with an end-over-end rotator and the final pH was always in the range  $7.0 \pm 0.1$ . Finally, the supernatants were separated by centrifugation and used for quantification of Gly or HA that remained in solution.

The effect of HA on the adsorption of Gly was investigated by performing Gly adsorption isotherms to goethite samples that were subjected first to HA adsorption. 0.7 mL of the stock goethite suspension were added to 15 mL polypropylene centrifuge tubes containing 10 mL of an aqueous solution of the desired HA concentration. The pH was adjusted and the suspensions were shaken for 6 h to produce the HA adsorption. Once HA was adsorbed on the goethite particles, Gly solutions of increasing concentrations were added to the tubes, the pH was readjusted if necessary, and the resulting suspensions were shaken again for 6 h. The supernatants were then separated by centrifugation and used for quantification of Gly and HA. All experiments were done at pH 7.0 in 0.1 M NaCl, where Gly and HA are in their anionic forms.

The concentration of Gly in the supernatant was measured by UV–vis spectrophotometry after a derivatization step with FMOC-Cl (fluorenylmethyloxycarbonyl chloride) in alkaline media. A full description of the method can be found elsewhere (Waiman et al., 2012). The spectra were recorded in the 200–900 nm wavelength range and the absorbance at 265 nm was used for quantification. The concentration of HA in the supernatant was also measured by UV–vis spectroscopy. The spectra were recorded and the HA concentration was then evaluated from the absorbance at 500 nm. In both cases, calibration curves were constructed with Gly and HA solutions prepared at pH 7.0 in 0.1 M NaCl. An Agilent 8453 UV–Vis diode array spectrophotometer equipped with a Hellma 1-cm quartz cell was used for absorbance readings.

### 2.3. ATR-FTIR measurements

ATR-FTIR spectra were acquired with a Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS detector, a SMART-ARK ATR accessory and a ZnSe crystal (area:  $10 \times 72 \text{ mm}$ , incident angle:  $45^\circ$ , total reflections: 12, trough cell). A film of goethite particles was prepared on the ZnSe crystal by placing  $210 \mu\text{L}$  of the  $9.63 \text{ g L}^{-1}$  goethite stock suspension on the crystal and evaporating to dryness at room temperature. The so-prepared film was covered with 1 mL of a 0.1 M NaCl solution and a blank spectrum was recorded. The NaCl solution was then replaced by either a HA or a Gly solution of the desired concentration and spectra were recorded as a function of time. Each spectrum is the result of the average of 256 scans, with a spectral resolution of  $4 \text{ cm}^{-1}$ . The time needed to collect each spectrum was 3 min. Gly and HA solutions were always prepared at pH 7.0 and in 0.1 M NaCl.

ATR-FTIR spectroscopy was used to perform two main types of experiments in order to investigate the effects of HA on Gly adsorption and desorption. They are described below.

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