Research article

Interaction between glyphosate and montmorillonite in the presence of artificial seawater

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ABSTRACT

Glyphosate (N-(phosphonomethyl) glycine) is one of the most widely used herbicides in the world. In the literature, there are several studies describing the interaction between glyphosate and clay minerals. However, there is a lack of data of this interaction in marine environments. In this research, we examined the adsorption of glyphosate onto montmorillonite in the presence of artificial seawater. Mössbauer data showed that the interaction of the phosphonate group of glyphosate with Fe2+ of montmorillonite prevents its oxidation to Fe3+. X-ray diffractograms showed that glyphosate adsorption takes place only onto the montmorillonite surface and not in its interlayers. Infrared spectroscopy data demonstrate that the interaction between glyphosate and montmorillonite could be through the amino group. FT-IR spectra of aqueous solutions of salts of seawater showed that Ca2+ interacts with glyphosate of the phosphonate group, thus causing an increase in its adsorption onto montmorillonite. However, glyphosate dissolved in 0.50 mol L−1 NaCl and 0.034 mol L−1 MgCl2 solutions showed the lowest adsorption onto montmorillonite. In addition, the adsorption of glyphosate onto montmorillonite decreased when the NaCl concentration increased. The results fitted the Sips isotherm model, probably because the Ca2+ interacts with glyphosate, making the adsorption process more homogeneous. Thus, n values for Freundlich and Sips isotherm models decreased with an increase in ionic strength. Glyphosate and ions of artificial seawater increased the pHpzc of montmorillonite.

1. Introduction

Glyphosate, also known as N-(phosphonomethyl) glycine (C3H8NO5P), has molecular weight of 169.1 g mol−1. It is a non-selective, systemic and post-emergent enzymatic inhibitor herbicide, toxicological class IV, meaning it has low toxicity (Andrei, 1999; Toni et al., 2006). Glyphosate was discovered by group of scientists led by Dr. John Franz at Monsanto in 1970 and commercial compositions of glyphosate have been presented as water-soluble salt since 1971 (Franz, 1985).

Behrens and Elakkad (1972) and Rioux et al. (1974) were one of the first to study the effects of glyphosate on noxious weeds, proving its efficiency in the enzymatic inhibition of plants, thus preventing its growth. When applied, glyphosate is absorbed by plant leaves acting as an inhibitor of the enzyme 5-enolpyruvyl-shikimate-3-phosphate synthetase (EPSPS), and thereby interferes with the biosynthesis of the aromatic amino acids phenylalanine, tyrosine and tryptophan and secondary compounds such as alkaloids and flavonoids (Anderson and Johnson, 1990; Roberts et al., 1998; Alibhai and Stallings, 2001; Schönbrunn et al., 2001).

Most of the applied glyphosate reaches the soil in its original form. Once in soil, it could be adsorbed by clay minerals (de Santana et al., 2006; Damonte et al., 2007; da Cruz et al., 2007; Pessagno et al., 2008; Khoury et al., 2010) or iron oxides (Dideriksen and Borggaard, 2007; Pessagno et al., 2008; Ahmed et al., 2018a; Orcelli et al., 2018; Pereira et al., 2019) or organic matter of the soil (Day et al., 1997; da Cruz et al., 2007; Gros et al., 2017; Ahmed et al., 2018b). Also, glyphosate could be decomposed by microorganism of the soils (Sprankle et al., 1975; Zhan et al., 2018). Glyphosate interacts with peptides/proteins and soil organic matter through carboxyl and phosphonate groups (Gros et al., 2017; Ahmed et al., 2018b). The interaction between glyphosate and peptides/proteins interfered in the formation of glyphosate-FMOC complex (Ahmed et al., 2018b). In addition,
glyphosate could interact with metals from the soils (Gros et al., 2019). However, even when adsorbed, glyphosate could be washed out to groundwater or rivers (Vereecken, 2005; Borggaard and Gimsing, 2008), and later reach the sea (Skeff et al., 2015). There are several processes that could wash out glyphosate from soils including: saline irrigation water, soluble fertilizers, weathering of rocks by rain (Dion et al., 2001; Vereecken, 2005; Borggaard and Gimsing, 2008). Depending on iron oxide composition in the soil, glyphosate could be more easily washed out of the soil (Orcelli et al., 2018; Pereira et al., 2019). However, the interaction between glyphosate and iron oxides is very complex, since glyphosate binds to each surface plane of goethite with different strengths (Ahmed et al., 2018a).

Glyphosate could be considered moderately persistent herbicide in marine environments under low light conditions and a highly persistent under dark conditions (Mercurio et al., 2014). Among the several effects of glyphosate on the metabolism of fishes, the followings could be high light hematologic and liver histological alterations, reduction in several enzymes and damage to DNA (do Carmo Langiano and Martinez, 2008; Moreno et al., 2014).

Several suspended minerals could be found in seawater such as carbonates, silicates, feldspars and clays (Velde, 1977; Bearman et al., 2004). Due to theirs high surface area and widely distribution in the world, clay minerals are one of the most important minerals in the herbicide adsorption studies. Montmorillonite, clay-mineral, belongs to the group of filosilicates. It is a 2:1 mineral, made up of two tetrahedral sheets of Si4+ with an octahedral sheet of Al3+ between them. They are bonded through the sharing of oxygens. Due to isomorphic substitutions of Al3+ by ions such as Mg2+ or Fe2+ and of Si4+ by Al3+, its surface is negatively charged over a wide pH range. In addition, cations and/or molecules must enter between the layers (Velde, 1977; Damonte et al., 2007).

pH, surface area and amount of metals are among of the several aspects that are important in the glyphosate adsorption onto clay minerals. The adsorption of glyphosate onto clay minerals decreased when the pH increased (Mcconnell and Hossner, 1985; Glass, 1987; da Cruz et al., 2007; Damonte et al., 2007; Khoury et al., 2010; Flores et al., 2018). Probably because of the increase of negative charges onto minerals and in the glyphosate molecule. However, in clay minerals saturated with Al3+, the formation of aluminum hydroxide polymers may occur in the interlayers of the clay, reducing the negative charge and providing more sites for adsorption of anions (Mcconnell and Hossner, 1985). Thus, the adsorption of glyphosate on these clays does not decrease with pH increasing. In clay minerals saturated with higher-charge cations was also observed higher glyphosate adsorption. Since the phosphonate group of glyphosate interacts with metals (Fe, Al, Cu), thus an increase of the content of these metals in clay increases the glyphosate adsorption (Mcconnell and Hossner, 1985; Motekaitis and Martell, 1985; Morillo et al., 1997, 2000; Ren et al., 2014). Surface area is also an important parameter for the adsorption of glyphosate (Mcconnell and Hossner, 1985; Glass, 1987; da Cruz et al., 2007). An increase in the surface of the clay increases the adsorption of glyphosate.

Since in the literature, there is a great dearth of studies on the interaction of glyphosate with minerals on marine environments and because montmorillonite is an important adsorber of organic micro pollutants, more studies are needed. Thus, in the present work we study the interaction with and adsorption of glyphosate onto montmorillonite with and without artificial seawater and salts using adsorption isotherms models, spectroscopic techniques and X-ray diffractometry.

2. Materials and methods

All the reagents were of analytical grade P.A. Milli-Q water was used in all experiments, which has a conductivity of 0.06 μS/cm.
2.2. UV spectrophotometry

A spectrophotometer UV-Vis Spectrum SP-2000UV was used in the quantification of glyphosate. This quantification was performed according to the method described by Bhaskara and Nagaraja (2006), which uses sodium molybdate as a catalyst for the reaction between glyphosate and ninhydrin, giving a violet compound with maximum absorbance at 570 nm.

To quantify glyphosate, in a test tube was added 1 mL of the sample, 1 mL of 2.5% (w/v) sodium molybdate solution and 1 mL of 2.5% (w/v) ninhydrin solution. The solution was stirred and heated in a water bath at 100 °C for 5 min. After cooling the solution, the glyphosate was quantified using the UV-Vis spectrophotometer at 570 nm. The limits of detection and quantification were 9.47 mg L⁻¹ and 32.63 mg L⁻¹, respectively. The calibration curve showed a coefficient of determination (R²) of 0.998.

2.2.3. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained using a Bruker FT-IR spectrophotometer, model Vertex 70, with Platinum ATR reflectance accessory. The spectral resolution was of 4 cm⁻¹ using 16 scans and the spectra were recorded from 400 to 4000 cm⁻¹.

2.2.4. Determination of pH at point of zero charge (pHpzc)

The pHpzc of montmorillonite was determined from its suspension. In two Eppendorf tubes with 2 mL was added 50 mg of montmorillonite. In one tube, 125 μL of ultrapure water was added in the other 125 μL of 0.1 mol L⁻¹ KCl solution. The samples were stirred for 30 min and after 24 h the pH was measured. This experiment was performed in triplicate. The pHpzc was calculated using the equation: pHpzc = 2 pH (1.0 mol L⁻¹ KCl) - pH (ultrapure water) (Uehara, 1979).

2.2.5. Na⁺, K⁺ and Ca²⁺ quantification

Na⁺, K⁺, and Ca²⁺ concentrations were measured by injecting the sample into a flame photometer (AJMicronal Flame Photometer - B 462). Standard curves were prepared by diluting a Na⁺, K⁺, and Ca²⁺ stock solution of 1000 mg L⁻¹ (Merck) to concentrations ranging from 10.0 mg L⁻¹ to 100 mg L⁻¹ (AWWA-APHA-WPCI, 2006).

2.2.6. Mg²⁺ quantification

Mg²⁺ and Ca²⁺ ions were quantified by complexation with EDTA at pH = 10 using eriochrome black T as indicator (Diehl et al., 1950). The concentration of Mg²⁺ was determined by subtracting the Ca²⁺ concentration obtained through the flame photometer.

2.2.7. X-ray diffraction

The samples were analyzed by powder X-ray diffraction using a Shimadzu equipment, model XRD 6000, using Cu Kα radiation and nickel filter, operating at 30 mA and 40 kV, in a step scan of 0.02° 20 for 0.6 s and amplitude of 5 to 65° 20. The samples were also analyzed as oriented aggregates and treated with ethylene-glycol-monoethyl-ether. This treatment was achieved by exposing them to a saturated atmosphere with ethylene glycol vapor at room temperature in a desiccator for a minimum of 12 h and then measuring using the XRD.

2.2.8. Mossbauer spectroscopy

Mossbauer spectroscopy was performed in transmission geometry, using a conventional Mössbauer spectrometer, operating in constant eleration mode, at room temperature. A ⁵⁷Co(Rh) source was used to generate the γ-rays, with an initial nominal activity of 50 mCi. A velocity range of ±11.4 mm s⁻¹ was used. The Mössbauer spectra were analyzed with a non-linear least-squares routine, with Lorentzian line shapes. All isomer shift (IS) data given were measured in relation to α-Fe.

2.2.9. Statistical analysis

The Tukey test was performed to analyze the adsorption differences, with a significance level of p < 0.05.

3. Results and discussion

The pHpzc of montmorillonite was 1.21 (Table 1), meaning that this mineral is positively charged when pH is below this value and is negatively charged when pH is above this value (Parés and de Bruyn, 1962). Carneiro et al. (2011) found a pHpzc value of 1.42 for unmodified montmorillonite. Flores et al. (2018) and Khoury et al. (2010) also found a similar result for natural montmorillonite pHpzc (2.7).

In the presence of artificial seawater, the pHpzc of montmorillonite value was not statistically different from the mineral without seawater ions (Table 1). Thus, the pHpzc value did not change, because the cation concentrations before and after artificial seawater were not statistically different from each other (Figure 1, p > 0.05). However, Farias et al. (2014) observed that Mg²⁺ adsorbed onto montmorillonite, but Ca²⁺ and K⁺ did not adsorb. It should be noted that the montmorillonite used by Farias et al. (2014) was sieved through 53 μm and saturated with sodium chloride. The montmorillonite used in this work was used as received.

The highest increase of pHpzc was in the presence of seawater plus glyphosate (Table 1). Besides the values between the cation concentrations before and after artificial seawater was mixed with glyphosate plus montmorillonite were not statistically different from each other (Figure 1, p > 0.05), probably glyphosate is carrying low quantity of cations to the surface of mineral increasing its pHpzc.

Montmorillonite, without further preparation, exhibits original baseline d001 reflection spacing of 13.41 Å and after treatment with ethylene glycol expands to 17.06 Å (Figure 2, Table 2), which means the ethylene glycol enters in the montmorillonite interlayers.

**Table 1. pH values at the point of zero charge (pHpzc) of montmorillonites before and after glyphosate adsorption.**

| Montmorillonite | without glyphosate | with glyphosate |
|----------------|--------------------|----------------|
| distilled water | 1.2 ± 0.1ᵃ         | 2.9 ± 0.5ᵇ     |
| seawater        | 2.0 ± 0.1ᵃ         | 4.4 ± 0.1ᵇ     |

The results are presented as mean ± standard deviation of mean. Each result was a mean of three experiments. Averages with distinct lowercase letters are statistically different from each other by the Tukey test (p < 0.05). These adsorptions were carried out at pH 7.0 with glyphosate initial concentration of 800 mg L⁻¹.
The addition of distilled water to montmorillonite expanded the d001 reflection to 15.32 Å and when treated with ethylene glycol to 17.23 Å. The addition of artificial seawater with or without glyphosate and 0.1 mol L\(^{-1}\) NaCl with or without glyphosate expanded the clay to values greater than the original, but lower than those with distilled water (Figure 2, Table 2). The treatment of these samples with ethylene glycol showed that it enters in the montmorillonite interlayers (Table 2). This small variation in basal montmorillonite spacing demonstrates that glyphosate did not enter in the montmorillonite interlayer. However, Khoury et al. (2010) and Flores et al. (2018) using the following conditions pH 2.0 and 30 mmol L\(^{-1}\) of glyphosate and pH 2.0 and 8.7 mmol L\(^{-1}\) of glyphosate, respectively, observed that glyphosate enters in the montmorillonite interlayers. The entrance of glyphosate in the montmorillonite interlayers was dependent on its concentration as well as net charge of it (Khoury et al., 2010). Ren et al. (2014) used montmorillonite modified with Fe\(^{3+}\) to remove glyphosate from wastewater. Under acidic

Table 2. Spacing of the d001 (Å) plane of montmorillonite and montmorillonite with distilled water, 0.1 mol L\(^{-1}\) NaCl and seawater with and without glyphosate before and after the treatment with ethylene glycol.

| Treatments                  | 25 °C | ethylene glycol |
|-----------------------------|-------|-----------------|
| M                           | 13.41 | 17.06           |
| M + distilled water         | 15.32 | 17.23           |
| M + 0.1 mol L\(^{-1}\) NaCl | 14.70 | 17.50           |
| M + seawater                | 14.64 | 17.13           |
| M + distilled water + GPS   | 14.13 | 17.52           |
| M + 0.1 mol L\(^{-1}\) NaCl + GPS | 14.64 | 17.37           |
| M + seawater + GPS          | 13.81 | 17.29           |

\(M\) = montmorillonite; GPS: glyphosate. The samples with glyphosate were obtained after an adsorption experiment with initial glyphosate concentration of 800 mg L\(^{-1}\). The addition of distilled water to montmorillonite expanded the d001 reflection to 15.32 Å and when treated with ethylene glycol to 17.23 Å. The addition of artificial seawater with or without glyphosate and 0.1 mol L\(^{-1}\) NaCl with or without glyphosate expanded the clay to values greater than the original, but lower than those with distilled water (Figure 2, Table 2). The treatment of these samples with ethylene glycol showed that it enters in the montmorillonite interlayers (Table 2). This small variation in basal montmorillonite spacing demonstrates that glyphosate did not enter in the montmorillonite interlayer. However, Khoury et al. (2010) and Flores et al. (2018) using the following conditions pH 2.0 and 30 mmol L\(^{-1}\) of glyphosate and pH 2.0 and 8.7 mmol L\(^{-1}\) of glyphosate, respectively, observed that glyphosate enters in the montmorillonite interlayers. The entrance of glyphosate in the montmorillonite interlayers was dependent on its concentration as well as net charge of it (Khoury et al., 2010). Ren et al. (2014) used montmorillonite modified with Fe\(^{3+}\) to remove glyphosate from wastewater. Under acidic
pH conditions the authors observed that both Fe$^{3+}$ and glyphosate enters in the montmorillonite interlayer. In addition, after heating montmorillonite at 550 °C, Damonte et al. (2007) observed that glyphosate enters in the montmorillonite interlayers under acidic pH. These conditions are very different from this work, 4.73 mmol L$^{-1}$ of glyphosate and pH 7.0, thus glyphosate has one positive charge at amino group, one negative charge at carboxyl group and two negative charges at phosphonate group (Figure 3). Because interlayers of montmorillonite are negatively charged, glyphosate enters more easily in the montmorillonite interlayers when its concentration is high and its molecule is positively charged (Khoury et al., 2010; Ren et al., 2014; Flores et al., 2018). Thus, in the present work we can affirm that sorption process of glyphosate onto montmorillonite was through adsorption, meaning glyphosate adsorbed onto the surface of the mineral.

In general, the experimental results were better fitted to the Sips isotherm model (Table 3, Figure 4). Also, for this isotherm model the confidence intervals were low (Table 4). In order to compare the validity of the isotherm equations more definitely, the normalized

![Figure 3](image_url). Molecular structure of glyphosate at different values of pH: pk$_1$ = 2.0; pk$_2$ = 2.6; pk$_3$ = 5.6; pk$_4$ = 10.6 (Sprankle et al., 1975).

### Table 3. Parameters of non-linear adsorption isotherm models for the adsorption of glyphosate onto montmorillonite.

| Solution          | Model  | K     | n | b     | R$^2$ | Δg (%) |
|-------------------|--------|-------|---|-------|-------|--------|
| Distilled water   | Lang   | 0.0784| - | 30.97 | 0.6545| 27.8   |
|                   | Freund | 26.350| 0.020| -     | 0.7615| 63.3   |
|                   | Sips   | 0.0492| 6.906| 29.91 | 0.9405| 7.2    |
|                   | 2-Sips | 1.9060| 4.784| 0.981 | 0.9405| 7.2    |
|                   |        | 0.0486| 6.999| 28.93 |       |        |
| 0.1 mol L$^{-1}$NaCl | Lang   | 0.0547| - | 32.46 | 0.8152| 19.0   |
|                   | Freund | 14.860| 0.117| -     | 0.5064| 36.9   |
|                   | Sips   | 0.0443| 2.246| 30.82 | 0.9443| 7.6    |
|                   | 2-Sips | 10380| 0.448| 0.937 | 0.9446| 7.5    |
|                   |        | 0.0431| 2.233| 29.89 |       |        |
| 0.5 mol L$^{-1}$NaCl | Lang   | 0.0009| - | 38.28 | 0.9453| 32.3   |
|                   | Freund | 0.2674| 0.609| -     | 0.9223| 29.5   |
|                   | Sips   | 0.0017| 1.390| 28.14 | 0.9513| 42.2   |
|                   | 2-Sips | 0.0033| 1.460| 6.624 | 0.3575| 98.4   |
|                   |        | 6.7280| 5.704| 7.372 |       |        |
| 0.01 mol L$^{-1}$CaCl$_2$ | Lang   | 0.0024| - | 80.44 | 0.9883| 13.9   |
|                   | Freund | 2.1870| 0.471| -     | 0.9667| 26.9   |
|                   | Sips   | 0.0021| 0.928| 85.64 | 0.9888| 10.7   |
|                   | 2-Sips | 0.0019| 5.886| 18.20 | 0.9988| 4.5    |
|                   |        | 0.0063| 1.066| 46.01 |       |        |
| 0.034 mol L$^{-1}$MgCl$_2$ | Lang   | 0.0110| - | 26.14 | 0.9430| 13.1   |
|                   | Freund | 4.7650| 0.237| -     | 0.9894| 12.8   |
|                   | Sips   | 0.0048| 0.538| 34.69 | 0.9828| 6.7    |
|                   | 2-Sips | 0.0059| 0.581| 32.04 | 0.9835| 5.8    |
|                   |        | 0.0168| 18.38| 0.543 |       |        |
| Seawater          | Lang   | 0.0053| - | 72.97 | 0.9799| 20.8   |
|                   | Freund | 3.9520| 0.4111| -     | 0.9268| 50.7   |
|                   | Sips   | 0.0063| 1.168| 67.13 | 0.9822| 15.0   |
|                   | 2-Sips | 0.0097| 1.539| 31.76 | 0.6273| 68.8   |
|                   |        | 0.5657| 2.596| 13.88 |       |        |

Each result was mean of three experiments. The solutions were stirred for 24 h at 30 °C, at pH 7.0 with 60 mg of montmorillonite. Lang: Langmuir; Freund: Freundlich; Sips: Sips one site; 2-Sips: Sips two sites. K (Langmuir) (L mg$^{-1}$) and K (Freundlich) (mg g$^{-1}$) (L g$^{-1}$): adsorbate-adsorbent affinities; b: maximum adsorption capacity (mg g$^{-1}$); n: empiric Freundlich constant.
standard deviation, $\Delta g$ (%), was calculated using Eq. (5) (Manohar et al., 2006).

$$\Delta g(\%) = 100 \sqrt{\frac{\sum (\theta^{\text{exp}} - \theta^{\text{cal}})^2}{N - 1}}$$  \hspace{1cm} (5)$$

where superscripts 'exp' and 'cal' show the experimental and calculated values and N is the number of measurements. It can be observed that the Sips and 2-sites Sips models showed the best fit in most cases, based on the $\Delta g$ values. However, the 2-site Sips parameters showed high confidence interval values (Table 4).

Langmuir and Freundlich isotherm models also presented a good fit for glyphosate dissolved in 0.5 mol L$^{-1}$NaCl solution, artificial seawater solution, CaCl$_2$ solution and MgCl$_2$ solution (Table 3). In addition, in general, confidence intervals were low (Table 4). Ren et al. (2014) observed that their results were better fit to the Freundlich isotherm model than the Langmuir isotherm model. They attributed this better fit in the Freundlich isotherm model to heterogeneity of montmorillonite adsorption sites. However, Pessagno et al. (2008) and Khoury et al. (2010) did not obtain a good fit using the Langmuir isotherm model and the Langmuir and the Freundlich isotherm models, respectively. It should be noted that they worked with glyphosate dissolved in high NaCl concentration. According to the authors the adsorption of glyphosate onto montmorillonite occurred in successive steps, meaning when a first monolayer was completed a second monolayer starts.

For the samples of glyphosate dissolved in distilled water, 0.1 mol L$^{-1}$NaCl solution, CaCl$_2$ solution and MgCl$_2$ solution, the data also fitted well.

**Table 4. Confidence intervals of the parameters presented at Table 1.**

| Solution          | Model    | K (Langmuir) (L mg$^{-1}$) | n (Freundlich) (mg g$^{-1}$) | b (Langmuir) (L mg$^{-1}$) |
|-------------------|----------|-----------------------------|-----------------------------|-----------------------------|
| Distilled water   | Lang     | 0.0981                      | -                           | 5.29                        |
|                   | Freund   | 11.69                       | 0.0157                      | -                           |
|                   | Sips     | 0.0053                      | 0.365                       | 2.36                        |
|                   | 2-Sips   | *                           | *                           | *                           |
| 0.5 mol L$^{-1}$NaCl | Lang     | 0.0443                      | -                           | 3.79                        |
|                   | Freund   | 11.007                      | 0.128                       | -                           |
|                   | Sips     | 0.0112                      | 1.454                       | 2.05                        |
|                   | 2-Sips   | *                           | *                           | *                           |
| 0.01 mol L$^{-1}$CaCl$_2$ | Lang     | 0.00068                     | -                           | 14.73                       |
|                   | Freund   | 0.3363                      | 0.1825                      | -                           |
|                   | Sips     | 0.00103                     | 0.9724                      | 5.26                        |
|                   | 2-Sips   | 0.0541                      | 40.62                       | 119.7                       |
|                   |          | 5.07                        | 258.2                       | 748.6                       |
| 0.034 mol L$^{-1}$MgCl$_2$ | Lang     | 0.00041                     | -                           | 1.94                        |
|                   | Freund   | 0.683                       | 0.022                       | -                           |
|                   | Sips     | 0.0021                      | 0.1577                      | 8.22                        |
|                   | 2-Sips   | 0.0078                      | 11.5                        | 755.2                       |
|                   |          | 231.2                       | *                           | 625.6                       |
| Seawater          | Lang     | 0.0015                      | -                           | 6.85                        |
|                   | Freund   | 2.765                       | 0.1125                      | -                           |
|                   | Sips     | 0.00208                     | 0.412                       | 9.35                        |
|                   | 2-Sips   | 2.169                       | 83.31                       | 8499                        |
|                   |          | *                           | *                           | 8398                        |

The results are given as ± the error margin. *error margin higher than 1.0E+5. Lang: Langmuir; Freund: Freundlich; Sips: Sips single site; 2-Sips: Sips dual site. K (Langmuir) (L mg$^{-1}$) and K (Freundlich) (mg g$^{-1}$) (L g$^{-1}$); adsorbate-adsorbent affinities; b: maximum adsorption capacity (mg g$^{-1}$); n: empiric Freundlich constant.
to the 2-site Sips isotherm model. However, the confidence intervals for these samples are very high (Table 4), what makes these results unreliable.

The highest values of maximum adsorption capacity were obtained for the samples containing Ca$^{2+}$ (artificial seawater, 0.010 mol L$^{-1}$-CaCl$_2$) (Table 3). The high glyphosate adsorption onto montmorillonite probably occurs due to the formation of a complex between Ca$^{2+}$ ions and glyphosate, which may facilitate glyphosate interaction with the mineral. Since the Ca$^{2+}$-glyphosate complex does not present a high stability constant, it is probable Ca$^{2+}$ is released to the solution after glyphosate adsorption (Madsen et al., 1978; Caetano et al., 2012). It should be noted that the stability of Fe$^{3+}$ or Al$^{3+}$/glyphosate complexes is higher than the stability of the Mg$^{2+}$-glyosphate complex (Caetano et al., 2012). FT-IR spectra of aqueous solutions of glyphosate plus salts of seawater presented a shoulder at 1126 cm$^{-1}$ for the sample containing Ca$^{2+}$ (Figure not shown). For all other samples this band was not observed. This is an indication that the phosphonate group of glyphosate interacts with Ca$^{2+}$ causing an increase of its adsorption onto montmorillonite. It should be noted that at pH 7.0, glyphosate has two negative charges at the phosphonate group and one negative charge at the carboxyl group (Figure 3), what makes it a good chelating for Ca$^{2+}$ ions (Gauvrit et al., 2001). No interaction between glyphosate and Mg$^{2+}$ was observed, probably because the stability of the Ca$^{2+}$/glyosphate complex is higher than the stability of the Mg$^{2+}$/glyosphate complex (Caetano et al., 2012).

In general, for the samples of glyphosate dissolved in distilled water, or 0.10 mol L$^{-1}$NaCl solution, there is a good agreement among the maximum adsorption capacity values obtained with Langmuir and Sips models (Table 3). However, for the other samples, maximum adsorption capacity values were different from each other (Table 3). In addition, an increase in NaCl concentration decreased the amount of glyphosate adsorbed onto montmorillonite. The amino group interacting with mineral it was the carboxyl group of glyphosate.

For the Sips and Freundlich isotherm models, the ionic strength influenced n values (Table 3). For the Sips isotherm model, the n values decreased from 6.906 (distilled water) to 1.168 (artificial seawater) and they were lower than 1 for the samples of glyphosate dissolved in CaCl$_2$ and MgCl$_2$ (Table 3). For the Freundlich isotherm model, all n values were lower than 1 (Table 3). The n parameter could be related to system heterogeneity (Do, 1998). The system heterogeneity means that the adsorbent or the adsorbate or both are heterogeneous. Usually n values for the Freundlich and Sips isotherm models are higher than 1. Therefore, the higher the value of n, the more heterogeneous is the system (Do, 1998). Therefore, in general, ions of artificial seawater decreased the heterogeneity of the glyphosate adsorption onto montmorillonite process, since montmorillonite did not adsorb ions of artificial seawater (Figure 1). Thus, probably, the complexation of glyphosate by Ca$^{2+}$ ions made the glyphosate adsorption process more homogeneous. It should be noted that the Ca$^{2+}$/glyphosate complex has higher stability when compared to Mg$^{2+}$ (Caetano et al., 2012).

There are two main regions in the infrared spectrum of glyphosate, one with bands from 800 cm$^{-1}$ to 1300 cm$^{-1}$ belonged to the phosphonate group and second with bands from 1300 cm$^{-1}$ to 1800 cm$^{-1}$ belonged to the amino and carboxyl groups (Figure 5). Besides, the main interaction between glyphosate and metal of minerals occurs throughout the phosphonate group (Barja and dos Santos Afonso, 1998; Sheals et al., 2002; Orcelli et al., 2018; Pereira et al., 2019). We could not confirm this interaction, because montmorillonite presents several bands in the region between 1300-800 cm$^{-1}$ due to Al-OH (bending) and Si-O (stretching in the plane and out of the plane) (Nakamoto, 1978; Tyagi et al., 2006). However, when the interaction is through the phosphonate group, the two predominant species are monodentate and bidentate phosphonate complexes (Damonte et al., 2007). The FT-IR spectrum of solid glyphosate showed the following bands 1332 cm$^{-1}$, 1420 cm$^{-1}$, 1467 cm$^{-1}$, 1482 cm$^{-1}$, and 1554 cm$^{-1}$ (Figure 5), that could be attributed to deformation CH$_2$ symmetric stretching CO$_2$ group CH$_3$, deformations NH$_3$ and stretching C=O (Miano et al., 1992; Barja and dos Santos Afonso, 1998). However, after glyphosate was adsorbed onto montmorillonite, the bands belonged to deformations NH$_3$ and stretching C=O vanished and the bands at 1420 cm$^{-1}$ and 1432 cm$^{-1}$ shifted to one band at 1411 cm$^{-1}$ (Figure 5). At pH (7.00) of the experiments the amino group of glyphosate was not deprotonated (Figure 3), thus the band at 1630 cm$^{-1}$ could be attributed to interaction of the amino group with montmorillonite (Sheals et al., 2002; Orcelli et al., 2018; Pereira et al., 2019). However, Dideriksen and Stipp (2003) observed that instead of the amino group interacting with mineral it was the carboxyl group of glyphosate.

Figure 5. FT-IR spectra of glyphosate, montmorillonite, and glyphosate adsorbed on montmorillonite. M = montmorillonite; GPS = glyphosate, M-GPS = glyphosate adsorbed onto montmorillonite. Glyphosate (800 mg L$^{-1}$) was dissolved in distilled water and adsorbed onto montmorillonite.
Figure 6. Mössbauer spectra for the montmorillonites. M = montmorillonite, W = distilled water; SW = seawater; GPS = Glyphosate. The samples with glyphosate were obtained after an adsorption experiment with initial glyphosate concentration of 800 mg L⁻¹.

Table 5. Mössbauer hiperfines parameters and subspectral areas for the montmorillonites.

| Samples | subspectrum | \(\Gamma^\alpha \pm 0.02\) (mm/s) | \(\Delta\sigma^\alpha \pm 0.01\) (mm/s) | \(\Delta\sigma^\beta \pm 0.02\) (mm/s) | \(\Delta\sigma^\delta \pm 0.01\) (mm/s) |
|---------|-------------|----------------|----------------|----------------|----------------|
| M       | Doublet 1 (Fe³⁺) | 0.59 | 0.36 | 0.57 | 77.7 |
|         | Doublet 2 (Fe²⁺) | 0.90 | 1.29 | 2.51 | 22.3 |
| M/W     | Doublet 1 (Fe³⁺) | 0.73 | 0.33 | 0.55 | 92.6 |
|         | Doublet 2 (Fe²⁺) | 0.70* | 1.18 | 2.75* | 7.4 |
| M/W/GPS | Doublet 1 (Fe³⁺) | 0.67 | 0.34 | 0.56 | 88.3 |
|         | Doublet 2 (Fe²⁺) | 0.71 | 1.19 | 2.71 | 11.7 |
| M/SW    | Doublet 1 (Fe³⁺) | 0.71 | 0.35 | 0.59 | 89.3 |
|         | Doublet 2 (Fe²⁺) | 0.48 | 1.17 | 2.75 | 10.7 |
| M/SW/GPS | Doublet 1 (Fe³⁺) | 0.64 | 0.33 | 0.58 | 80.2 |
|         | Doublet 2 (Fe²⁺) | 1.09 | 1.23 | 2.67 | 19.8 |

M = montmorillonite, W = distilled water; SW = seawater; GPS = Glyphosate. The samples with glyphosate were obtained after an adsorption experiment with initial glyphosate concentration of 800 mg L⁻¹.\(^\text{1}\)Half-width of spectral lines; \(^\text{2}\)Isomer shift related to \(\alpha\)-Fe at room temperature; \(^\text{3}\)Quadrupole splitting. *Parameters set in the adjustment.
For all samples, two doublets were observed, one corresponding to Fe$^{3+}$ and the other to Fe$^{2+}$ (Figure 6, Table 5). For montmorillonite in the presence of distilled water or seawater, the doublet area corresponding to Fe$^{2+}$ decreased approximately 67% and 50%, respectively, when compared to montmorillonite without further preparation (Table 5). The oxidation of Fe$^{2+}$ to Fe$^{3+}$ occurred because the dissolved oxygen in the water. The area of the doublet corresponding to Fe$^{2+}$ presented the lowest decreasing for the sample of glyphosate dissolved in artificial seawater (Table 5). This could be an evidence that glyphosate is protecting Fe$^{2+}$ against oxidation by oxygen. It should be noted that the complex between Fe$^{3+}$ and glyphosate plays important roles in the transport of iron through cellular membrane (Motekiatis and Martelli, 1985; Tilquin et al., 2000).

4. Conclusions

After the adsorption of glyphosate onto montmorillonite its pH$_{pzc}$ increased, probably because glyphosate is carrying a small number of cations to the montmorillonite surface. However, it should be noted that the cation concentrations before and after artificial seawater was mixed with montmorillonite were not statistically different from each other (p > 0.05).

Glyphosate did not enter in the interlayer, because, at pH 7.0, glyphosate has an excess of three negative charges and the montmorillonite interlayer is also negatively charged. Thus, probably, glyphosate has an excess of three negative charges and the montmorillonite layer is negatively charged. Consequently, the fabricated doublet area corresponding to Fe$^{3+}$ presented the lowest decreasing for the sample of glyphosate dissolved in artificial seawater (Table 5). This could be an evidence that glyphosate is protecting Fe$^{2+}$ against oxidation by oxygen. It should be noted that the complex between Fe$^{3+}$ and glyphosate plays important roles in the transport of iron through the cellular membrane (Motekiatis and Martelli, 1985; Tilquin et al., 2000).

Declartions

Author contribution statement

Rodrigo C. Pereira: Performed the experiments; Analyzed and interpreted the data.
Antonio C. S. da Costa, Flavio F. Ivashita, Andrea Paesano Jr: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.
Dimas A. M. Zaia: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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