



## 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  $\text{Fe}^{2+}$  of montmorillonite prevents its oxidation to  $\text{Fe}^{3+}$ . 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  $\text{Ca}^{2+}$  interacts with glyphosate of the phosphonate group, thus causing an increase in its adsorption onto montmorillonite. However, glyphosate dissolved in 0.50 mol L<sup>-1</sup> NaCl and 0.034 mol L<sup>-1</sup> MgCl<sub>2</sub> 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  $\text{Ca}^{2+}$  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  $\text{pH}_{\text{pzc}}$  of montmorillonite.

## 1. Introduction

Glyphosate, also known as N-(phosphomethyl) glycine (C<sub>3</sub>H<sub>8</sub>NO<sub>5</sub>P), has molecular weight of 169.1 g mol<sup>-1</sup>. 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 Stipp, 2003; Gimsing 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 (Sprinkle 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,

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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 their 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 fillosilicates. It is a 2:1 mineral, made up of two tetrahedral sheets of Si<sup>4+</sup> with an octahedral sheet of Al<sup>3+</sup> between them. They are bonded through the sharing of oxygens. Due to isomorphic substitutions of Al<sup>3+</sup> by ions such as Mg<sup>2+</sup> or Fe<sup>2+</sup> and of Si<sup>4+</sup> by Al<sup>3+</sup>, 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 clays 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 Al<sup>3+</sup> ions, 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.

### 2.1. Materials

#### 2.1.1. Montmorillonite

Montmorillonite KSF (CAS 1318-93-0) was purchased from Acros-Organics-NJ, USA and it was used as received.

#### 2.1.2. Artificial seawater

Artificial seawater was made by dissolving the following salts in 1.0 L of distilled water: 28.57 g sodium chloride, 3.88 g magnesium chloride, 1.787 g magnesium sulphate, 1.308 g calcium sulphate, 0.832 g potassium sulphate, 0.103 g potassium bromide and 0.0282 g boric acid (Bearman et al., 2004).

### 2.2. Methods

#### 2.2.1. Adsorption of glyphosate onto montmorillonite

In order to obtain the adsorption isotherms, in 15 ml Falcon tubes a volume of 10 ml of glyphosate solutions ranging from 100 to 2000 mg L<sup>-1</sup> were mixed with 60 mg of montmorillonite (triplicates). This procedure was used for glyphosate dissolved in distilled water, 0.10 mol L<sup>-1</sup>NaCl; 0.50 mol L<sup>-1</sup>NaCl; 0.01 mol L<sup>-1</sup>CaCl<sub>2</sub>; 0.034 mol L<sup>-1</sup>MgCl<sub>2</sub>; and artificial seawater. The pH of the samples was adjusted to 7.0 using 0.10 mol L<sup>-1</sup> NaOH or 0.10 mol L<sup>-1</sup> HCl. Because this value is like the seawater pH (Bearman et al., 2004). The tubes were stirred for 24 h and then centrifuged for 15 min at 6,000 rpm. The aqueous phase was used for glyphosate quantification (Bhaskara and Nagaraja, 2006) and the solid was lyophilized for further analysis. This procedure was repeated without glyphosate.

The results of glyphosate adsorption onto montmorillonite were fitted to non-linear isotherm models: Langmuir, Freundlich, Langmuir-Freundlich-1 (1-site-Sips) and Langmuir-Freundlich-2 (2-site Sips) (Sips, 1948, 1950; Do, 1998; Jeppu and Clement, 2012).

Non-linear Langmuir isotherm model

$$\theta = \frac{k_{eq}bC}{(1 + C)} \quad (1)$$

where  $C$  (mg L<sup>-1</sup>) is concentration of glyphosate in solution after the equilibrium,  $\theta$  (mg g<sup>-1</sup>) is the concentration of glyphosate adsorbed onto montmorillonite (difference between initial glyphosate concentration and concentration after the equilibrium) by mass unity,  $b$  (mg g<sup>-1</sup>) is the theoretical limit of adsorbed glyphosate onto montmorillonite,  $k_{eq}$  (L mg<sup>-1</sup>) is equilibrium constant (adsorbate-adsorbent).

Non-linear Freundlich isotherm model

$$\theta = K_f C^n \quad (2)$$

where  $K_f$  is adsorption capacity of Freundlich and  $n$  is the index of heterogeneity.

Non-linear Langmuir-Freundlich-1 (one-site Sips) isotherm model

$$\theta = \frac{b(KC)^n}{1 + (KC)^n} \quad (3)$$

where  $b$  (mg g<sup>-1</sup>) is the theoretical limit of adsorbed glyphosate onto montmorillonite.  $K$  (L/mg) is the affinity constant for adsorption and  $n$  is the index of heterogeneity.

Non-linear Langmuir-Freundlich-2 (two-sites Sips) isotherm model

$$\theta = \frac{b_1(K_1C)^{n_1}}{1 + (K_1C)^{n_1}} + \frac{b_2(K_2C)^{n_2}}{1 + (K_2C)^{n_2}} \quad (4)$$

where  $b_1$  and  $b_2$  (mg g<sup>-1</sup>) are the theoretical limit of the two sites of adsorbed glyphosate onto montmorillonite.  $K_1$  and  $K_2$  are the affinity constant for adsorption  $n_1$  and  $n_2$  are the index of heterogeneity.

**Table 1.** pH values at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of montmorillonites before and after glyphosate adsorption.

	without glyphosate	with glyphosate
Montmorillonite in distilled water	$1.2 \pm 0.1^a$	$2.9 \pm 0.5^{a,b}$
Montmorillonite in seawater	$2.0 \pm 0.1^a$	$4.4 \pm 0.1^b$

The results are presented as mean  $\pm$  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  $800 \text{ mg L}^{-1}$ .

### 2.2.2. 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  $100^\circ\text{C}$  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  $9.47 \text{ mg L}^{-1}$  and  $32.63 \text{ mg L}^{-1}$ , respectively. The calibration curve showed a coefficient of determination ( $R^2$ ) 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  $4 \text{ cm}^{-1}$  using 16 scans and the spectra were recorded from 400 to  $4000 \text{ cm}^{-1}$ .

### 2.2.4. Determination of pH at point of zero charge ( $\text{pH}_{\text{pzc}}$ )

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

### 2.2.5. $\text{Na}^+$ , $\text{K}^+$ and $\text{Ca}^{2+}$ quantification

$\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  concentrations were measured by injecting the sample into a flame photometer (AJMicronal Flame Photometer - B 462). Standard curves were prepared by diluting a  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  stock solution of  $1000 \text{ mg L}^{-1}$  (Merck) to concentrations ranging from  $10.0 \text{ mg L}^{-1}$  to  $100 \text{ mg L}^{-1}$  (AWWA-APHA-WPCI, 2006).

### 2.2.6. $\text{Mg}^{2+}$ quantification

$\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were quantified by complexation with EDTA at  $\text{pH} = 10$  using eriochrome black T as indicator (Diehl et al., 1950). The concentration of  $\text{Mg}^{2+}$  was determined by subtracting the  $\text{Ca}^{2+}$  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  $\text{Cu K}\alpha$  radiation and nickel filter, operating at 30 mA and 40 kV, in a step scan of  $0.02^\circ 2\theta$  for 0.6 s and amplitude of  $5$  to  $65^\circ 2\theta$ . 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. Mössbauer spectroscopy

Mössbauer spectroscopy was performed in transmission geometry, using a conventional Mössbauerspectrometer, operating in constant eleration mode, at room temperature. A  $^{57}\text{Co}(\text{Rh})$  source was used to generate the  $\gamma$ -rays, with an initial nominal activity of 50 mCi. A velocity range of  $\pm 11.4 \text{ mm s}^{-1}$  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  $\alpha\text{-Fe}$ .

### 2.2.9. Statistical analysis

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

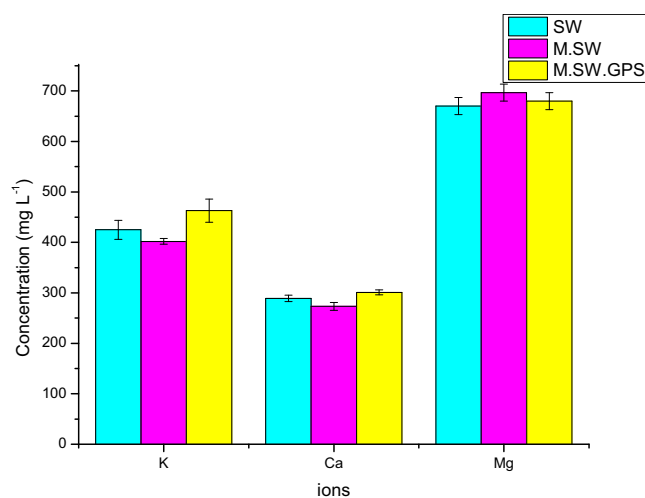
## 3. Results and discussion

The  $\text{pH}_{\text{pzc}}$  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 (Parks and de Bruyn, 1962). Carneiro et al. (2011) found a  $\text{pH}_{\text{pzc}}$  value of 1.42 for unmodified montmorillonite. Flores et al. (2018) and Khoury et al. (2010) also found a similar result for natural montmorillonite  $\text{pH}_{\text{pzc}}$  (2.7).

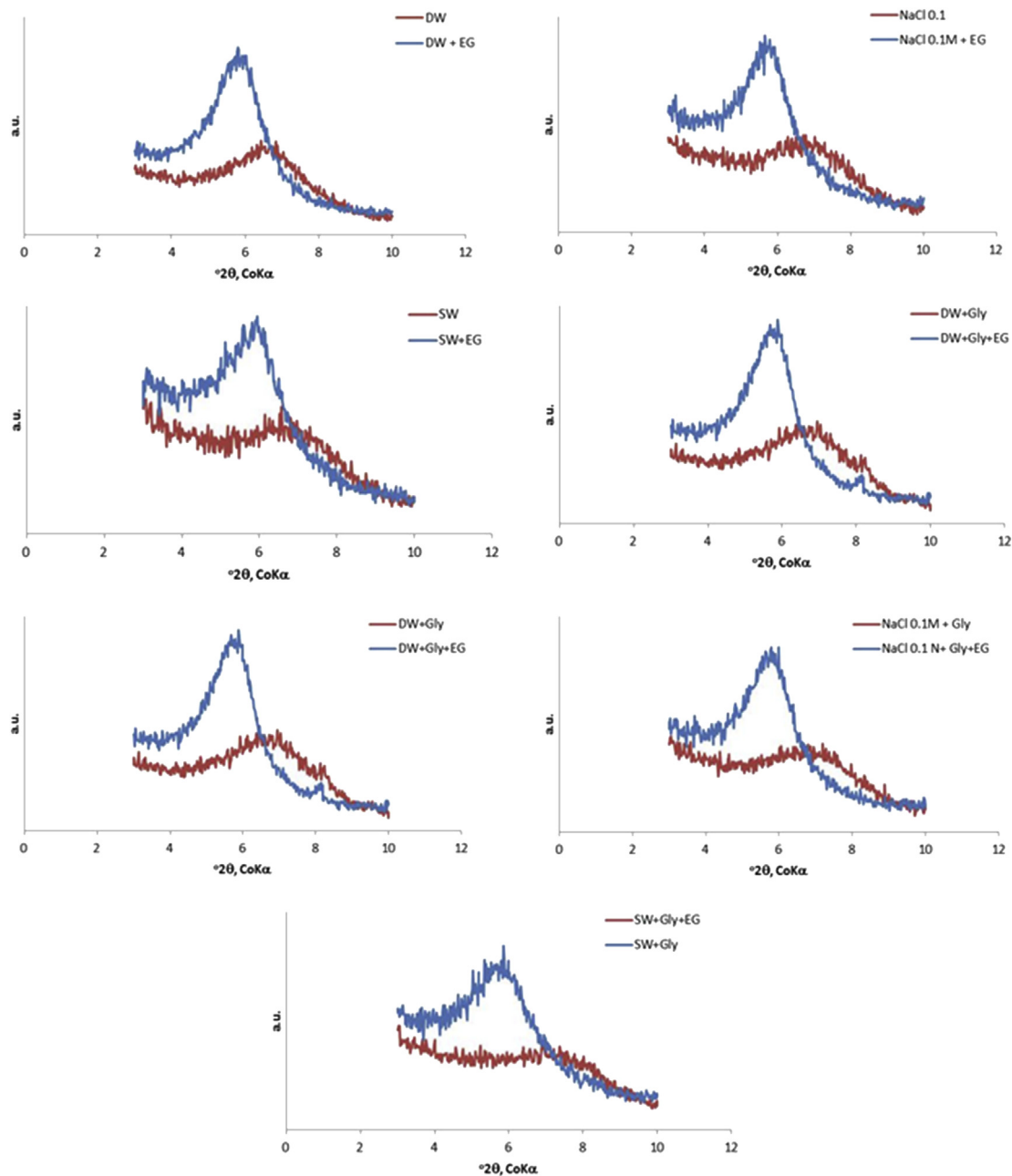
In the presence of artificial seawater, the  $\text{pH}_{\text{pzc}}$  montmorillonite value was not statistically different to the mineral without seawater ions (Table 1). Thus, the  $\text{pH}_{\text{pzc}}$  value did not change, because the cation concentrations before and after artificial seawater were not statistically different from each other (Figure 1,  $p > 0.05$ ). However, Farias et al. (2014) observed that  $\text{Mg}^{2+}$  adsorbed onto montmorillonite, but  $\text{Ca}^{2+}$  and  $\text{K}^+$  did not adsorb. It should be noted that the montmorillonite used by Farias et al. (2014) was sieved through  $53 \mu\text{m}$  and saturated with sodium chloride. The montmorillonite used in this work was used as received.

The highest increase of  $\text{pH}_{\text{pzc}}$  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  $\text{pH}_{\text{pzc}}$ .

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



**Figure 1.** Concentration of  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions ( $\text{mg L}^{-1}$ ) after adsorption onto montmorillonite using artificial seawater. The results are presented as mean  $\pm$  standard deviation of mean. The number of experiments was three. SW = artificial seawater, M-SW = montmorillonite plus artificial seawater, M-SW-GPS = montmorillonite plus glyphosate ( $800 \text{ mg L}^{-1}$ ) dissolved in artificial seawater. Artificial seawater was prepared as described by Bearman et al. (2004).



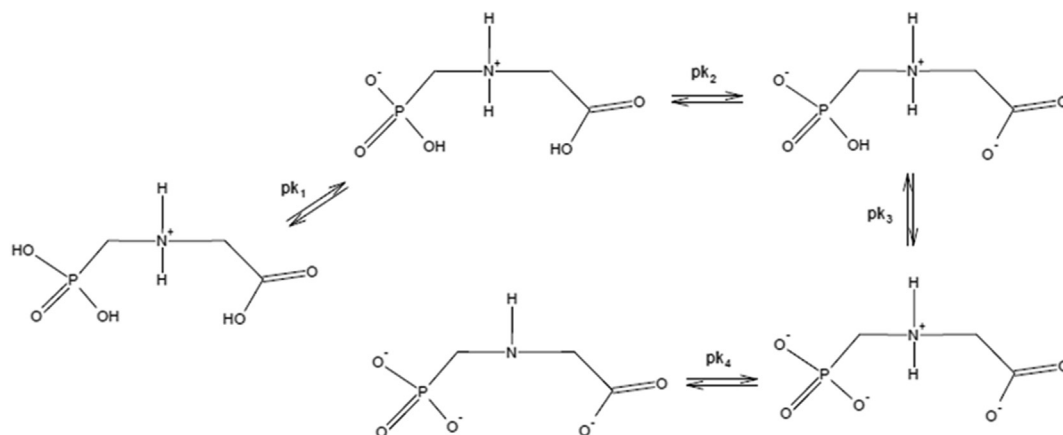
**Figure 2.** X-rays diffraction of treated montmorillonite with distilled water (DW), ethylene-glycol (EG), sea water (SW), glyphosate (Gly) and sodium chloride (NaCl 0.1M).

**Table 2.** Spacing of the d001 (Å) plane of montmorillonite and montmorillonite with distilled water, 0.1 mol L<sup>-1</sup> 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 <sup>-1</sup> NaCl	14.70	17.50
M + seawater	14.64	17.13
M + distilled water + GPS	14.13	17.52
M + 0.1 mol L <sup>-1</sup> 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<sup>-1</sup>.

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<sup>-1</sup> 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<sup>-1</sup> of glyphosate and pH 2.0 and 8.7 mmol L<sup>-1</sup> 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<sup>3+</sup> to remove glyphosate from wastewater. Under acidic



**Figure 3.** 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.

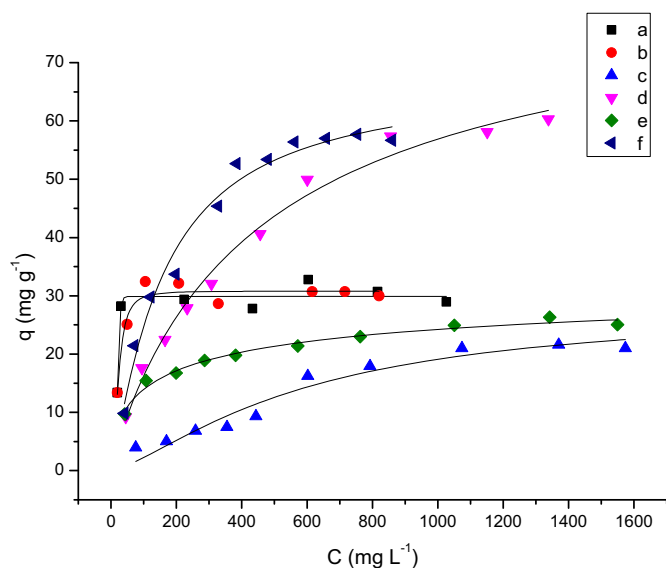
Solution	Model	K	n	b	R <sup>2</sup>	Δg (%)
Distilled water	Lang	0.0784	-	30.97	0.6545	27.8
	Freund	26.350	0.020	-	0.7615	63.3
	Sips	0.0492	6.906	29.91	0.9405	7.2
	2-Sips	1.9060 0.0486	4.784 6.999	0.981 28.93	0.9405	7.2
0.1 mol L <sup>-1</sup> NaCl	Lang	0.0547	-	32.46	0.8152	19.0
	Freund	14.860	0.117	-	0.5064	36.9
	Sips	0.0443	2.246	30.82	0.9443	7.6
	2-Sips	10380 0.0431	0.448 2.233	0.937 29.89	0.9446	7.5
0.5 mol L <sup>-1</sup> 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 6.7280	1.460 5.704	6.624 7.372	0.3575	98.4
0.01 mol L <sup>-1</sup> CaCl <sub>2</sub>	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 0.0063	5.886 1.066	18.20 46.01	0.9988	4.5
0.034 mol L <sup>-1</sup> MgCl <sub>2</sub>	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 0.0168	0.581 18.38	32.04 0.543	0.9835	5.8
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 0.5657	1.539 2.596	31.76 13.88	0.6273	68.8

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<sup>-1</sup>) and K (Freundlich) (mg g<sup>-1</sup>) (L g<sup>-1</sup>): adsorbate-adsorbent affinities; b: maximum adsorption capacity (mg g<sup>-1</sup>); n: empiric Freundlich constant.

pH conditions the authors observed that both Fe<sup>3+</sup> 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<sup>-1</sup> 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 4.** The fit of the non-linear Sips one site model to the data for adsorption of glyphosate onto montmorillonite with a) distilled water b) 0.10 mol L<sup>-1</sup>NaCl c) 0.50 mol L<sup>-1</sup> NaCl d) 0.01 mol L<sup>-1</sup>CaCl<sub>2</sub> e) 0.034 mol L<sup>-1</sup>MgCl<sub>2</sub> and f) artificial seawater. Each result was a mean of three experiments. The solutions were stirred for 24 h at 30 °C, at pH 7.0 with 60 mg of montmorillonite. C (mg L<sup>-1</sup>) is the concentration of glyphosate in solution after the equilibrium, q (mg g<sup>-1</sup>) was the amount of glyphosate adsorbed onto montmorillonite.

standard deviation, Δg (%), was calculated using Eq. (5) (Manohar et al., 2006).

$$\Delta g(\%) = 100 \times \sqrt{\frac{\sum [(\theta^{exp} - \theta^{cal}) / \theta^{exp}]^2}{N - 1}} \tag{5}$$

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 Δg values. However, the 2-site Sips parameters showed high confidence interval values (Table 4).

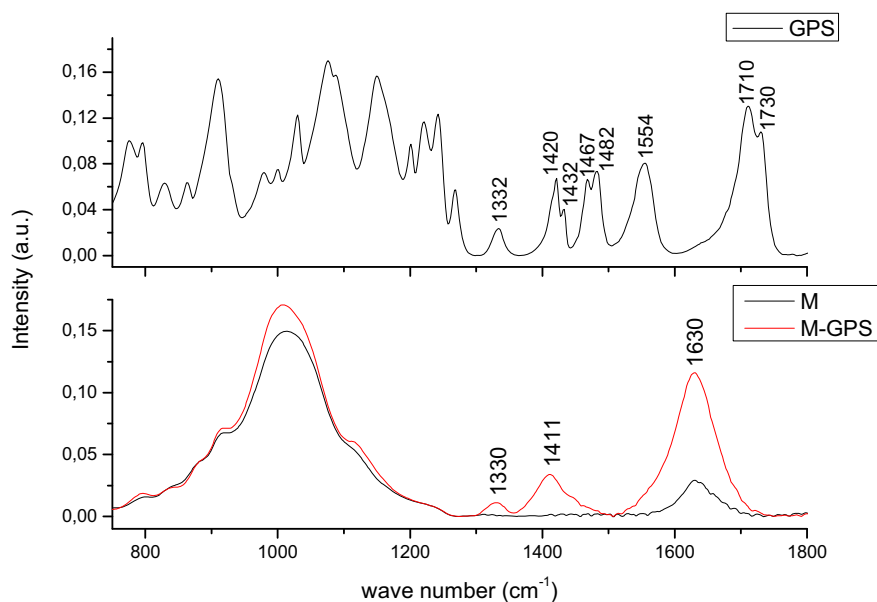
Langmuir and Freundlich isotherm models also presented a good fit for glyphosate dissolved in 0.5 mol L<sup>-1</sup>NaCl solution, artificial seawater solution, CaCl<sub>2</sub> solution and MgCl<sub>2</sub> solution (Table 3). In addition, in general, confidence intervals were low (Table 4). Ren et al. (2014) observed that their results were better fitted in 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 obtained 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<sup>-1</sup> NaCl solution, CaCl<sub>2</sub> solution andMgCl<sub>2</sub> solution, the data also fitted well

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

Solution	Model	K	n	b
Distilled water	Lang	0.0981	-	5.29
	Freund	11.69	0.0157	-
	Sips	0.0053	0.365	2.36
	2-Sips	*	*	*
		*	*	*
0.1 mol L <sup>-1</sup> NaCl	Lang	0.0443	-	3.79
	Freund	11.007	0.128	-
	Sips	0.0112	1.454	2.05
	2-Sips	*	*	6923
		5.07	258.2	7486
0.5 mol L <sup>-1</sup> NaCl	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
		*	*	76.18
0.01 mol L <sup>-1</sup> CaCl <sub>2</sub>	Lang	0.00061	-	8.14
	Freund	1.2739	0.0881	-
	Sips	0.00076	0.3237	19.73
	2-Sips	0.00023	1.457	5.63
		0.00435	0.681	40.33
0.034 mol L <sup>-1</sup> MgCl <sub>2</sub>	Lang	0.0041	-	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<sup>-1</sup>) and K (Freundlich) (mg g<sup>-1</sup>) (L g<sup>-1</sup>): adsorbate-adsorbent affinities; b: maximum adsorption capacity (mg g<sup>-1</sup>); n: empiric Freundlich constant.



**Figure 5.** FT-IR spectra of glyphosate, montmorillonite, and glyphosate adsorbed onto montmorillonite. M = montmorillonite; GPS = glyphosate, M-GPS = glyphosate adsorbed onto montmorillonite. Glyphosate ( $800 \text{ mg L}^{-1}$ ) was dissolved in distilled water and adsorbed onto montmorillonite.

to the 2-site Sips isotherm model. However, the confidence intervals for these samples are very high (Table 4), what makes these results unreliable.

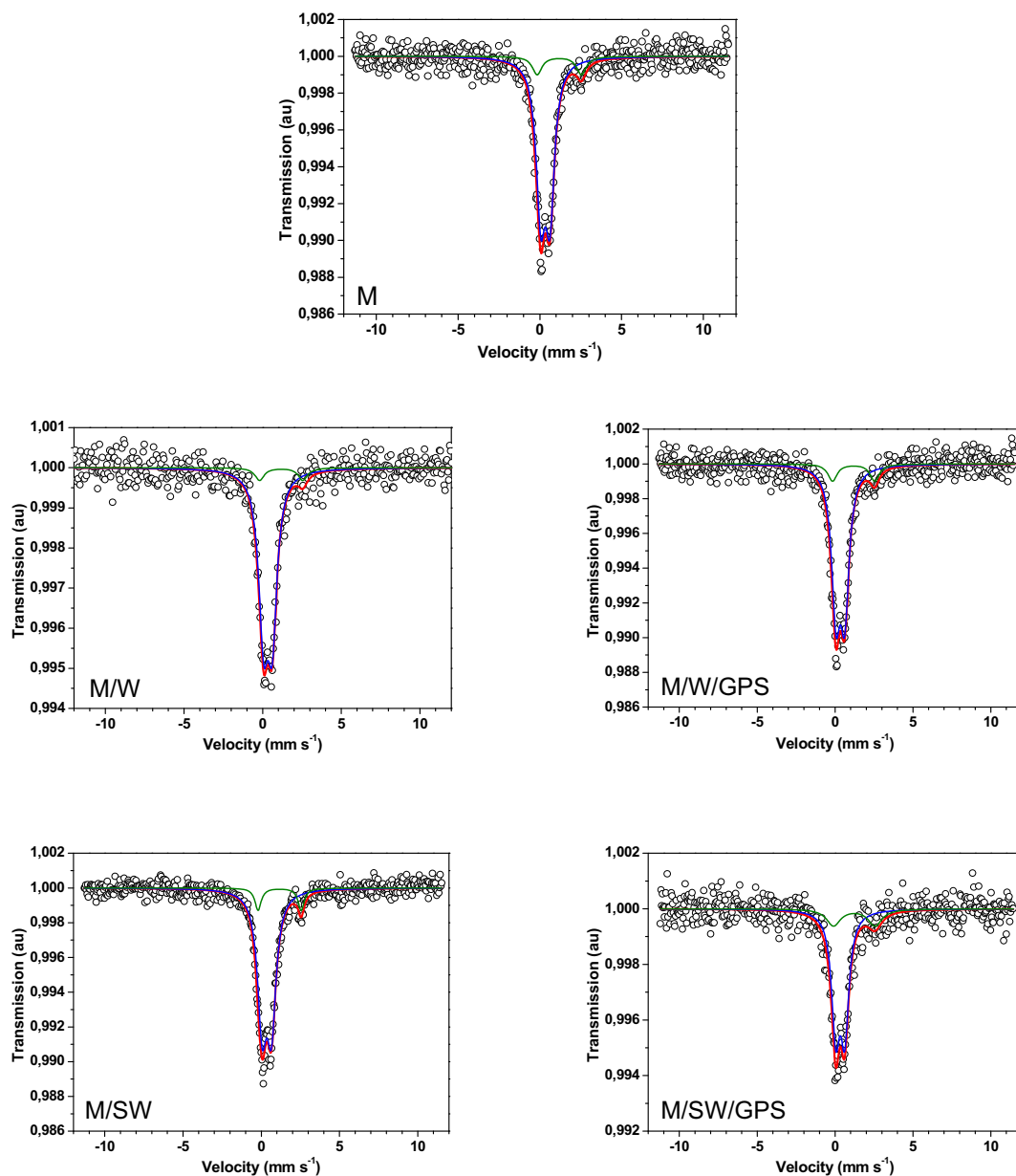
The highest values of maximum adsorption capacity were obtained for the samples containing  $\text{Ca}^{2+}$  (artificial seawater,  $0.010 \text{ mol L}^{-1}$ - $\text{CaCl}_2$ ) (Table 3). The high glyphosate adsorption onto montmorillonite probably occurs due to the formation of a complex between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

In general, for the samples of glyphosate dissolved in distilled water, or  $0.10 \text{ mol L}^{-1}$  NaCl solution, there is a good agreement among the maximum adsorption capacity values obtained with Langmuir and Sips (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 (Table 3, Figure 4).

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  $\text{CaCl}_2$  and  $\text{MgCl}_2$  (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  $\text{Ca}^{2+}$  ions made the glyphosate adsorption process more homogeneous. It should be noted that the  $\text{Ca}^{2+}$ -glyphosate complex has higher stability when compared to  $\text{Mg}^{2+}$  (Caetano et al., 2012).

There are two main regions in the infrared spectrum of glyphosate, one with bands from  $800 \text{ cm}^{-1}$  to  $1300 \text{ cm}^{-1}$  belonged to the phosphonate group and second with bands from  $1300 \text{ cm}^{-1}$  to  $1800 \text{ cm}^{-1}$  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  $1300$ - $800 \text{ cm}^{-1}$  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  $1332 \text{ cm}^{-1}$ ,  $1420 \text{ cm}^{-1}$ ,  $1432 \text{ cm}^{-1}$ ,  $1467 \text{ cm}^{-1}$ / $1482 \text{ cm}^{-1}$ / $1554 \text{ cm}^{-1}$  and  $1730 \text{ cm}^{-1}$  (Figure 5), that could be attributed to deformation  $\text{CH}_2$ , symmetric stretching  $\text{CO}_2$ , group  $\text{CH}_2$ , deformations  $\text{NH}_2^+$  and stretching  $\text{C}=\text{O}$  (Miano et al., 1992; Barja and dos Santos Afonso, 1998). However, after glyphosate was adsorbed onto montmorillonite, the bands belonged to deformations  $\text{NH}_2^+$  and stretching  $\text{C}=\text{O}$  vanished and the bands at  $1420 \text{ cm}^{-1}$  and  $1432 \text{ cm}^{-1}$  shifted to one band at  $1411 \text{ cm}^{-1}$  (Figure 5). At pH (7.00) of the experiments the amino group of glyphosate was not deprotonated (Figure 3), thus the band at  $1630 \text{ cm}^{-1}$  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 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  $800 \text{ mg L}^{-1}$ .

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

Samples	subspectrum	( $\Gamma^a \pm 0.02$ ) (mm/s)	( $IS^b \pm 0.01$ ) (mm/s)	( $QS^c \pm 0.02$ ) (mm/s)	( $A^d \pm 1$ ) (%)
M	Doublet 1 ( $Fe^{3+}$ )	0.59	0.36	0.57	77.7
	Doublet 2 ( $Fe^{2+}$ )	0.90	1.29	2.51	22.3
M/W	Doublet 1 ( $Fe^{3+}$ )	0.73	0.33	0.55	92.6
	Doublet 2 ( $Fe^{2+}$ )	0.70*	1.18	2.75*	7.4
M/W/GPS	Doublet 1 ( $Fe^{3+}$ )	0.67	0.34	0.56	88.3
	Doublet 2 ( $Fe^{2+}$ )	0.71	1.19	2.71	11.7
M/SW	Doublet 1 ( $Fe^{3+}$ )	0.71	0.35	0.59	89.3
	Doublet 2 ( $Fe^{2+}$ )	0.48	1.17	2.75	10.7
M/SW/GPS	Doublet 1 ( $Fe^{3+}$ )	0.64	0.33	0.58	80.2
	Doublet 2 ( $Fe^{2+}$ )	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  $800 \text{ mg L}^{-1}$ . <sup>a</sup>Half-width of spectral lines; <sup>b</sup>Isomer shift related to  $\alpha$ -Fe at room temperature; <sup>c</sup>Quadrupole splitting. \*Parameters set in the adjustment.



For all samples, two doublets were observed, one corresponding to  $\text{Fe}^{3+}$  and the other to  $\text{Fe}^{2+}$  (Figure 6, Table 5). For montmorillonite in the presence of distilled water or seawater, the doublet area corresponding to  $\text{Fe}^{2+}$  decreased approximately 67% and 50%, respectively, when compared to montmorillonite without further preparation (Table 5). The oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  occurred because the dissolved oxygen in the water. The area of the doublet corresponding to  $\text{Fe}^{2+}$  presented the lowest decreasing for the sample of glyphosate dissolved in artificial seawater (Table 5). This could be an evidence that glyphosate is protecting  $\text{Fe}^{2+}$  against oxidation by oxygen. It should be noted that the complex between  $\text{Fe}^{2+}$  and glyphosate plays important roles in the transport of iron through cellular membrane (Motekaitis and Martell, 1985; Tilquin et al., 2000).

#### 4. Conclusions

After the adsorption of glyphosate onto montmorillonite its  $\text{pH}_{\text{pzc}}$  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 interacts with montmorillonite through phosphonate and amino groups. These groups are probably interacting with montmorillonite surface metals ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) and with silanol/hydroxyl groups.

Among the isotherm models tested in this work, Sips isotherm model presented the best results. The  $n$  values for the Freundlich and Sips isotherm models decreased with an increase in the ionic strength. Because of the cations of the artificial seawater, the adsorption process of glyphosate onto montmorillonite was more homogeneous.

FT-IR spectra of glyphosate adsorbed onto montmorillonite indicates that glyphosate could interact with montmorillonite through the amino group.

An increase in NaCl concentration, from  $0.1 \text{ mol L}^{-1}$  to  $0.5 \text{ mol L}^{-1}$ , decreased the glyphosate adsorption onto montmorillonite.

The interaction between  $\text{Ca}^{2+}$  and glyphosate in aqueous solution occurs through the phosphonate group. Because of this interaction, an increase in glyphosate adsorption onto montmorillonite occurred, when glyphosate was dissolved in  $0.01 \text{ mol L}^{-1}$   $\text{CaCl}_2$  solution or artificial seawater. However, when glyphosate was dissolved in  $0.50 \text{ mol L}^{-1}$  NaCl or  $0.034 \text{ mol L}^{-1}$   $\text{MgCl}_2$  solutions the lowest adsorption onto montmorillonite occurred.

Mössbauer spectroscopy showed that glyphosate protected  $\text{Fe}^{2+}$  from being oxidized by oxygen.

#### Declarations

##### Author contribution statement

Rodrigo C. Pereira: Performed the experiments; Analyzed and interpreted the data.

Antonio C. S. da Costa, Flávio 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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##### Competing interest statement

The authors declare no conflict of interest.

##### Additional information

No additional information is available for this paper.

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