Rapid quantification of residual glyphosate in water treated with layered double hydroxides using liquid chromatography

Quantificação rápida de glifosato residual em água tratada com hidróxidos duplos lamelares usando cromatografia líquida

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ABSTRACT

High performance liquid chromatography and an optimized colorimetric method were applied to determine the residual glyphosate in waters treated with double lamellar hydroxides such as $Mg_xAl_yCO_3.nH_2O$. The chromatographic determination was by means of derivatization with 9-fluorenylmethylchloroformiate and running time less than 2 minutes, faster than analogous methods in the literature. The colorimetric method was performed by optimizing the Ruhemann purple method. The chromatographic and colorimetric methods presented LOQ of 1.05 and 2.08 μg / mL and LOD of 0.31 and 0.84

μg / mL, respectively. The percentages of recovery of the methods are between 93 to 105% with RSD less than 2.35% for the chromatographic method and 6% for the colorimetric. Both methods depend on the temperature. The double hydroxide $Mg_1Al_1CO_3.nH_2O$ has the highest percentage of charge density (5.54 nm^2) and the best performance in removing glyphosate from the aqueous medium.

Keywords: High performance liquid chromatography with detection by photodiode array, Ruhemann colorimetric method, glyphosate, layered double hydroxides.

RESUMO

Cromatografia líquida de alta eficiência e um método colorimétrico otimizado foram aplicados para determinar o glifosato residual em águas tratadas com hidróxidos duplos lamelares, como $Mg_xAl_yCO_3.nH_2O$. A determinação cromatográfica foi por meio de derivatização com 9-fluorenilmetilcloroformiato e tempo de corrida menor que 2 minutos, mais rápido que métodos análogos na literatura. O método colorimétrico foi realizado otimizando o método do púrpura de Ruhemann. Os métodos cromatográficos e colorimétricos apresentaram LQ de 1,05 e 2,08 μg / mL e LD de 0,31 e 0,84 μg / mL, respectivamente. As porcentagens de recuperação dos métodos estão entre 93 a 105% com RSD menor que 2,35% para o método cromatográfico e 6% para o colorimétrico. Ambos os métodos dependem da temperatura. O hidróxido duplo $Mg_1Al_1CO_3.nH_2O$ tem a maior porcentagem de densidade de carga (5,54 nm^2) e o melhor desempenho na remoção do glifosato do meio aquoso.

Palavras-chave: Cromatografia líquida de alto desempenho com detecção por arranjo de fotodiodo, método colorimétrico de Ruhemann, glifosato, hidróxidos duplos lamelares.

1 INTRODUCTION

N-(phosphonomethyl)-glycine, better known as glyphosate, is the active component of the globally used Roundup® herbicide. It is the most widely used herbicide of its type, employed on crops such as rice, soybean, tobacco and sugarcane [BARBARA, Gilson., FERRO, Dagmar Aparecida de marco. MATURADORES EM CANA DE AÇÚCAR: COMPARAÇÃO ENTRE OS PRINCÍPIOS ATIVOS DOS PRODUTOS TRINEXAPAQUE-ETILICO (MODDUS) E GLIFOSATO (ROUNDUP). Brazilian Journal Of Development, Vol 6, No 7 (2020). DOI:10.34117/bjdv6n7-487], among others. Generally, it is applied on large crops by aspersion using airplanes, but on small crops it is manually applied.[1-4] Once applied, part of the glyphosate is absorbed by the plants and another part goes directly to the soil, where it is subject to several processes, including microbiological degradation, complexation to metal cations and percolation.[5-9] Thus, it can contaminate surface and underground water resources that are relevant both for human and animal consumption. The continuously rising usage of glyphosate in recent decades has caused concern both from governmental and nongovernmental health and environmental entities around the globe, since investigations have indicated that

glyphosate may contribute to chronic kidney disease in young workers as well as autism in children.[10] It is known that lixiviation of glyphosate in the soil can contaminate groundwater, with severe consequences for human and agricultural water supply. However, the limit on concentration of glyphosate in potable water varies from one country to another. For instance, in Brazil that limit is 0.5 μg/mL according to Brazilian Health Ministry, Consolidation Edict (2017), whereas in the USA it is 0.7 μg/mL according to United States Environmental Protection Agency (US EPA); EPA 8000D, National Primary Drinking Water Regulation, United States of America (2017).[11,12] The removal of glyphosate from water is not an easy task, so sophisticated and costly methods, such as ion exchange using resins, must be applied.[13] In this context, the use of anionic clays, such as the layered double hydroxides (LDH), for the removal of pollutants is promising.[14-16] LDHs are versatile anionic clays of the hydrotalcite mineral type that present in their lamellar structure the metals M (II) and M (III) occupying octahedral sites .[17] Because of the importance of glyphosate in agriculture and the global economy, counterbalanced by the need to protect water quality, several methods have been developed for its detection and measurement, mainly chromatographic and spectroscopic. A major difficulty in the detection and quantification of glyphosate is the fact that it does not have a chromophore group, which precludes its direct detection by photometric detectors.[18] As an alternative, different glyphosate derivatization schemes have been proposed and tested, aiming at the introduction of chromophore groups in the glyphosate molecule, such as by reaction with 9-fluorenylmethylchloroformiate (FMOC-Cl), which was employed in this work.[19] Several reaction schemes that employ FMOC-Cl to detect and/or quantify glyphosate have been described in the literature, with somewhat contradictory results, and parameters such as reaction time and temperature, pH, limit of detection and of quantification need to be optimized in order to validate each method .[20,21] Besides the mentioned methods, in the 1990s the Ruhemann colorimetric method was adapted for the quantification of glyphosate. This method is based on the reaction of ninhydrin and molybdate with amino acids under heating .[22] However, some adaptations have been made to the Ruhemann method to improve its efficiency.[23,24] It is relatively simple and cheaper than chromatographic methods, but as will be described here, its reproducibility of reaction with glyphosate is strongly dependent on the cooling rate of the samples. The objectives of this work were three-fold: (a) to develop statistically robust analytical protocols for the detection and quantification of glyphosate in water solutions, using both high performance liquid chromatography with detection by photodiode array

(HPLC-PDA), and an optimized Ruhemann colorimetric method, to evaluate the linearity, accuracy and precision, limits of detection and quantification, effect of reaction time, temperature and pH, and concentration of reactants; (b) to synthesize and characterize LDHs with different Mg/Al ratios for the treatment of water contaminated with glyphosate; and (c) to evaluate the performance of the analytical methods for the quantification of residual glyphosate in water treated with LDHs.

2 EXPERIMENTAL

All analytical measurements were carried out according to the USEPA 8000D (2017) directives. The precision and accuracy of the analytical methods were determined by the analysis of a set of seven replicates and evaluated by relative standard deviation (RSD). The accuracy of the methods was calculated by comparing the measured concentrations with the nominal concentrations, expressed as mean recovery percent (%). The limit of detection (LOD) was defined as the least intense sample point that could be quantified with precision < 20% and accuracy between 70 and 130%.

2.1 *ANALYTICAL CURVES*

All measurements were carried out with seven-fold replicates. For the chromatographic method, the analytical curve was constructed from seven standard solutions at glyphosate at concentrations of 5, 10, 20, 40, 60, 80 and 100 µg/ml, prepared from a 1 mg/mL stock solution. For the colorimetric method, the curve was constructed from concentrations of 10, 20, 40, 60, 80 and 100 µg/ml.

2.2 *DERIVATIZATION OF GLYPHOSATE*

Borate buffer at pH 10, glyphosate and FMOC-Cl standard solutions were mixed and stirred for 15 minutes at 45 ºC. The concentration of FMOC-Cl was two-fold that of the glyphosate, and the reactional volume for the derivatization was 3 mL, composed of at least 65% acetonitrile, 25% freshly prepared borate buffer and the corresponding volumes of glyphosate and FMOC-Cl. If necessary, the volume was completed with acetonitrile. HPLC measurements were carried out with a Shimadzu Prominence LC-20AT chromatograph, equipped with an SPD-M20A detector, CTO-20A oven, and SIL-10AF-CBM20A autosampler. For the measurements, an Allure C18 organic acid column (15 cm x 4.6 mm x 5 µm) was used, purchased from Restek. The mobile phase (B solvent) was acetonitrile, and phosphate buffer was the A solvent, at pH 2.5 and a flow of 1.3

mL/min at 40 °C. The injection volume was 20 µL during 4 minutes. Glyphosate was detected at 260 nm.

2.3 *OPTIMIZED RUHEMANN COLORIMETRIC METHOD*

Standard solutions at concentrations of 0.25, 0.5, 1.0, 1.5 and 2.5% m/v of ninhydrin and sodium molybdate and a standard solution of glyphosate (1 mg/ml) were prepared for the analytical curve. In glass tubes, 1 mL of the ninhydrin solution, 1 mL of the sodium molybdate solution and the corresponding volume of the glyphosate solution were added. If necessary, deionized water was added to complete the final volume of 3 mL. Solutions were heated in a water bath at 100 ºC for 10 minutes in order to obtain reproducible and reliable results. Then the reaction was quenched in an ice bath until reaching room temperature, and absorbance was measured at 570 nm (Shimadzu UV-1800).

2.4 *SYNTHESIS OF THE LDHS AT THE 1:1, 2:1 AND 3:1 MG/AL RATIOS*

The LDHs were synthesized according to Constantino *et al.*[25] and were characterized by powder XRD (Rigaku Ultima IV, Cu kα), FTIR (Bruker Vertex 70, 4cm^{-1}, in ATR mode) and ^{27}Al solid-state NMR (Bruker Avance II spectrometer, operating with a 9.4 T magnet, equipped with a standard 4 mm probe). The Mg/Al ratios were determined by atomic absorption (SpectrAA 55B atomic absorption system). The characterization data of LDHs are available upon request to the authors.

2.5 *GLYPHOSATE ADSORPTION AND EXTRACTION*

The performance of the LDHs prepared in this work for the removal of glyphosate from water was investigated at pH 9, in batch experiments, using 1.5 mg/mL of glyphosate and 1 mg/mL of each adsorbent. The contact time was 2, 6, 12 or 24 h, under constant stirring of 200 rpm, at room temperature. The profile of glyphosate adsorption was evaluated by the residual concentration of glyphosate in solution after contact with the adsorbent. Glyphosate was extracted from the aqueous suspensions containing the LDH by centrifuging (6000 rpm, 10 min, and room temperature) and filtering the supernatants in 0.25 µm membranes. The glyphosate concentrations were determined by the chromatographic and colorimetric protocols developed and validated in this work. For the suspensions of the LDH with the best performance, it was also necessary to pre-

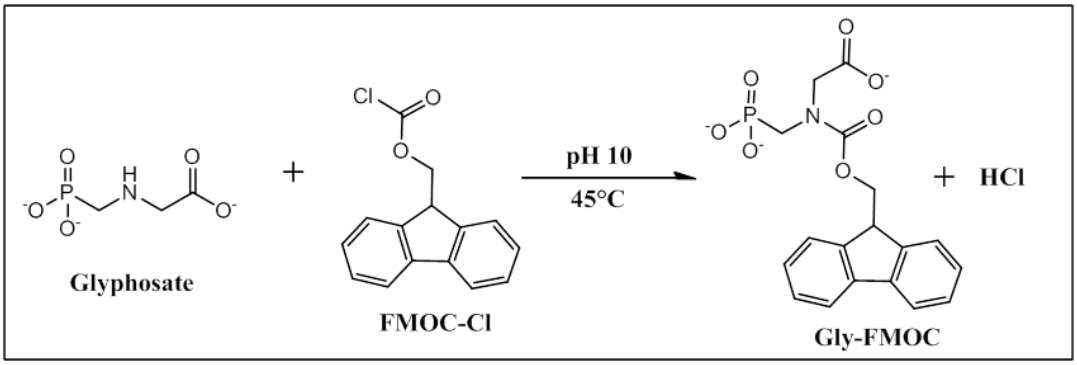
concentrate the residual glyphosate filtered solutions to about half of the initial volume, using a rotary evaporator at ~80°C.

3 RESULTS AND DISCUSSION

3.1 *DERIVATIZATION OF GLYPHOSATE*

Since the glyphosate molecule does not contain chromophore groups, after the extraction the pesticide was reacted with FMOC-Cl (Figure 1) to detect the derivatization product by HPLC-PDA. As pointed out in the experimental section, the experimental conditions were optimized to attain a better derivatization reaction, as well as to improve the resolution of the chromatographic peaks.

Figure 1: Scheme of the derivatization of glyphosate with FMOC-Cl.



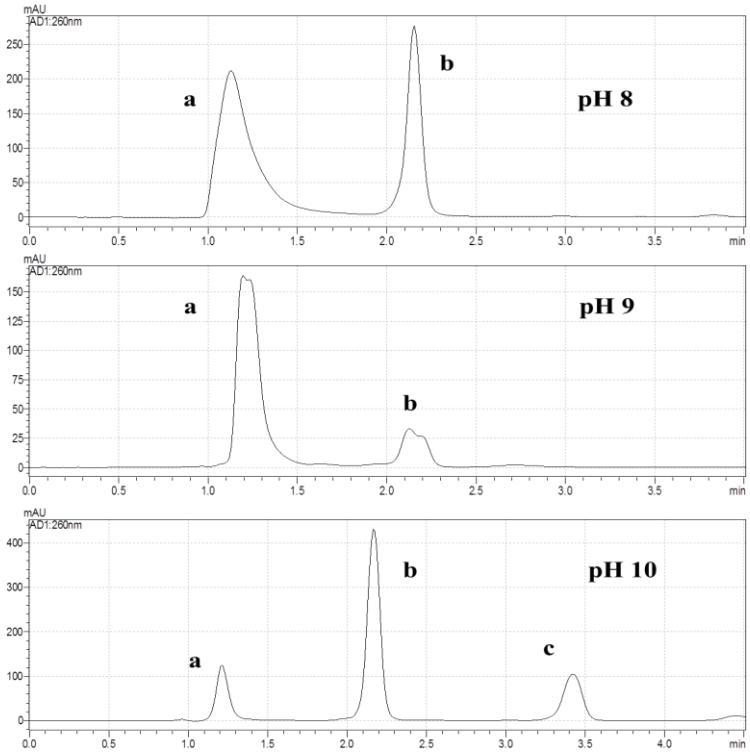
The optimum result for the derivatization of glyphosate was obtained with a mixture of 65% acetonitrile and 35% aqueous solution of glyphosate and buffer. This condition was necessary since glyphosate is sparingly soluble in organic solvents and FMOC-Cl is insoluble in water.

3.2 *INFLUENCE OF THE BORATE BUFFER ON THE DERIVATIZATION OF GLYPHOSATE*

Solutions containing glyphosate have an acid pH close to 2.5. Glyphosate is commonly found in the form of zwitterion. According to studies reported in the literature, glyphosate has different structures in different pH ranges. Choosing an optimum pH value for the HPLC measurements is thus crucial for the correct quantification of glyphosate, and also for the symmetry of the chromatographic peaks. The literature also reports that for each pKa there exists a distribution of structural species of glyphosate, each of which may react differently with FMOC-Cl.[26] Since the derivatization process is not selective against a specific structure of glyphosate, all structural species at a given pH will react,

but their products will interact with the chromatographic column in different forms, thus deforming the peaks. That asymmetry of the chromatographic peaks can the partially attenuated by strictly controlling the pH. In this work, it was found that the optimum pH value was 10, as shown in Figure 2.

Figure 2: Comparison of the chromatograms measured for the derivatization of glyphosate with FMOC-Cl at pH 8, 9 and 10. (a) FMOC-glyphosate, (b) FMOC-OH and (c) FMOC-Cl (residual).



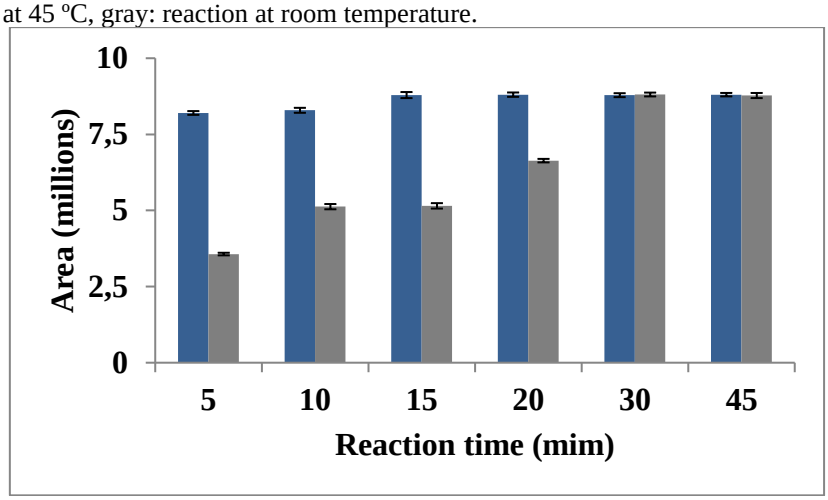
The choice of such a high pH value was not only associated with minimizing the number of glyphosate structures available for derivatization, but also to guarantee high solubility of glyphosate, due to its high anionic charge. The retention times for FMOC-glyphosate and FMOC-OH were, respectively, 1.24 and 2.14 at pH 8, 1.9 and 2.15 at pH 9, and 1.20 and 2.16 at pH 10. The formation of FMOC-OH occurred at all pH values. The literature reports that FMOC-OH is a degradation product o FMOC-Cl in basic media.[20]

3.3 *INFLUENCE OF TIME AND TEMPERATURE ON THE DERIVATIZATION OF GLYPHOSATE*

The effect of time on the derivatization of glyphosate was investigated from 5 to 45 minutes at room temperature and 45 °C, as shown in Figure 3. The literature reports different derivatization times, varying from 5 to 30 minutes, either at room temperature

or under heating.[18, 20, 27, 28] The best reactional condition found in this work is 15 minutes at 45 °C. As shown in Figure 3, after 15 minutes at this temperature the system did not present significant variations, thus indicating that equilibrium was reached. On the other hand, at room temperature the conversion was complete only after 30 minutes.

Figure 3: Correlation between the reaction time and the area under the chromatographic peak. Blue: reaction under heating at 45 ºC, gray: reaction at room temperature.



3.4 *STABILITY OF THE DERIVATIZATION PRODUCTS*

The stability of the glyphosate-FMOC adducts was investigated by obtaining the chromatograms 2, 6 and 24 hours after the derivatization reaction. Samples were kept either at room temperature or 5 ºC. The chromatograms obtained for both storage conditions are available upon request to the authors. Loss of stability was defined as the broadening or asymmetry of the chromatographic peak. The chromatograms show that with both storage conditions, degradation was observed after 6 h, and was faster when the storage was at room temperature.

3.5 *INFLUENCE OF EXPERIMENTAL CONDITIONS AND STABILITY OF THE PRODUCTS IN THE OPTIMIZED RUHEMANN COLORIMETRIC METHOD*

For the concentration range from 10 to 100 μg/mL, the best condition for ninhydrin and molybdate was 1%. Ninhydrin and molybdate concentrations of 0.5, 1, 2.5 and 5% were tested. The concentration of 5%, prescribed by the literature, afforded deep purple solutions whose absorbance was higher than unity.[22] Those authors also indicated that 5 minutes at 25 ºC is sufficient for the formation of Ruhemann's purple, but in order to get reproducible absorbance values, it was found that the optimum reaction temperature was no lower than 100 °C to enable completing the reaction in 10 minutes, followed by ice bath quenching. The stability of the Ruhemann purple products was also found to be

critically dependent on those parameters. The purple solutions prepared as described above were stored at room temperature and under refrigeration, and in both conditions the formation of precipitates was observed after 10 h. These precipitates were not further investigated. Concerning the influence of borate buffer (pH 10) in the formation of Ruhemann's purple, no significant differences between samples prepared in the presence or absence of buffer were found.

3.6 *VALIDATION OF METHODS*

The accuracy and precision of the analytical curves at three concentration levels were established, respectively, by the percentage of glyphosate recovery and by calculating the coefficient of variation (or relative standard deviation, RSD). According to the USEPA 8000D standard, the recovery percentage must be in the range 70 – 130%. Table 1 shows that the recovery percentage of the chromatographic method was in the 93 – 105% range, whereas for the colorimetric method, the recovery percentages ranged from 94 to 103%. Thus both methods presented good accuracy. Also, the RSD values lower than 2.35% and 6%, respectively for the chromatographic and the colorimetric methods, indicated good precision.

Table 1: Evaluation of precision and accuracy for the analytical methods.

	gly [µg/mL]	recovery (%)	RSD (%)
HPLC	**100**	**99**	**2.359**
	40	**105**	**0.686**
	5	**93**	**0.320**
Colorimetric	**100**	**100**	**0.189**
	40	**94**	**0.932**
	10	**99**	**5.550**

The limit of detection (LOD) and limit of quantification (LOQ) of both methods were calculated as 3 and 10 times the signal-to-noise ratio, respectively. The LOQ reached by the chromatographic method was 1.05 µg/mL, and the LOQ of the colorimetric method was 2.80 µg/mL. The LOD values were, respectively, 0.31 and 0.84 µg/mL. The recent literature reports similar values for the chromatographic limits.[21] Regarding the colorimetric method, the literature reports LOD values of 0.04 µg/mL and 0.093 µg/mL, which are lower than the LOD value found in this work. However, in the experimental conditions of this work, this LOD was not reached, even when it was followed the experimental conditions described in the literature, and the purple adduct was not detected for glyphosate concentrations lower than 0.37 µg/mL for any concentration of ninhydrin and molybdate.[29] The parameters of linearity, reproducibility and repetitiveness of both

methods were obtained by the R^2 values and inter-day and intraday analysis, as shown in Table 2.

Table 2: Evaluation of linearity, reproducibility and repetitiveness of both analytical methods.

HPLC-PDA				
Curve	**ax**	**b**	**R^2**	**SD fc (%)**
First day	**82709.61**	**72115.09**	**0.998976**	**5%**
	82754.96	**68813.04**	**0.999165**	**6%**
	82815.05	**59686.56**	**0.998919**	**5%**
Second day	**83404.03**	**56954.41**	**0.999061**	**6%**
	82780.94	**59361.12**	**0.999107**	**6%**
Third day	**82282.41**	**82827.86**	**0.998891**	**7%**
	82627.62	**84112.55**	**0.998655**	**6%**
RSD	**< 1%**	**-**	**-**	**0.35%**
Colorimetric method				
Curve	**ax**	**b**	**R^2**	**SD fc (%)**
First day	**0.00926**	**0.01886**	**0.99508**	**10%**
	0.00928	**0.02947**	**0.99759**	**10%**
	0.00877	**0.04396**	**0.99750**	**14%**
Second day	**0.00856**	**0.05230**	**0.99728**	**14%**
	0.00852	**0.05598**	**0.99661**	**13%**
Third day	**0.00846**	**0.02929**	**0.99026**	**16%**
	0.00865	**0.03419**	**0.99955**	**9%**
RSD	**3%**	**-**	**-**	**2%**

3.6 *EVALUATION OF LDH IN THE ADSORPTION OF GLYPHOSATE: APPLICATION OF THE ANALYTICAL METHODS*

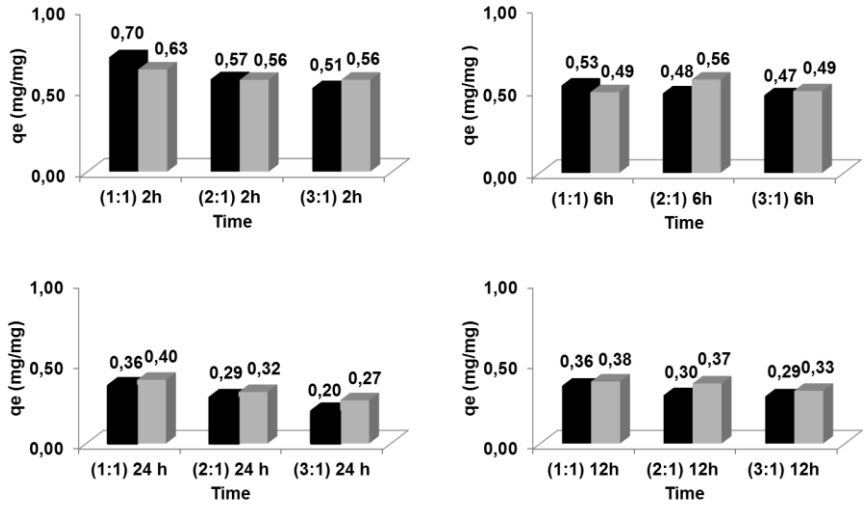
The adsorption of anionic species, such as the glyphosate anions, by the LDHs occurs due to the positively charged hydroxylated lamellae. That positive charge is formed by the substitution of divalent cations with trivalent ones, that is, the addition of Al^{3+} raises the positive net charge of the lamellae, and as a consequence, the adsorption capacity of the LDH. Thus, the objective of synthesizing LDHs with different Mg/Al ratios is to promote different positive net charges of the lamellae, aiming at optimum adsorption of glyphosate. This effect was confirmed for the materials synthesized in this work, as observed by the C_d values. Thus, the order of adsorption capacity as a function of the positive net charge would be 1:1 > 2:1 > 3:1.[30] Figure 6 presents a series of the equilibrium adsorbed quantity of glyphosate, q_e (defined as $C_e - C_0$) of the three LDHs, as a function of contact time, and by type of analytical method.

3.7 *EVALUATION OF LDH IN THE ADSORPTION OF GLYPHOSATE: APPLICATION OF THE ANALYTICAL METHODOLOGIES*

The adsorption of anionic species, as the glyphosate anions, by the LDH occurs due to the positively charged hydroxylated lamella. That positive charge is formed by the

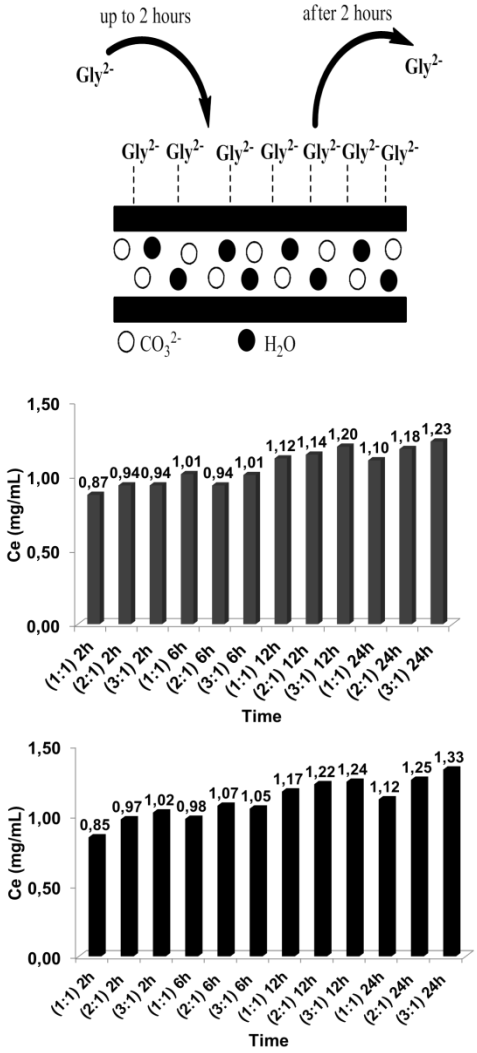
substitution of divalent cations for trivalent ones, that is, the addition of Al^{3+} raises the positive net charge of the lamella, and as a consequence, the adsorption capacity of the LDH. Thus, the objective of synthesize LDH with different Mg/Al ratios is to promote different positive net charges of the lamella, aiming an optimum adsorption of glyphosate. Such effect was confirmed for the materials synthesized in this work, as observed by the C_d values. Thus, the order of adsorption capacity as a function of the positive net charge would be 1:1 > 2:1 > 3:1. Figure 4 presents a series of the equilibrium adsorbed quantity of glyphosate, q_e (defined as $C_e - C_0$) of the three LDH, as a function of contact time, and by type of analytical method.

Figure 4: Comparison of adsorbed quantity of glyphosate (qe) of each LDH as a function of contact time. From upper left, in clockwise motion: 2h, 6h, 24h and 12h. Black bars are for the colorimetric method, and grey bars are for the HPLC method.



It was observed that both methods presented the same profile when considering the quantity of glyphosate adsorbed by the LDHs. The performance of the methods was compared by the Pearson correlation coefficient (r^2), which was 0.92, indicating a strong correlation between the methods. The small discrepancies can be attributed to the inherent uncertainty of each method, as discussed in the validation section, as well as to systematic errors. The graphs presented in Figure 5 indicate that the optimum contact time was 2 h for the three LDHs, and the LDH with Mg/Al ratio of 1:1 presented the highest adsorption capacity. For longer contact times there was a decrease in the adsorbed quantity of glyphosate, attributed to desorption processes, as shown schematically in Figure 5.

Figure 5: (a) Scheme for the adsorption-desorption of glyphosate at the LDH. (b) Residual glyphosate in solution as a function of time. Gray bars: measured by HPLC; Black bars: measured by colorimetry.



4 CONCLUSION

Rapid determination of residual glyphosate in water treated with three LDH clays synthesized with distinct charge density (Cd) values was carried out by HPLC-PDA using FMOC-Cl as chromogenic agent. An optimized Ruhemann purple colorimetric method was also tested, with good results. Both methods were validated according to the USEPA 8000D directives, and were able to detect glyphosate in the concentration ranges for drinking water required by the USEPA (0.7 μg/mL) and Brazilian Health Ministry (0.5 μg/mL). The HPLC and the colorimetric methods presented good accuracy and reproducibility in the tested conditions, with LOQ of 1.05 and 2.80 μg/mL and LOD of 0.31 and 0.84 μg/mL, respectively. The recovery percentage values indicate that both the chromatographic and colorimetric methods have good precision and accuracy, indispensable aspects of any analytical method. The R^2 values for the replicates, calculated on three different days, also confirm that both methods have good linearity and

are reproducible. Both the HPLC and the colorimetric methods are temperature dependent, and the colorimetric one does not work at room temperature, despite some reports in the literature. The stability of the reactional medium was < 6 h for the chromatographic method, and <10 h for the colorimetric method. The chromatographic method described in this work is faster than any similar method described in the literature.

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