CHAPTER 29

An overview of the adsorption of glyphosate by different materials, natural, hybrid and composite

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ABSTRACT

The present work brings a compilation of selected data on aspects involving the adsorption of glyphosate in aqueous medium by in different materials. According to the information reported, the pH of the medium plays a fundamental role in the formation of glyphosate anions, thus affecting its behavior in adsorption by different materials. It was found that the Langmuir and Freundlich isothermal models respond more satisfactorily to the glyphosate adsorption process as a function of the type of adsorbent, and that the adsorption mechanisms respond to a greater degree to a pseudo-second-order kinetic model . Finally, it was found that clays, hybrid materials containing clays and biochar, were the matrices with the best adsorptive potential for glyphosate.

Keywords: Glyphosate, Adsorption, Lamellar double hydroxides, Adsorbent materials.

1 INTRODUCTION

Environmental safety in the control of soil and water contamination are priorities, and currently are increasingly worrying society. In fact, ensuring access to clean water and preserving aquatic life are Sustainable Development Goals (SDGs) of the UN 2030 Agenda. (AGENDA, 2018) The increase in world demand for food is reflected in the means of production and expansion of the use of different tools in agriculture such as pesticides, as well as a greater demand in the consumption of water in irrigation processes. The presence of various contaminants in water and food has also been widely debated by governmental and non-governmental organizations around the world. The pollution of water bodies is mainly due to the presence of heavy metals, dyes and organic compounds existing in the most diverse pesticides. These contaminants, especially organic compounds, come from agriculture where they are constantly applied in order to control and eliminate pests present in the most diverse crops. In recent decades, large amounts of pesticides have been applied to crops, and with this many other compounds inherent to the degradation process of these substances have been present in the environment. Many of these compounds are not biodegradable and can accumulate in living organisms causing severe damage to human health and the ecosystem. Among the substances most used as pest control agents are organochlorines and organophosphates. However, amid this wide variety of molecules, glyphosate deserves special attention. According to CONAMA Resolution number 396, of April 3, 2008, for water to be considered potable and safe for human supply, it must not present certain compounds and metals in quantities greater than those established by national guidelines for the control of pollutants. Thus, to keep a check on the rates of contaminants, different technologies have been

developed and are still being studied. In this sense, we can affirm that adsorption emerges as an effective alternative, since several materials can be applied as adsorbents, and the adsorptive capacity of each of these materials is related to their structural properties of the surface. Thus, this work aimed to present an overview from the compilation of data present in studies published in the literature in the last five years involving the adsorption of glyphosate in different materials.

2 LITERATURE REVIEW

2.1 GENERAL ASPECTS ABOUT GLYPHOSATE

Glyphosate (N-(phosphonomethyl)glycine) is a post-emergent, systemic, non-selective herbicide with a broad spectrum of action, and undoubtedly the most widely used in Brazil and in the world due to its unique properties, since it is the only one capable of inhibiting the enzyme 5-enolpiruvilshikimato-3-phosphate synthase (EPSPs), present in the shikimic acid pathway which in turn is responsible for the production of amino acids fundamental for the development and maintenance of the vital functions of the plants where it is absorbed in greater proportion by the leaves and in less quantity through the roots. (ANNETT; HABIBI; HONTELA, 2014; BORGGAARD; GIMSING, 2008; VALLE et al., 2019).

In general, glyphosate is applied to crops by means of airplanes or constal bombs. Once applied a portion is absorbed by the plants and another is available in the soil, where it can go through different chemical, physical and biological processes. The behavior of glyphosate in soil is affected by different aspects since this complex matrix consists of minerals, organic matter, microorganisms and water. Thus, the properties of the soil can be modified according to changes in any of the components, and in turn influence the adsorption of compounds added to it (VEREECKEN, 2005).

The high sorption capacity of glyphosate in the soil can occur by different pathways, such as: complexation with metal oxides, hydrogen bonds, ion exchange in clays and interactions with humic acids (PEREIRA et al., 2019; SHEALS; SJÖBERG; Persson, 2002; Veterinary, 2007). Their solubility of the compounds in water is also a determining factor in their sorption profile in the soil. Thus, the lower the solubility of the compost in water, the greater the potential for retention by the soil. However, glyphosate does not follow this rule, as it is a water-soluble compound strongly adsorbed by soil. In addition to the possibilities of interaction of glyphosate with the soil previously mentioned, another mechanism can corroborate for its fixation, such as: this is the case of the possibility of van de Waals interactions (YAMADA, 2007). According to the literature, the adsorption of glyphosate by bentonite, illite, kaolinite, iron and aluminum hydroxides is initially associated with the cation exchange capacity of clays and also of hydroxides. For example, it was observed that bentonite, because it presents a higher cation exchange coefficient (CTC) than the other minerals mentioned, would present a higher

adsorption capacity. However, kaolinite and ilite showed greater adsorptive potential. Thus, it was concluded that glyphosate would be bound to iron ions (in the case of kaolinite) present in the structures of minerals (DOUGLAS; GAINES, 2014; YAMADA, 2007). The complexing capacity with metals present in the soil can lead to inactivation of glyphosate. The literature also reports complexation potential is associated with the size of the cationic radius, thermodynamic and imbalance factors and also observed that the highest complexing efficiency and inactivation of glyphosate in the soil were obtained for compounds formed with Al 3+, Fe ^{3}+, Fe 2+ and Mg 2^{+} (YAMADA, 2007)

Prata et al. (PRATA, LAVORENTI, *et al*., 2000) also observed that the adsorption of glyphosate by soils is not directly affected by the presence or absence of organic matter. However, they realized that there was no desorption of glyphosate after leaching from the soil, and glyphosate was mostly retained as residues bound with the mineral fraction containing Fe 3+ and Al^{3+}. The interaction of glyphosate with humic acids present in the soil was studied by Piccolo et al. (PICCOLO; CELANUS; Arienzo 2008; PICCOLO; CELANUS; Conte, 1996). They observed that organic matter had the ability to adsorb large amounts of glyphosate due to interactions such as hydrogen bonds. However, it has been found that unlike minerals, humic acids can easily desorb glyphosate retained due to the disruption of these bonds.

Another important aspect associated with glyphosate is its ability to present different structures depending on the pH of the medium where it is inserted. The studies on the ionization constants of glyphosate were carried out theoretically by Peixoto and collaborators, and were later confirmed experimentally by Liu et al. and indicated that glyphosate can be completely protonated and in the anionic forms gli-, gli ^{2}- and gli ^{3}- , as shown in Figure 1 (PEIXOTO et al., 2015; LIU et al., 2016). The existing percentage of each structure will vary according to the pH range, so major structures are only expected at exact values of transition pH, that is, within a pH range the proportion between the different structures will increase or decrease as the pH value moves away from or approaches the transition pH where a given structure prevails. For example, at the pH value between 7 – 8, observed in physiological medium, and in groundwater and surface water not submitted to chemical treatment, the dominant species will be gli^{2-}. For pH values equal to or greater than 10 the gli^{3-} structure will tend to be predominant (PEIXOTO et al., 2015). A disadvantage when working within pH ranges is that the thermodynamic data reflect the behavior of a group of structures and not just a majority. When working on defined pH values, where the coexistence of different structures is minimal, there is a better understanding of the kinetic, thermodynamic and equilibrium aspects involved in the study.

Figure 1. Chemical structures of glyphosate as a function of pKa. (Adapted from PEIXOTO et al. 2015)
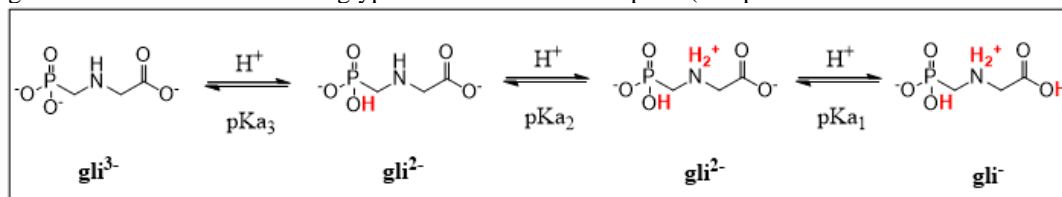
2.1.1 Glyphosate Consumption in Brazil

Between 2014 and 2018, glyphosate was the most commercialized active ingredient in Brazil, corresponding to 35% of the total of pesticides, which represent more than 940 thousand tons (IBAMA, 2020). Table 1 presents the glyphosate consumption data in the period 2014 – 2018 and, as can be seen, the consumption of Brazil corresponds to a large percentage of the total of all products applied, which makes glyphosate by far the most widely used pesticide in the national territory. The high consumption of glyphosate makes its presence in various systems increasingly larger. Certainly, its accumulation in the environment in the form of undegraded glyphosate or its degradation products, generate great damage to the environment, such as: contamination of soil and tributaries and the health of man. The dynamics of glyphosate, whether in soil or water, largely depends on its physicochemical properties (VALLE et al., 2019).

Table 1. Consumption (in tons) of glyphosate in Brazil between the years 2014 to 2018.

Year	Glyphosate consumption (tonnes)	Total herbicide consumption (tonnes)	Glyphosate consumption (%)
2014	194.877,84	508.556,84	38,3
2015	194.939,60	521.525,40	37,4
2016	185.602,22	541.861,09	34,3
2017	173.150,75	539.944,95	32,1
2018	195.056,025	549.280,44	35,5
Total	943.626,43	2.607.642,83	35,5

2.1.2 Risks of glyphosate for human health

Several studies around the world have been conducted to assess the harm of glyphosate to human health. Chronic exposure to glyphosate is associated with different comorbidities, such as: attention deficit/hyperactive disorder (ADHD), colitis, diabetes, heart disease, intestinal inflammation, multiple sclerosis, obesity, depression, Alzheimer's disease (SAMSEL; SENEFF, 2013), autism (JE; SENEFF, 2015), birth defects (PAGANELLI et al., 2010), brain and breast cancer (SHIM; MIYNAREK; VAN WIJNGAARDEN, 2009), celiac disease and gluten intolerance (SAMSEL; SENEFF, 2015) chronic kidney disease (JAYASUMANA; GUNATILAKE; SENANAYAKE, 2014), allergies (SLAGER et al., 2010), among others.

2.1.3 Glyphosate legislation

Brazilian laws are generally more flexible regarding the tolerance of pesticide components in water compared to European ones, for example. This is since Brazil has historically maintained a characteristic of an agro-exporting country. Since the 2000s, Brazil, taking turns with the United States, are the largest consumers of pesticides in the world, consuming about 20% of the world's production of these products. The most surprising thing is that in Brazil large quantities of these toxic substances are freely allowed, and in some cases, there is no technical monitoring by competent bodies that designates the conditions of use, thus favoring the increase of soil contamination and especially of water sheets (HOTTES et al., 2021, 2022).

Within a standard of potability, there is a maximum allowable amount of the presence of pesticides and this amount varies from pesticide to pesticide and from country to country. In relation to glyphosate, European legislation allows a total of only 0.1 μg/L of this substance in water intended for human consumption (HOTTES et al., 2022). According to USEPA, the US controlling body, the allowable amount of glyphosate within water potability standards is 700 μg/L (HOTTES et al., 2021, 2022). In Brazil, current legislation considers the presence of up to 500 μg/L of glyphosate to be safe for humans ("Water Quality", 2008). It is observed through the comparison between the values, that according to the Brazilian legislation, we are consuming glyphosate in a proportion 5000 times higher than that of the Europeans. Even though, Brazilian laws are soft and undemanding, public authorities tend to push the responsibility of pollution to farmers, arguing that they do not respect the limits of application or promote improper applications (HOTTES et al., 2021, 2022).

2.2 SOME ADSORBENT MATERIALS

2.2.1 Lamellar double hydroxides (HDLs)

Lamellar double hydroxides are a class of two-dimensional (2D) anionic clays. HDLs are hydrotalcite-type compounds and have a chemical structure similar to that of the mineral brucite, where divalent cation sites are replaced by trivalent cations, such substitution being performed by a wide range of cations, which gives HDLs a variety of composition and very wide preparation (MISHRA; DASH; PANDEY, 2018a). The positively charged layers due to the cationic substitution process can be stabilized by the presence of different anions in the interlamellar region, as well as water molecules responsible for helping to maintain the structural cohesion of the system (EXTREMERA et al., 2012). A wide diversity of compounds can be interspersed, such as: inorganic and organic anions, complex anions, biomolecules, polymers, among others (ABDELLAOUI et al., 2017; IFTEKHAR et al., 2018; ZUBAIR et al., 2017).

The representation of the structure of HDL can be seen in Figure 2, its general chemical formula being expressed by $[M^{2+} M^{3+}(X) (OH)2]^{X+}(A)_{X/m} \cdot mH_2O$. The di and trivalent cations are represented by M^{2+} and M^{3+}, while the anions are equivalent to A^{m-} (JULIANTI et al., 2017). In general the value of X ranges from a range of 0.2 to 0.33, which leads to a molar ratio M^{2+}/M^{3+} between 2 and 4. However, other reasons can also be formed, but in these cases there is the possibility of the presence of different phases beyond HDL (IFTEKHAR et al., 2018).

Figure 2: Generic schematic of the structure of lamellar double hydroxide.
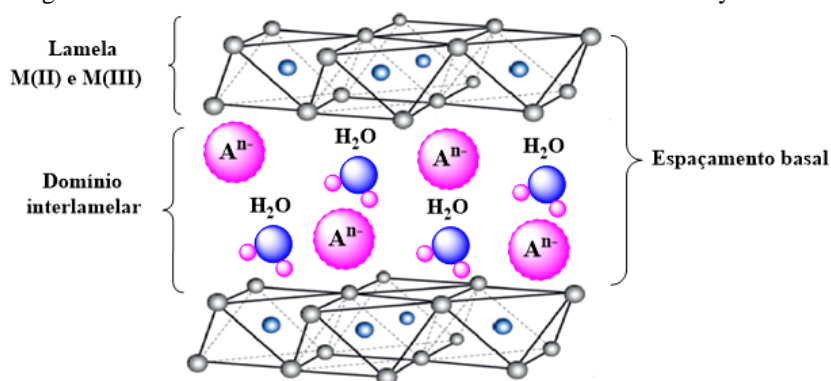
HDLs-type materials have gained great interest due to their various possible applications, such as: catalysis, slow-release agents of drugs and pesticides (CHUBAR et al., 2017; CREPALDI, 1998; MISHRA; DASH; PANDEY, 2018a), supercapacitors (CAI et al., 2015), water treatment (ABDELLAOUI et al., 2017; BHARALI; DEKA, 2017), among others. Especially its use as adsorbent agents of pollutants intended for the treatment of effluents has been gaining special attention, due to its low toxicity and cost, high surface area, anionic exchange capacity and variety of structure architecture (YANG et al., 2016).

The versatility of composition and structure of HDLs has made them promising adsorbent materials for the removal of the most varied types of contaminants from effluents. Nanostructured HDLs can be used to eliminate wastewater pollutants, mainly through adsorption and ion exchange mechanisms (LUNDEHØJ et al., 2019; Yang et al., 2016; ZHANG et al., 2019). Adsorption of pollutants into HDL is an efficient and cost-effective approach. In addition, the combination of HDLs with materials such as carbon nanostructures, anions, surfactants, iron nanoparticles and polymers provided a significant improvement in the surface characteristics and adsorption performance of HDLs (CHUBAR et al., 2017; MISHRA; DASH; Pandey, 2018b; ZUBAIR et al., 2017). In fact, these hybrids are increasingly arousing interest to investigate their adsorption performance for the elimination of various hazardous pollutants from aqueous solutions (MISHRA; DASH; PANDEY, 2018b).

This review describes the use of hybrids containing HDL as adsorbent materials in the removal of glyphosate present in the medium and also brings a comparison in function of the adsorptive

capacity of HDLs with different solids applied in the removal of glyphosate. We address the effect of some factors that affect adsorption, in addition to its adsorption performance and adsorbent/adsorbate interaction mechanism.

2.2.2 Biochar

Biochar can be defined as carbonized or pyrolyzed biomass, produced for application in the soil in order to improve its properties while providing the sequestration of C. The sequestration of C occurs due to the presence of biochemically recalcitrant and predominantly aromatic carbon in the biochar. Biochar obtained by biomass pyrolysis degrades much more slowly, creating a carbon stock in the soil, about 1500 to 2000 times more stable than a non-pyrolyzed organic material, residing in the soil for several hundred to thousands of years. The presence of internal organic structures similar to that of graphite contributes to biochar maintaining its recalcitrance for a longer period of time, characterizing a more efficient C sequestration system (CLOUGH et al., 2013; DING et al., 2016).

Due to its excellent properties, such as: high surface area, porosity, low cost and easy obtainment, non-toxic, structural variability and easy handling, biochar has been studied as a potential adsorption agent of organic and inorganic pollutants (CHEN et al., 2019b; WEBER; Quicker, 2018; XIANG et al., 2020).

2.2.3 Aluminosilicate clay minerals

Clays are formed in their essence by clay minerals, which are aluminosilicates hydrated mainly of iron, magnesium and occasionally aluminum (UDDIN, 2017). The structures of clay minerals are formed from two fundamental groups: tetrahedral (SiO_4) and octahedral (AlO_8) groups of oxygen atoms or ions and hydroxyl ions, around small cations (KHURANA et al., 2015). The tetrahedral groups bind to each other to form continuous hexagonal sheets, the tetrahedral leaves. The octahedral groups also bind hexagonally, forming octahedral sheets. Among the wide variety of silicate clays, those of the smectites group stand out (UDDIN, 2017). Within the smectite group, special attention can be paid to montmorillonite, a clay mineral consisting of the overlapping of two hexagonal sheets formed by tetrahedral silicate groups (SiO_4), with a central sheet formed by octahedral groups ($Al_2(OH)_6$), joined together by oxygen atoms common to the two leaves (2:1). Clay minerals such as montmorillonite have been and still are being widely studied as adsorbent agents due to their good characteristics, such as: high natural abundance, low cost, nontoxic and good surface area (BAILEY; LEKKERKERKER; MAITLAND, 2015; Khurana et al., 2015; KLOPROGGE; KOMARNENI; AMONETTE, 1999; PERELOMOV et al., 2021; UDDIN, 2017)

2.3 EVALUATION OF GLYPHOSATE ADSORPTION BY DIFFERENT MATERIALS

When compared to other compounds and ions, glyphosate is still a little-studied absorbate. In part, the difficulty of its study is due to the large structural variation suffered by the compound as a function of pH as previously reported in the text, which can be a major problem when we are dealing, for example, with lamellar double hydroxides (HOTTES et al., 2022). The text brings some more recent studies published in the last five years but does not fail to mention some works prior to this period that were considered precursors of studies involving glyphosate.

Hottes et al (2022) investigated the mobility of glyphosate in calcined lamellar double hydroxide and found that glyphosate adsorption was increasing as a function of increasing medium temperature. In addition, the authors also verified that the presence of different anions in the medium directly affects the adsorption of glyphosate by the solid, and that such interference was more expressive with the increase in the concentration of competing ions in the medium.

Chen et al. (2019) evaluated the adsorption of glyphosate on a composite consisting of cellulose and $MnFe_2O_4$. The authors point out that, individually, cellulose and inorganic solid presented adsorptive capacity lower than the composite material formed by the union of the two components, indicating the existence of a synergistic effect between them.

Yang et al. (2018) evaluated the photodegradation process of glyphosate using goethite and magnetite and observed that the former had a better glyphosate degradation/adsorption capacity. This fact can be evidenced thanks to the higher zero charge potential of goethite when compared to magnetite.

Recent studies evaluate the mobility of glyphosate in environmental systems by studying its adsorption and its metabolites in natural clays, such as montmorillonite (FLORES; TORRES SÁNCHEZ; DOS SANTOS AFONSO, 2018), goethita and magnetite (ARROYAVE et al., 2016). This is an important aspect of contaminant hydrology since classical times. In the future, more investigations are likely to emerge using other types of soil samples. Other studies have now progressed to examine the effect of other chemical species on glyphosate-clay adsorption in the system. These include phosphates, fulvic acid and humic acid (ARROYAVE et al., 2016). Competitive adsorption systems like this help show adsorbent affinity for the specific adsorbate in the presence of other species (IGHALO et al., 2020). HDL-containing hybrids provide a new research window to explore the excellent adsorption trend of different toxic pollutants on HDL from aqueous solutions. However, other materials have also been shown to be potentially efficient with regard to adsorption of the herbicide glyphosate. Table 2 summarizes the results of equilibrium and kinetic modeling. In most cases, the best-fit isotherm model was Langmuir (monolayer) or Freundlich (multiple layers). The

nature of the adsorbent plays an important role in determining whether the adsorption is mono- or multi-layer.

Table 2: Comparison of the different types of materials applied in the adsorption of the herbicide glyphosate.

Material type	q_{max} (mg/g)	Isotherm/kinetics	Reference
MgAl-ODL	158,22	Langmuir/2nd order	(HOTTES et al., 2022)
NiAlNO 3-HDL	180,00	Langmuir/2nd order	(KHENIFI et al., 2010)
Soil	161,3	Langmuir/2nd order	(SEN et al., 2017)
Activated carbon	48,80	Langmuir	(NOUROUZI; CHUAH; Choong, 2010)
Biochar	123,03	Freundlich/1st order	(HERATH et al., 2016)
Biochar	44,00	Freundlich/2nd order	(MAYAKADUWA et al., 2015)
Biochar	40,49	Langmuir/2nd order	(JIANG et al., 2018)
Industrial waste	113,60	Langmuir	(HU; ZHAO; SOROHAN, 2011)
Graphene-$MnFe_2O_4$	39,90	Freundlich/1st order	(YAMAGUCHI et al., 2016)
Graphene-Fe_2O_3	46,80	Langmuir/2nd order	(SANTOS et al., 2019)
biopolymer	10,88	Freundlich/2nd order	(CARNEIRO et al., 2015)
Resin-$Cu(OH)_2$	113,70	Langmuir/2nd order	(ZHOU et al., 2017)
Activated carbon-magnetic powder	119,61	Langmuir/2nd order	(YU et al., 2021)
Graphene oxide	70,07	Langmuir/2nd order	(LI et al., 2018)
$MnFe2O4@CAC$	164,00	Freundlich/2nd order	(CHEN et al., 2019a)
Montimorilonite	-	Freundlich and Sips	(PEREIRA et al., 2020)
Magnetite	6,70	Langmuir/1st order	(YANG et al., 2018)
Chitosan	35,10	Langmuir	(RISSOULI et al., 2017)
Chitin	14,10	Langmuir	(RISSOULI et al., 2017)

3 CONCLUSION

The adsorptive potentials of carbon-based materials, clays, polymers and resins for glyphosate removal in solution had their values compared. It was observed that polymers and resins are the best class of adsorbents for adsorption of glyphosate in aqueous medium. Glyphosate adsorption is usually more appropriately modeled by Freundlich or Langmuir isotherms, depending on the nature of the adsorbent. Pseudo-second-order and first-order kinetics were also the best fits to model glyphosate adsorption kinetics. This is an indicator that glyphosate adsorption is dependent on the number of metal ions present in the solution, as well as anchor points on the adsorbent surface.

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