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Analysis of the adsorption capacity of glyphosate in German railway systems

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Report submitted to the School of Chemistry of the Instituto Tecnológico de Costa Rica as a partial requirement to obtain the degree of Environmental Engineer with a licentiate degree.

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DEDICATION

A mi madre, que siempre ha estado presente, apoyándome y motivándome a cumplir mis metas.

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LIST OF ACRONYMS AND ABBREVIATIONS

ADI	Acceptable Daily Intake
AMPA	Aminomethylphosphonic acid
BfUL	Saxon State Laboratory for Environment and Agriculture
BMDV	Federal Ministry for Digital Affairs and Transport
BMEL	Federal Ministry of Food and Agriculture
BVL	Federal Office of Consumer Protection and Food Safety
CO₂	Carbon Dioxide
CEC	Cation Exchange Capacity
DB	Deutsche Bahn
EC	Electrical Conductivity
EFSA	European Food Safety Authority
EBA	Federal Railway Authority
FMOC-Cl	9-fluorenyl methoxycarbonyl chloride
HTWD	University of Applied Sciences Dresden
IARC	International Agency for Research on Cancer
KG	Korngemisch
O₂	Oxygen
SOM	Soil Organic Matter
TEC	Instituto Tecnológico de Costa Rica

ABSTRACT

Glyphosate is a widely used herbicide globally and has been extensively employed for weed control in railway systems over several decades. The inherent low organic matter content and runoff capacity of these systems pose a risk of glyphosate runoff, ultimately reaching nearby aquatic bodies. This investigation focuses on studying the adsorption capacity of glyphosate in railway systems by analyzing four different soils by kinetic and isotherm tests. Batch experiments were conducted using glyphosate solutions with a concentration of 8 mg/L, and soils with particle sizes below 2 mm were examined. The adsorption kinetics of glyphosate in KG1.1 soil demonstrated a better fit to the pseudo second model, with equilibrium reached in 24 hours in 0.1 M KCl and 48 hours in artificial rainwater. Adsorption isotherm results were evaluated using the Langmuir and Freundlich models. The Langmuir model exhibited a better fit for the KG1.1 soil, revealing a modeled adsorption capacity of 0.25 mg/g. In contrast, the Freundlich model yielded better results for the fine material from the ballast, indicating a modeled adsorption capacity of 0.25 mg/g. The KG1.2 and KG2 soils exhibited poor fits to both models, with experimental adsorption capacities of 0.14 mg/g and 0.06 mg/g, respectively. The influence of pH on the adsorption process was investigated, highlighting that optimal adsorption conditions occur at pH 4. The effect of temperature on the adsorption capacity was analyzed, where no statistically significant effect was observed. The analysis of adsorption capacity in rail systems indicates a relatively low to moderate adsorption capacity of glyphosate. In order to better assess the risks associated with glyphosate presence in nearby aquifers, it is recommended to accurately determine the chemical and biological composition of soils (e.g., SOM, TOC, metals content) from railroads and to study the transportation dynamics of glyphosate in these systems by conducting column tests and modelling.

Key words: Railway systems soil, adsorption, glyphosate.

RESUMEN

El glifosato es un herbicida altamente utilizado en todo el mundo, el cual se ha empleado ampliamente para el control de las malas hierbas en los sistemas ferroviarios durante varias décadas. El bajo contenido en materia orgánica y la capacidad de escorrentía inherentes a estos sistemas suponen un riesgo de escorrentía de glifosato que, en última instancia, alcanza los cuerpos acuáticos cercanos. Esta investigación se centra en el estudio de la capacidad de adsorción del glifosato en sistemas ferroviarios mediante el análisis de cuatro suelos distintos por medio de pruebas de cinética e isotermas de adsorción. Se realizaron experimentos de tipo batch utilizando soluciones de glifosato con una concentración de 8 mg/L, y se examinaron suelos con tamaños de partícula inferiores a 2 mm. La cinética de adsorción del glifosato en el suelo KG1.1 demostró un mejor ajuste al modelo de pseudo segundo orden, alcanzándose el equilibrio en 24 horas en KCl 0.1 M y en 48 horas en agua de lluvia artificial. Los resultados de la isoterma de adsorción se evaluaron utilizando los modelos de Langmuir y Freundlich. El modelo Langmuir mostró un mejor ajuste para el suelo KG1.1, revelando una capacidad de adsorción modelada de 0.25 mg/g. Por el contrario, el modelo Freundlich arrojó mejores resultados para el material fino del lastre, indicando una capacidad de adsorción modelada de 0.25 mg/g. Los suelos KG1.2 y KG2 mostraron un mal ajuste a ambos modelos, con capacidades de adsorción experimentales de 0.14 mg/g y 0.06 mg/g, respectivamente. Se investigó la influencia del pH en el proceso de adsorción, destacando que las condiciones óptimas de adsorción se dan a pH 4. Se analizó el efecto de la temperatura en la capacidad de adsorción, donde no se observó ningún efecto estadísticamente significativo. El análisis de la capacidad de adsorción en sistemas ferroviarios indica una capacidad de adsorción relativamente baja a moderada del glifosato. Para evaluar mejor los riesgos asociados a la presencia de glifosato en los acuíferos cercanos, se recomienda determinar con precisión la composición química y biológica de los suelos (por ejemplo, SOM, TOC, contenido en metales) de los sistemas ferroviarios y estudiar la dinámica de transporte del glifosato en estos sistemas mediante la realización de ensayos en columna y la modelización.

Palabras clave: Suelo de sistemas ferroviarios, adsorción, glifosato.

1 INTRODUCTION

In railway systems is necessary to remove the vegetation growing along the railroad tracks to ensure their proper maintenance and guarantee the safety of rail traffic. There are various mechanical methods to eliminate these unwanted plants, using hot water, liquid nitrogen, radiation, steam, among others (Torstensson, 2001). However, chemical herbicides are most frequently employed for weed management, and European railroad operators mostly rely on glyphosate for this purpose (Cederlund, 2022). According to the European Commission (2023), as of now, glyphosate has been approved for usage only as herbicide in the European Union until December 2023. However, according to the same author, there is an ongoing analysis being conducted by the European Commission to determine whether glyphosate should be renewed or not beyond this period.

Glyphosate has gained global recognition and widespread use due to its effectiveness and low toxicity, making it a popular choice for weed control in urban areas (Hanke et al., 2010). It was also noted by Hanke et al. that the application of glyphosate on hard surfaces (e.g., asphalt, concrete, and gravel) for maintenance purposes is a significant contributor to its presence, given the limited retention capacity of such areas. In the context of railway systems, the utilization of glyphosate poses a potential contamination risk to water bodies (Torstensson, 2001). High concentrations of glyphosate in water sources can lead to disruptions in aquatic organisms (Martínez Bellido, 2018). Moreover, the impact of glyphosate extends beyond water bodies, potentially affecting the soil and posing risks to human health (Salazar López & Aldana Madrid, 2011).

According to Vo et al. (2015) the microbial biomass found in track areas is considerably lower compared to agricultural soil, with only one-tenth of the biomass present. They also state that this disparity can be attributed to factors such as the coarse texture of ballast and embankment materials, as well as their low organic and nutrient contents. Vo et al. conclude that consequently, herbicides like glyphosate, commonly used in railway embankments, tend to have better mobility and extended persistence. Based on Vereecken (2005) in instances of heavy rainfall occurring shortly after herbicide application, there is a possibility of preferential flow and rapid transport of pesticides. The study noted that as the soil becomes saturated, the volume of drainage increases. According to Borggaard & Gimsing (2008)

glyphosate, along with its metabolite aminomethylphosphonic (AMPA), can be transported from terrestrial to aquatic environments in both dissolved and particle-bonded forms. This movement occurs through processes such as leaching in subsurface runoff and overland flow in surface runoff. In the same context, Borggaard & Gimsing point out that subsurface leachates eventually reach drainage and groundwater systems, while surface runoff transports these compounds directly into open waters like streams and lakes. Due to these factors, there is a need to investigate the adsorption capacity of glyphosate in soils from railway systems. The primary goal of this project was to analyze the adsorption capacity of glyphosate in railway soils. This was achieved by conducting batch tests to determine the specific adsorption characteristics of glyphosate in the soil samples.

1.1 OBJECTIVES

1.1.1 General objective

Analyze the adsorption capacity of glyphosate in soils within German railway systems, from its use in vegetation control on these systems.

1.1.2 Specific objectives

Determine the adsorption characteristics of glyphosate in different types of soil obtained from railway systems.

Analyze the adsorption capacity of glyphosate in railway systems under simulated rainwater conditions.

2 LITERATURE REVIEW

2.1 SITUATION OF GLYPHOSATE IN GERMANY: USAGE, REGULATIONS, IMPACT ON HEALTH AND ENVIRONMENT

In the 1920s, herbicides were introduced for weed control in railway tracks in Germany (Schweinsberg et al., 1999). The same author mentioned that since 1996, Deutsche Bahn (DB) has exclusively used glyphosate in various formulations. Glyphosate is applied selectively to individual plants with a maximum application rate of 0.29 g/m² in the ballast bed and embankment, typically once or twice a year (spring and late summer) (Burkhardt et al., 2008). However, the use of glyphosate has resulted in contamination of nearby surface and groundwater. Nevertheless, no herbicides from this application were found in the public drinking water supplies directly, with the exception of a few instances following activated carbon filtering (Schweinsberg et al., 1999).

In a study conducted by Conrad et al. (2017), which analyzed 399 urine samples collected between 2001 and 2015, it was found that 31.8% of the samples contained glyphosate concentrations at or above the quantification limit of 0.1 µg/L. For the metabolite AMPA, this was the case for 40.1% of the samples. The acceptable daily intake (ADI) for glyphosate, as determined by the European Food Safety Authority (EFSA), is 0.5 mg/(kg.day). Conrad et al. further highlights that according to EFSA's risk assessment, none of the glyphosate concentrations measured in the samples pose a health concern. However, the International Agency for Research on Cancer (IARC) has classified glyphosate as Group 2A, indicating that it is "probably carcinogenic to humans".

According to Voss (2023), DB has announced that it will no longer use glyphosate starting from 2023, effectively implementing the phase-out plan announced in 2019. In late 2022, the EU Commission extended the approval of glyphosate until December 2023. Voss comments that the approval for the use of pelargonic acid was granted in February 2023 by the Federal Office of Consumer Protection and Food Safety (BVL), in coordination with the responsible Federal Ministry of Food and Agriculture (BMEL) and the Federal Ministry for Digital Affairs and Transport (BMDV). However, the use of pelargonic acid is still subject to approval by the Federal Railway Authority (EBA).

2.2 GLYPHOSATE APPLICATION IN RAILWAY SYSTEMS

2.2.1 Structure of railway systems and potential transport pathways of glyphosate

2.2.1.1 Railway system structure

The structure of railway systems consists of several essential components that fulfill specific purposes, contributing to the overall functionality and stability of the tracks. Figure 2.1 shows the main components of these systems. The functions of these components are defined below.

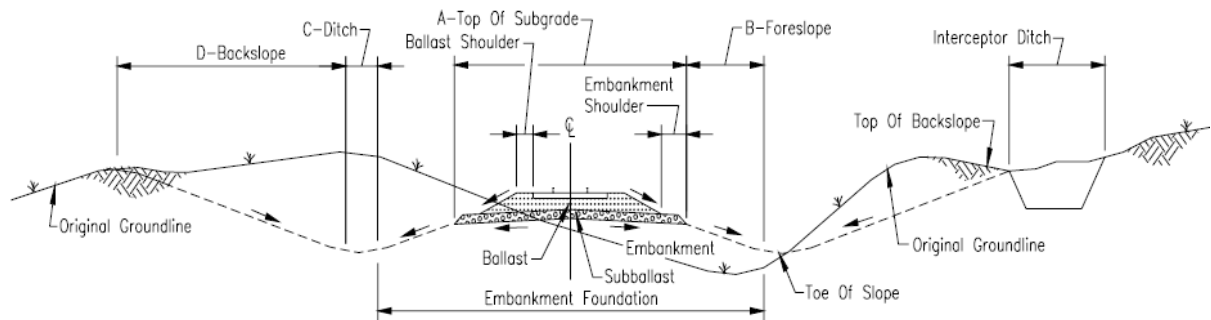


Figure 2.1. Cut and fill section components (AREMA, 2010).

According to AREMA (2010), the purposes of the main segments of the railway systems are:

- A) Top of Subgrade: To serve as the foundation for the sub-ballast, ties, rails, and service roads.
- B) Foreslope: To securely sustain the subgrade of the road and track. to install subgrade at a safe height above the drainage levels specified in the design.
- C) Ditch: To transport watershed runoff and seepage into the cut while limiting the deterioration of the track's subgrade.
- D) Backslope: Resultant excavation face located between outer ditch line and natural ground line.
- E) Interceptor Ditches: Used to transport runoff from the watershed they serve and keep it out of the cut.

According to AREMA (2010) and Vo et al. (2015), the infrastructure of a railway is comprised of a track superstructure and a track substructure. The authors mention that the superstructure is the combination of rail, cross ties, additional track materials, and special track materials that make up a track system. AREMA and Vo et al. also explain that the

substructure is the strata of granular materials that are put in place to enable drainage, anchorage of the track superstructure in the three dimensions of space, load distribution and transfer from the track superstructure to the roadbed below. These functions enable precise system-free alignment, slope, and cross-level adjustments of the railway superstructure and protecting the materials of the roadbed from climatic forces. In the same context, the authors mention that a typical ballasted substructure comprises ballast as a top layer of the foundation of single-sized rocks, on which the superstructure is set at a depth between 150-550 mm; sub-ballast as a lower stratum of the substructure composed of well-graded crushed rock or a sandy gravel mixture, situated beneath the ballast section and to a depth between 90-450 mm; and an underlying subgrade layer (natural or amended soil).

2.2.1.2 Routes for glyphosate transportation

Glyphosate application in railway infrastructure involves the precise application of herbicide to the railway tracks and ballast using specialized spray trains operated by trained personnel (Torstensson, 2001). After application, glyphosate can take various routes of transportation. According to Vo et al. (2015), the movement of contaminants, including glyphosate, is significantly influenced by rainfall, which determines their migration across rail tracks and embankments. Vo et al. point out that generally, the ballast and sub-ballast layers exhibit higher permeability compared to the subgrade, causing contaminants to migrate downward and accumulate at the interface between the sub-ballast layer and the subgrade. Moreover, a study by Cederlund (2022) found limited lateral transport of glyphosate. The same author mentions that this could be attributed to the proposed control of pesticide leaching from railways, including glyphosate, through particle-bound or particle-associated transport, predominantly occurring through preferential flow paths. Such mechanisms are likely less significant for lateral transport in saturated zones.

Based on Vo et al. (2015), during periods of low rainfall intensity (below 15-20 mm), rainwater may accumulate within the track bed, with a substantial portion being absorbed or evaporated without generating runoff. On the other hand, Vo et al. also make note that intense rainfall can result in the washout of contaminants into drainage systems or their infiltration into adjacent soil. Consequently, the retention time of pollutants within rail tracks can vary significantly, ranging from half a day to three months, depending on the location. Noteworthy

levels of glyphosate were identified in the findings of Cederlund (2022) after approximately three years of sampling, indicating that the process of glyphosate migration through the railway ballast and subgrade, eventually reaching groundwater, may take an even longer duration.

As stated by Vo et al. (2015), rainwater falling on the ballast quickly drains into the sub-ballast layer and subsequently flows into drainage systems, which can be a network of parallel pipework or natural ditches located alongside the embankment toe. Vo et al. further explain that the potential for runoff pollution is influenced by various factors, including precipitation patterns, runoff flow dynamics, substance properties, and their interaction with surrounding soils. The same author mentions that the discharge of glyphosate into runoff is determined not only by its sources and characteristics but also by its interactions with the soil environment. Vo et al. conclude that the unsaturated soil near the track bed can serve as both a filter and a pathway for the transport of pollutants, with flow dynamics depending on soil texture, structure, water content, and tension.

Furthermore, the erosion of rail embankments can result in the removal of sediments, which may pose a pollution risk depending on their particle size. Additionally, heavy metals and organic compounds have a tendency to bind to particles, facilitating the transport of pollutants into aquatic environments (Vo et al., 2015).

2.3 HERBICIDE GLYPHOSATE- PROPERTIES AND IMPACT ON SOIL, WATER BODIES AND HUMAN HEALTH

2.3.1 Physical-chemical properties

Glyphosate, also known as N-(phosphonomethyl)glycine, is an organic acid comprising a glycine unit and a phosphonomethyl group. Its chemical formula is $C_3H_8NO_5P$, and the visual representation of its structure can be observed in Figure 2.2 (Mensink et al., 1994). It is an effective herbicide against weed, belonging to the class of organophosphorus anionic herbicides (Martínez Bellido, 2018). Due to its amphoteric nature, glyphosate can exist as several ionic species depending on the pH level. It is used in numerous crops and is available in multiple commercial formulations. In the primary formulation as Roundup, glyphosate is contained as isopropylamine salt (Mensink et al., 1994). Some of the physical and chemical properties of glyphosate are listed in Table 2.1.

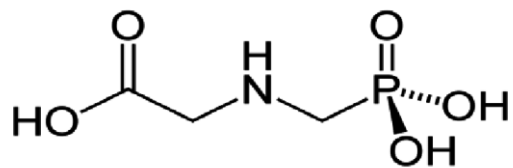


Figure 2.2. Chemical structure of N-(phosphonomethyl)glycine, or glyphosate.

Table 2.1. Physical and chemical properties of glyphosate.

Parameter	Data
Physical state	Crystalline powder
Colour	White
Odour	None
Density	0.5 g mL ⁻¹
Molecular weight	169.1 g mol ⁻¹
Melting point	185.5°C
Solubility in water at 25°C	12 g/L
pH in 1% solution	2.5
pKa values	<2, 2.6, 5.6, 10.6
Flammability	Not flammable
Explosiveness	Not explosive

2.3.2 Cation exchange capacity

The cation exchange capacity (CEC) of soils refers to their ability to adsorb and exchange cations (Tan, 2011). It is determined by factors such as the surface area and surface charge of clay particles. The same author points out that various cations exhibit different levels of efficacy in exchanging adsorbed cations. The amount of cations adsorbed is not always equivalent to the amount exchanged. Tan also noted that divalent ions tend to be more strongly held than monovalent ions, resulting in a more challenging exchange process for them compared to monovalent ions.

When a sorbate is a weak acid or weak base, as it is the case of glyphosate, its presence can exist either in a neutral state or an ionized state, which is determined by the pH of the solution (Worch, 2012). In the same context, Worch points out that the proportion of ionic and neutral forms is influenced by the acidity constant of the solute, often represented by

pKa, and the pH of the aqueous phase. Ionized species are more soluble and less hydrophobic compared to their neutral counterparts. Continuing with Worch's argument, the sorption behavior differs between the ionic and nonionic species, with neutral species expected to exhibit stronger sorption compared to ionized species.

Glyphosate, due to its anionic nature in the relevant pH range of soils, can only adhere to surfaces that possess variable charges rather than permanent negative charges found on layer silicates (Figure 2.3) (Borggaard & Gimsing, 2008). The functional groups present in glyphosate, namely amine, carboxylate, and phosphonate, have the capability to form strong coordination bonds with metal ions, resulting in the formation of bidentate and tridentate complexes. This unique characteristic places glyphosate in the infrequently encountered category of chelating herbicides (Ololade et al., 2014; Dollinger et al., 2015). Glyphosate is associated with four ionic equilibrium constants, specifically $pK_{a1}=0.8$, $pK_{a2}=2.23$, $pK_{a3}=5.46$, and $pK_{a4}=10.14$, which are linked to its functional groups. These constants indicate that as the pH increases, the net charge of the glyphosate molecule becomes more negative. When the pH exceeds the zero-point charge of a mineral, hydrous-oxide surfaces exhibit a prevalence of negative charges. Consequently, the presence of negative charges on both hydrous-oxide surface sites and glyphosate molecules leads to a decrease in adsorption (Sidoli et al., 2016).

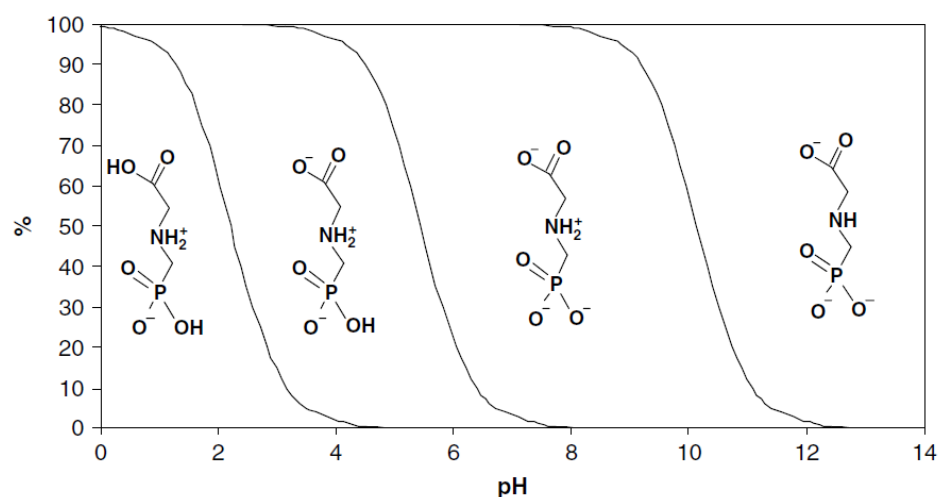


Figure 2.3. Glyphosate species distribution in relation to pH (Bjerrum diagram) (Borggaard & Gimsing, 2008).

2.3.3 Glyphosate impact on soil, water bodies and human health

According to Salazar López & Aldana Madrid (2011), applying a pesticide to a system sets in motion a series of interactions between the pesticide and the surrounding environment. Different media, including plants, water, soil, and the atmosphere, are involved in this interaction. Salazar López & Aldana y Madrid further explain that the duration and disappearance of the pesticide's effects are determined by its specific structure and physicochemical properties. As a result, the pesticide can linger in the environment, primarily accumulating in water and soil. Eventually, it can enter the food chain, progressing through different levels and ultimately affecting humans.

Martínez Bellido (2018) states that the destiny of glyphosate in soils relies on the specific properties of the soil itself. Additionally, the presence of other substances, such as iron oxide or various minerals, plays a significant role. The same author notes that glyphosate is strongly adsorbed by soil organic matter (SOM) and has limited soil mobility. Hence, glyphosate undergoes degradation, transforming into its metabolite AMPA and eventually decomposing into carbon dioxide (CO₂). According to Salazar López & Aldana Madrid (2011), another potential scenario involves the demobilization of glyphosate in the soil through competition with phosphorus. In this case, the herbicide could potentially be transferred to non-target plants, and this transfer is influenced by various soil characteristics. The same authors highlight that factors such as the soil's ability to fix phosphorus, the iron content available to plants, pH levels, CEC, sand content, and the amount of organic matter present in the soil all contribute to this process.

According to Martínez Bellido (2018), through leaching, glyphosate can contaminate water resources like surface water and groundwater. The same author states that high concentrations of glyphosate in surface water can cause alterations in aquatic organisms. Some of the effects are inhibition of growth of algae and fish, abnormalities in sea urchin hatching, histopathological changes in fish gills, vacuolation of hepatocytes, nuclear pyknosis in liver and kidney, and alteration of sexual activity. Additionally, Salazar López & Aldana Madrid (2011) remark that it has been demonstrated that glyphosate dissipates quickly in lentic systems. It is suggested that sediment adsorption and biodegradation are the primary causes of glyphosate loss in the water column.

Glyphosate has been demonstrated to have damaging effects on the human body. It exhibits to be toxic to human cells, to act as an endocrine disruptor in aromatase activity, to alter DNA structure in other cell types like mammalian cells and to cause cell death in the liver (Salazar López & Aldana Madrid, 2011). It may also contribute to the development of chronic conditions that have teratogenic, oncogenic, and hepatorenal consequences. Moreover, it is classified as a probable carcinogenic substance belonging to Group 2A (Martínez Bellido, 2018).

2.3.4 Biodegradation

The rate at which herbicides are degraded by microorganisms in field conditions is influenced by various environmental factors. According to Ashton (1982), favorable conditions that support the growth of microorganisms responsible for degradation accelerate the degradation rate, while conditions that inhibit their growth slow down the process. The same author states that soil factors such as temperature, pH, CEC, fertility, structure, type, moisture content, organic matter, O₂, CO₂, and other parameters play significant roles. Additionally, the same author writes that microorganisms employ a range of biochemical reactions, such as oxidation, reduction, hydrolysis, hydroxylation, decarboxylation, dehalogenation, dealkylation, and conjugation with normal metabolites like sugars, amino acids, or peptides, to degrade herbicides.

According to Carlisle & Trevors (1988), glyphosate degradation is primarily driven by microbial processes, while chemical degradation and photodecomposition have minor roles in soil breakdown, though photolysis may be more relevant in aquatic environments. The nonherbicidal components of glyphosate may enhance its degradation by stimulating soil microbial activity. In the same context, Carlisle & Trevors point out that the rate at which glyphosate degrades is linked to the soil respiration rate, which serves as an indicator of microbial activity. Carlisle & Trevors (1988) mention that the half-life of glyphosate in soil varies greatly, ranging from less than a week to several years, and is influenced by soil binding capacity and microbial activity levels. Additionally, the same authors state that the primary metabolite of glyphosate is aminomethylphosphonic acid (AMPA), while several minor metabolites, including N-methylaminomethylphosphonic acid, glycine, N, N-

dimethylaminomethylphosphonic acid, and hydroxymethylphosphonic acid, have also been identified, collectively accounting for less than 1% of the total applied glyphosate.

Temperature could affect glyphosate transportation and biodegradation Cederlund (2022). They propose that dry conditions during summer season could impede the degradation of glyphosate, consequently increasing the potential for leaching once autumn rains commence. The same author concludes that this can be attributed to reduced microbial activity in soil caused by limited bioavailability of organic molecules and the increased energy expenditure required by microorganisms to maintain osmotic pressure under drought conditions.

2.4 ADSORPTION OF GLYPHOSATE

2.4.1 Adsorption: Terms and definitions

Adsorption, commonly employed in practical applications, consist in a process where Substances that are present in a liquid phase are adsorbed, or collected, on a solid phase and then removed from the liquid phase through the mass transfer (Crittenden et al., 2012). The same author defines that the term *adsorbent* refers to the substance that adsorbs onto a surface, whereas *adsorbate* refers to the solid onto which the substance is adsorbed. Crittenden et al. (2012)also mention that diffusion is the mechanism that moves dissolved species into the porous solid adsorbent granule during the adsorption process, where they are adsorbed onto the large inner surface of the adsorbent. This can be seen in Figure 2.4.

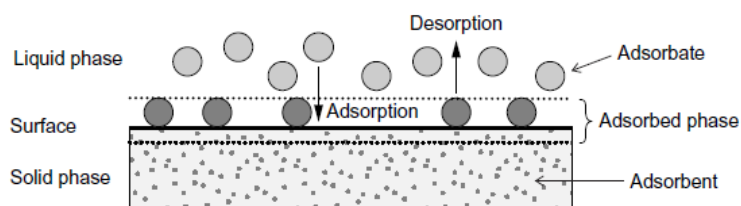


Figure 2.4. Basic adsorption terms (Worch, 2012).

Adsorption equilibrium, adsorption kinetics, and adsorption dynamics make up the three basic components of the application-focused theory of adsorption (Worch, 2012). Additionally, Worch (2012) highlights that the dependency of the amount adsorbed on the adsorbate concentration and temperature is described by the adsorption equilibrium. According to the same author the adsorption kinetics, or the increase in loading with time or,

alternately, the drop in liquid phase concentration with time, is the study of how the adsorption process changes with time.

Adsorbents can be categorized as either naturally occurring or artificially produced through industrial manufacturing and activation procedures. Clay minerals, natural zeolites, oxides, and biopolymers are examples of common natural adsorbents (Worch, 2012). According to the same author, geoadsorbents are solids with a mixture of organic and mineral components. Worch (2012) also states that the mineral components primarily consist of oxidized substances and clay minerals. These components, owing to the surface charge, exhibit a strong affinity for adsorbing ionic species. On the other hand, Worch (2012) highlights that the organic fractions present in geoadsorbents have the ability to bind organic solutes, particularly hydrophobic compounds.

The adsorption onto geoadsorbents depends on its porosity (Worch, 2012). Three categories of pores are distinguished: macropores, mesopores, and micropores (Table 2.2). The same author states that macropores and mesopores primarily play a role in facilitating mass transfer within the adsorbent particles, while the volume of micropores predominantly influences the internal surface area and, consequently, the adsorption capacity. As the micropore volume increases, the internal surface area also increases. Essentially, it is important to note that when dealing with very small pores and large adsorbate molecules, there may be limitations in the extent of adsorption due to size exclusion.

Table 2.2. Classification of porosity (Worch, 2012).

Pore type	Pore radius range
Macropores	>25 nm
Mesopores	1 nm ... 25 nm
Micropores	<1 nm

2.4.1.1 Adsorption kinetics

The advancement of the adsorption process over time is referred to as adsorption kinetics. Diffusion processes to the adsorbent's outer surface and within its porous particles typically serve to limit the rate of adsorption (Worch, 2012).

To analyze the adsorption kinetics, an amount of solution (V_L) is introduced to interact with a mass of adsorbent (m_A), and the consequent change in concentration over time is

determined. Throughout the adsorption process, the concentration falls from the initial value (c_0) to reach the equilibrium concentration (c_{eq}) (Worch, 2012). Considering that, for every time interval during the experiment, the material balance in equation (1).

$$\bar{q}(t) = \frac{V_L}{m_A} [c_0 - c(t)] \quad (1)$$

Then the kinetic curve can be expressed as:

$$\bar{q} = f(t) \quad (2)$$

Where \bar{q} is the average solid phase concentration (amount adsorbed).

From the equations (1) y (2), typical kinetic curves can be seen in the following figure:

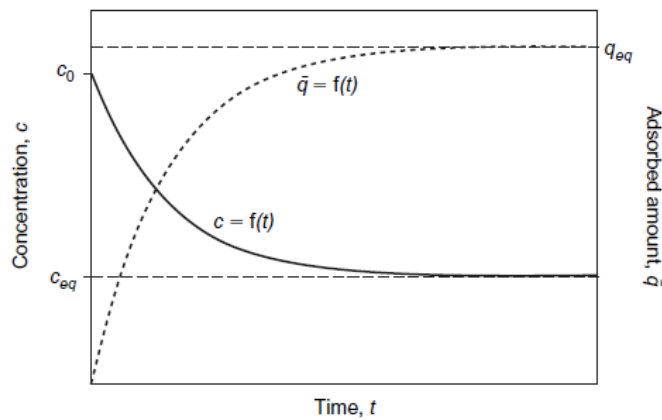


Figure 2.5. Kinetic curves. Progression of concentration and loading over time (Worch, 2012).

2.4.1.2 Adsorption isotherms

The strength of the adsorbate/adsorbent interaction determine the equilibrium position in a system under study, which is also greatly influenced by the characteristics of the adsorbate and adsorbent as well as the aqueous solution (such as temperature, pH, and the presence of competing adsorbates) (Worch, 2012). In the same context, Worch (2012) points out that the three parameters adsorbate concentration, adsorbate amount (adsorbate loading), and temperature collectively determine each adsorption equilibrium state. The same author further explains that it is customary to maintain a constant temperature and represent the equilibrium connections as an adsorption isotherm.

This equilibrium relationship is expressed in equation (3):

$$q_{eq} = f(c_{eq}), T = \text{constante} \quad (3)$$

From the above equation, an adsorption isotherm can be obtained as shown in Figure 2.6

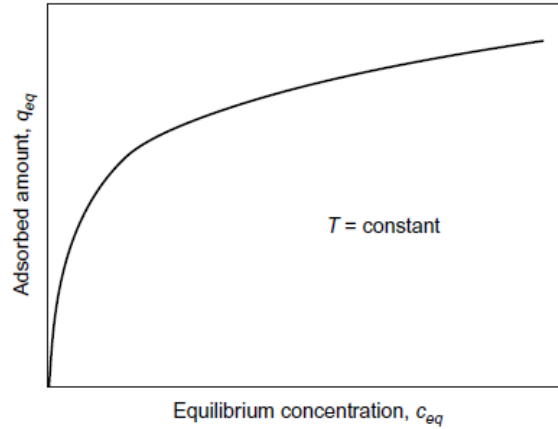


Figure 2.6. Adsorption isotherm (Worch, 2012).

The **Langmuir isotherms** considers that the equilibrium between the surface and solution is described as a reversible chemical equilibrium between species (Crittenden et al., 2012). Adsorption occurs in proportion to the portion of the adsorbent surface that is available, while desorption is proportional to the portion of the adsorbent surface that is occupied (Ayawei et al., 2017). This can be expressed in equation (4) in linear form.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

Where C_e is the equilibrium adsorbate concentration (mg/g) and the K_L is the Langmuir constant associated with adsorption capacity (mg/m). This constant can be correlated to changes in the adsorbent's surface area and porosity, indicating that a greater surface area and a pore volume will lead to an increased adsorption capacity (Ayawei et al., 2017).

According to the equation (5), the separation factor R_L , a dimensionless constant, can be used to describe the basic properties of the Langmuir isotherm.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

Where C_0 is the initial adsorbate concentration (mg/g).

The values of R_L provide insights into the nature of adsorption. Adsorption is unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$, and irreversible when $R_L = 0$ (Ayawei et al., 2017).

The **Freundlich isotherm** was first proposed as an empirical equation, which describes the data for heterogeneous adsorbents (Crittenden et al., 2012). This isotherm

provides an expression that characterizes the surface heterogeneity and the exponential distribution of active sites and their energies (Ayawei et al., 2017). It can be written as the linear version in the equation (6):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where the parameter K_F represents the adsorption capacity (L/mg), while $1/n$ represents the adsorption intensity. Additionally, $1/n$ provides information about the relative energy distribution and heterogeneity of adsorption sites (Ayawei et al., 2017).

2.4.2 Adsorption capacity of glyphosate in railway systems

Glyphosate exhibits distinct sorption characteristics in soil compared to other pesticides (Borggaard & Gimsing, 2008). The same authors further explain that unlike most pesticides that are moderately to weakly sorbed by SOM, glyphosate strongly sorbs to soil minerals. This is due to glyphosate's small size and possession of three polar functional groups (carboxyl, amino, and phosphonate groups). According to the same authors, within the typical soil pH range of 4-8, glyphosate forms mono- and divalent anions that have a high affinity for trivalent cations, such as Al^{3+} and Fe^{3+} . Borggaard & Gimsing (2008) also mention that this sorption behavior can be influenced by the presence of phosphate, as glyphosate and phosphate may compete for surface sites, affecting glyphosate sorption and mobility in phosphate-rich soils. Hence, the concentration of phosphate plays a crucial role in determining the extent of glyphosate sorption, with phosphate being capable of completely desorbing glyphosate in some cases due to similar adsorption mechanisms (Gimsing & Borggaard, 2002).

In areas like courtyards, railroads, and roads, the top layer of soil, which typically contains organic matter and micro-organisms, is usually removed and replaced with gravel layers of various types (Strange-Hansen et al., 2004). The same author states that in such systems, glyphosate adsorption is expected to be lower compared to soils, primarily due to the lower clay content, reduced presence of iron and aluminum oxides, and higher pH levels. Consequently, the same author concludes that pesticide mobility is likely to be higher in these areas due to increased infiltration rates, lower adsorption, and presumably lower mineralization rates. When herbicides like glyphosate are applied to these hard surfaces, such

as during treatments of roadways or courtyards, adsorption occurs mainly through physical and chemical sorption. Under unfavorable conditions, especially when rain follows shortly after application, herbicides may runoff into surface water (Spanoghe et al., 2005).

3 MATERIALS AND METHODS

This section provides a comprehensive account of the procedures implemented in the study. The initial step involved the selection of the glyphosate quantification method. Subsequently, the study focused on assessing the behavior of glyphosate through the evaluation of its removal via adsorption in diverse anthropogenic influenced soils sourced from railway systems. The experimental tests were carried out in simulated conditions that replicated the effects of rainfall events, as the presence of rainwater is significant in influencing the transport of contaminants across railroad tracks and embankments. The experiments took place at the Department of Water Sciences, University of Applied Sciences Dresden (HTWD).

3.1 GLYPHOSATE QUANTIFICATION

The methodology employed at HTWD for the quantification of glyphosate in water samples was developed by Waiman et al. (2012). The method involves the derivatization of the sample using 9-fluorenyl methoxycarbonyl chloride (Fmoc-Cl), followed by absorbance measurement at a wavelength of 265 nm (Figure 3.1).

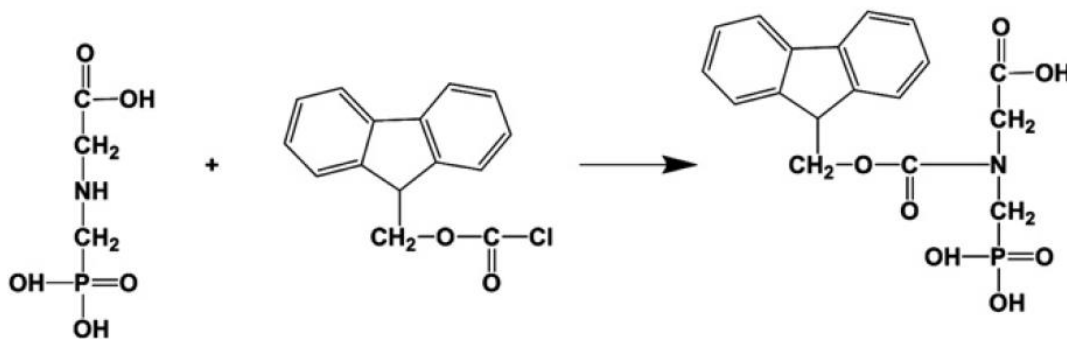


Figure 3.1. Reaction of glyphosate + Fmoc-Cl to give derivatized glyphosate (Waiman et al., 2012).

To construct a calibration curve, aqueous solutions of glyphosate were prepared in a supporting electrolyte composed of 0.1 M KCl. A calibration curve was successfully

generated, allowing the quantification of glyphosate in a concentration range from 1 mg/L to 20 mg/L (Appendix 1).

A stock solution was prepared using glyphosate analytical standard (PESTANAL®, 98.5%) in ultrapure water with a concentration of 180 mg/L. From the stock solution, a series of dilution were prepared, ranging from 1 to 20 mg/L, which served as data points for constructing the calibration curve. The glyphosate dilution (3 mL) was mixed with 0.5 mL of sodium tetraborate decahydrate buffer (ROTI®, pH 9.180 ± 0.02) in 15 mL polypropylene tubes. Subsequently, 0.5 mL of a 1.0 g/L solution of FMOCCl (obtained from Apollo Scientific, UK) was added, using acetonitrile (ROTISOLV®, 99.9%) as a solvent. The mixture was homogenized by manual stirring. The mixture was left to react at room temperature for a period of 2 hours. After the reaction, the resulting solution was mixed with 4.0 mL of dichloromethane (ROTISOLV®, 99.9%), followed by shaking and centrifugation at 1558 g for 6 minutes to achieve phase separation between dichloromethane and water due to their immiscibility. The aqueous phase, which contained the derivatization product, was withdrawn. Finally, the absorbance of the aqueous phase was measured using a spectrophotometer (WTW photoLab®, 6600 UV-VIS) to measure the presence of glyphosate in the sample. This procedure was repeated for the measurement of the samples collected in the following adsorption tests performed.

Throughout the measurement procedure, potential health risks were identified, particularly in relation to the use of compounds such as FMOCCl, acetonitrile, and dichloromethane. Due to the generation of fumes during their handling, additional precautions were necessary. Although a fume extraction cabinet was employed during the measurements, it was observed that significant exposure to the emitted dichloromethane fumes persisted. Consequently, to ensure the safety of personnel involved, a decision was made to procure and utilize a 620, 620S respirator equipped with an AX type gas filter.

For the experiments, a glyphosate concentration of 8 mg/L was selected. This concentration falls within the quantification range of the chosen method. With an anticipated maximum glyphosate removal of 80% during the tests, it becomes measurable. However, under real conditions, such high concentrations of glyphosate are not expected to be present in railway systems. In a study conducted by Zentrum für Schienenverkehrsforschung beim

Eisenbahn-Bundesamt (2022) near the railway, at a distance of 2.5 m, the maximum measured concentration was 16.56 $\mu\text{g/L}$.

3.2 DETERMINATION OF BASIC WATER QUALITY PARAMETERS

Throughout the experiments, the pH and electrical conductivity (EC) values of the samples were measured at both the beginning and the end of the experiments. For the measurements it was used a multi-parameter meter (WTW, Multi 3430). The measurements were conducted for various solutions, including glyphosate at a concentration of 8 mg/L, KCl, and artificial rainwater, both individually and in contact with the adsorbents.

3.3 PREPARATION OF ARTIFICIAL RAINWATER FOR SORPTION EXPERIMENTS

Considering that natural rainwater can vary its composition in terms of organic matter, ions, pH, and presence of contaminants, an artificial rainwater was prepared in the laboratory. The aim was to maintain consistent rainwater conditions across all experiments, which would not have been feasible with natural rainwater due to its variable parameters. Therefore, a controlled rainwater source with constant parameters was utilized for the experiments to examine the adsorption behavior of glyphosate under rainfall event conditions.

Artificial rainwater stock was prepared by dissolving magnesium sulfate, sodium sulfate, potassium nitrate, ammonium nitrate and calcium chloride in 2 L of ultrapure water. To ensure a composition closer to natural rainwater, data on various parameters of rainwater in Saxony were collected from the Saxon State Laboratory for Environment and Agriculture (BfUL). To simulate the salinity and pH of rainwater, specific ions were added to the solution. The concentrations used in the preparation of the dissolution are shown in Appendix 5. These concentrations result in pH and EC values of approximately 5.6 and 19.2 $\mu\text{S/cm}$, respectively, closely resembling the characteristics of natural rainwater. For each adsorption test, the artificial water stock solution was diluted according to the required volume of the test, using a dilution factor of 0.01.

3.4 ADSORBENTS PREPARATION

The selected soil samples used as adsorbents in this study were obtained from various depths and locations within the railway systems in Germany, reflecting anthropogenic influences. One such soil type is known as Korngemisch (KG), which forms a crucial part of the protective layer in railway systems. Korngemisch 1 (KG1) is a composite material consisting of a mixture of sands and rocks with varying sizes lower than 56 mm (IFM Dr. Schellenberg Rottweil GmbH, 2016). Two types of KG1 were utilized in this study, sourced from different ages and locations. The first type, labeled KG1.1, originated from an unknown source, with an estimated age of more than 10 years since it was extracted from railroad tracks. The second type, labeled KG1.2, displays a composition of fill, gravel, sandy, crushed aggregate, round aggregate at a depth of 0.90 m, geosynthetic, and a moisture content ranging from loose to medium dense, with a gray-brown color. In addition to KG1, another soil type investigated in this study is known as KG2. Korngemisch 2 (KG2) also forms part of the protective layer in railway systems but demonstrates a higher runoff capacity compared to KG1. KG2 is characterized by fill, gravel, sandy composition, slight siltiness, and a moist, gray appearance. Lastly, the ballast used for the extraction of the fine material demonstrates characteristics of backfill and gravel. The Table 3.1 shows more information of the characteristics of the soils. The soils utilized in this investigation, along with their corresponding information, were provided by GEPRO Ingenieurgesellschaft mbH, and HTWD.

Table 3.1. Characteristics of the soils KG1.1, KG1.2, KG2 and ballast.

	KG1.1	KG1.2	KG2	Ballast
Track	Unknown	2324	5841	5402
Location	Unknown	Neuwied	Ingolstadt	Ludwigslut
Depth	Unknown	0.70-0.90 m	0.40-0.60 m	0.00-0.60 m
Granulometry				
Silt %	5.35	2.61	1.7	Unknown
Sand %	52.48	45.02	80.3	Unknown
Gravel %	42.17	52.37	18.1	Unknown

3.4.1 KG1.1

The soil was sieved to obtain a particle size below 2 mm. Subsequently, that adsorbent fraction was washed with deionized and ultra-pure water to remove any presence of unwanted particles, such as leaves or plastics. The soil was then dried at a temperature of 105°C for 24 hours. After completing this process, the soil was again sieved to obtain the same particle size.

Initially, dry soil was used for the initial adsorption kinetics test, however, a significant amount of air bubbles was observed in the soil micropores. The air presence was confirmed by putting 30 g of soil in contact with 50 mL of ethanol into a glass bottle. Vacuum was then applied, and the presence of a significant quantity of bubbles released was observed. To eliminate air from the soil, 20 g of soil were placed in contact with 50 mL of ultrapure water, and it was applied vacuum pressure until the escape of air bubbles ceased. The water was decanted to remove the excess water. The soil obtained after treatment was stored in a sealed container under humid conditions. The process was repeated as necessary to obtain an adequate quantity of treated soil for the remaining experiments. Furthermore, the soil moisture percentage was determined by measuring 20 g of soil in triplicate, drying at 105°C and measuring the final weight of the dry soil. It was obtained a moisture percentage of 17.15 ± 0.38 , which was taken into consideration to adjust the required weight for subsequent trials.

3.4.2 KG1.2, KG2 and Fine material (ballast)

For soil samples KG1.2, KG2 and fine material, a process similar to the one described in the previous section 3.4.1 was followed. However, there was one exception - the soils were not washed to prevent any loss of fine material and organic matter present in them. As for the ballast, the fine material fraction was extracted by brushing, and subsequently, the identical sieving and drying process, as detailed earlier, was applied.

3.5 ADSORPTION KINETICS

Glyphosate adsorption kinetics was studied using batch tests in duplicate using the KG1.1 adsorbent dry and humid. 200 mL of a glyphosate solution with a concentration of 8 mg/L was added to 250 mL glass bottle, along with 2 g of adsorbent. One bottle served as a

blank containing only the solvent of the solution (KCl 0.1 M or artificial rainwater), 8 more bottles contained the glyphosate solution and adsorbent. Different kinetics experiments were conducted in a digital orbital shaker (Heathrow Scientific™) operating at 100, 130, 155, 180 and 200 rpm in each case, while a thermostat maintained a constant temperature of 20 °C throughout the experiments. Samples were collected from each bottle at two specific contact times, spanning intervals from 2 minutes to 3 days. A 12 mL syringe was used to withdraw 6 mL of the supernatant, which was subsequently filtered using a 0.45 µm syringe polyethersulfone white PES filter (CHROMAFIL®). The samples were then analyzed to measure the residual content of glyphosate. Following the methods outlined by De Jonge et al. (2001) and Strange-Hansen et al. (2004), the first test run at 180 rpm consisted utilizing KG1.1 soil that had been moistened with 0.1 M KCl solution for 24 hours before the test. The test with artificial rainwater was conducted using humid KG1.1 (treated for air removal) at an agitation speed of 180 rpm, which had demonstrated a more favorable equilibrium point in previous tests.

Experimental kinetic data were fitted to the pseudo-first order, pseudo-second order, Elovich, and second order models (Eqs. (7), (8), (9) and (10), respectively).

$$\log(Q_e - Q_t) = -\frac{k_1}{2.303}t + \text{Log}(Q_e) \quad (7)$$

$$\frac{t}{Q_t} = \frac{1}{Q_e}t + \frac{1}{k_2 Q_e^2} \quad (8)$$

Where k_1 (L/h) y k_2 (g/mg-h) are the adsorption rate constants; t is the time (h); Q_e (mg/g) y Q_t (mg/g) are the amounts of glyphosate adsorbed at equilibrium and at time t , respectively.

$$Q_t = \frac{1}{\beta} \ln(t) + \frac{1}{\beta} \ln(\alpha\beta) \quad (9)$$

Where Q_t (mg/g) is the amount of glyphosate adsorbed at time t (h); α (mg/g-min) is the initial adsorption rate; and β (g/mg) is the desorption constant.

$$\frac{1}{C_1} = k_2 t + \frac{1}{C_0} \quad (10)$$

Where k_2 (L/mg-h) is the rate constant and C_0 and C_t (mg/L) represent the initial concentration and solute concentration at time t (h), respectively.

3.6 PH AND TEMPERATURE EFFECT

In order to explore the impact of pH and temperature on the adsorption of glyphosate, a series of tests were carried out, involving the adjustment of these parameters to assess the corresponding changes in adsorption behavior. Humid KG1.1 served as the adsorbent material in the adsorption studies.

3.6.1 Effect of pH on glyphosate adsorption

In the first experiment, a solution of glyphosate was prepared in 0.1 M KCl at a concentration of 8 mg/L. Six bottles of borosilicate glass 3.3 were used, with one bottle serving as a blank and the remaining five bottles intended to evaluate different pH values. Each bottle contained 200 mL of the solution along with 2 g of KG1.1 soil as the adsorbent material. To achieve the desired pH values of 2, 4, 5, 7, and 10, 0.1 M HCl and/or 0.1 M NaOH were added accordingly. The initial pH and EC of each bottle were measured. Following the preparation, each sample was placed on an orbital shaker, set at a speed of 180 rpm, and maintained at a temperature of 20 °C. The samples were shaken continuously for 24 hours. At the end of the shaking period, the final pH and conductivity of each sample were measured, and the resulting concentration of glyphosate in each sample was determined.

In a second experiment, artificial rainwater was utilized, with a fixed concentration of 8 mg/L of glyphosate. Two sets of seven borosilicate glass bottles 3.3 were prepared, with one bottle serving as a blank. In each bottle, 200 mL of solution together with 2 g of KG1.1 soil were placed. To achieve the desired pH values of 3, 4, 5, 6, 7, and 8, 0.1 M HCl and 0.1 M NaOH were used for pH adjustment. The initial pH and conductivity of each bottle were measured. The containers were kept at a constant temperature of 20°C for 48 hours while being continuously shaken at a fixed speed of 180 rpm. Throughout the test period, the pH values were periodically adjusted to ensure the desired values were maintained. At the end of the 48-hour period, the final pH and conductivity of each sample were measured, and representative samples were collected for analysis of residual glyphosate.

3.6.2 Effect of temperature on glyphosate adsorption

The temperature value utilized in the adsorption tests was modified to account for the large temperature variations seen in Germany in order to evaluate the effect of temperature on glyphosate adsorption. An experiment at 10°C using KG1.1 was performed to compare with the original temperature of 20°C. Two sets of samples were prepared, each consisting of four samples: one serving as a control (blank) and the other three containing a glyphosate solution in 0.1 M KCl with a concentration of 8 mg/L. Subsequently, they were shaken for a duration of 24 hours at a speed of 180 rpm. The pH and EC of the samples were measured at both the beginning and end of the experiment. After the 24-hour period, samples were collected, and the remaining glyphosate content was determined.

3.7 ADSORPTION ISOTHERMS

In order to assess the adsorption capacity of glyphosate herbicide in railway systems, adsorption isotherms were conducted on different soil types: KG1.1, KG1.2, KG2, and fine material (ballast). These tests were designed to simulate the conditions of a rainfall event, and as such, the glyphosate solutions were prepared using artificial rainwater as the solvent for all samples. The obtained data was subjected to fitting analysis using the Langmuir and Freundlich models to determine the optimal fit option.

3.7.1 Isotherms of KG1.1

The batch test consisted of nine bottles of borosilicate glass 3.3. One bottle was designated as a blank, while the remaining eight bottles were used for testing the adsorption of a 200 mL solution containing 8 mg/L of glyphosate. To each of these eight bottles, varying masses of KG1.1 soil were added (g): 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 6.0. The bottles were agitated for 48 hours in an orbital shaker at 180 rpm and a constant temperature of 20 °C. At the end of the test, a sample of 8 mL was filtered by a 0.45 µm syringe polyethersulfone filter and the final concentration of glyphosate was determined. This procedure was applied to KG1.1, KG1.2, KG2 and the fine material from ballast. The original pH of the samples was maintained, having an initial value of 4.2 and changing after the addition of the soil's samples. The test was carried out in duplicate.

4 RESULTS AND DISCUSSION

4.1 ADSORPTION KINETICS

The data of glyphosate were fitted to the pseudo first order, pseudo second order, Elovich, and second order models. Among them, the pseudo-second order model fitted better with the experimental and modeled data shown in Table 4.1. The experimental results for the adsorption capacity closely align with the results from the kinetic model. The adsorption stage could be controlled by a chemisorption reaction in accordance with this concept, which suggests that glyphosate adsorption most likely takes place at particular adsorption sites on the surface (Guler & Sarioglu, 2014). When comparing the data obtained using KCl 0.1 M and rainwater, distinct variations in the binding strengths of glyphosate were observed between the two conditions. Specifically, there was a higher value of k_2 for glyphosate binding in the case of KCl 0.1 M.

The adsorption capacity data obtained from the experiment were compared to the data modeled using the pseudo-second order model. Figure 4.1 and Figure 4.2 show the adsorption kinetics of soil KG1.1 previously moistened for 24 hours and after air removal treatment, respectively. In both cases KCl 0.1 M was used as the solvent of the glyphosate solution. A rotational speed of 180 rpm was determined to be the most acceptable after testing various speeds. In the case of moistened soil, the equilibrium point was reached after 24 hours. For the same case, it was established that the adsorption capacity was 0.41 ± 0.04 mg/g, and the removal percentage was 49.0 ± 4.6 %. In the case of KG1.1 with removed air, the equilibrium point was reached after 48 hours of agitation. It was determined that the adsorption capacity was 0.20 ± 0.01 mg/g, and that the removal percentage was 35.6 ± 2.7 %. Moist soil exhibits a higher adsorption capacity compared to soil from which air has been removed. Although equilibrium was attained at 48 hours, a potential measurement error may have occurred at 26 hours, as the results between hours 20-23 and hours 44-48 show similar trends. Nonetheless, to ensure consistency, a contact time of 48 hours was maintained for subsequent experiments.

The utilization of artificial rainwater as a solvent for the glyphosate solution yielded into the results shown Figure 4.3. The equilibrium was achieved after a period of 48 hours. The resulting adsorption capacity was calculated to be 0.25 ± 0.03 mg/g, with a glyphosate removal percentage of 39.3 ± 5.0 % from KG1.1 soil. When comparing these results with the

results obtained using 0.1 M KCl, there is a slight increase in the adsorption capacity of the soil. An increase suggests the potential existence of characteristics in artificial rainwater that promote stronger interactions between glyphosate and the soil matrix, leading to improved adsorption performance.

In comparison to other glyphosate adsorption studies, such as the investigation conducted by Cáceres-Jensen et al. (2009), notable distinctions emerge. In their study, they achieved an adsorption of up to 98.8% of glyphosate within a mere 10 minutes after attaining equilibrium, with the equilibrium point reached between 10 to 120 minutes. However, it is crucial to acknowledge that the soils employed in their research possessed distinct characteristics, notably a high organic carbon content, which distinguishes them from the soil implemented in the present study.

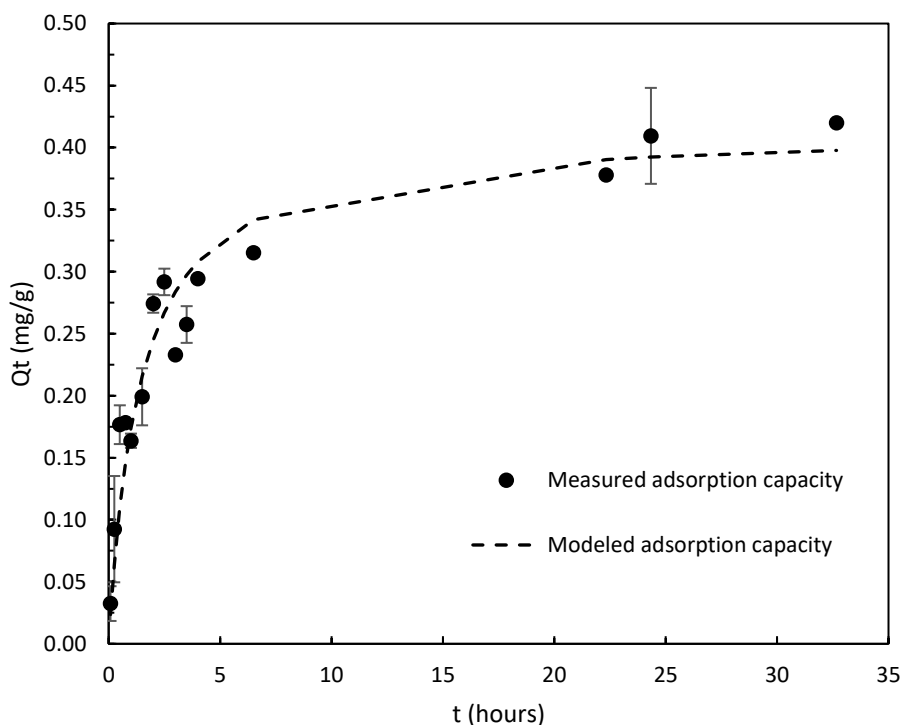


Figure 4.1. Effect of contact time on glyphosate adsorption capacity. Soil KG1.1 moistened 24 hours: 2 g, glyphosate initial concentration: 8 mg/L, KCl 0.1 M, 180 rpm, and 20°C.

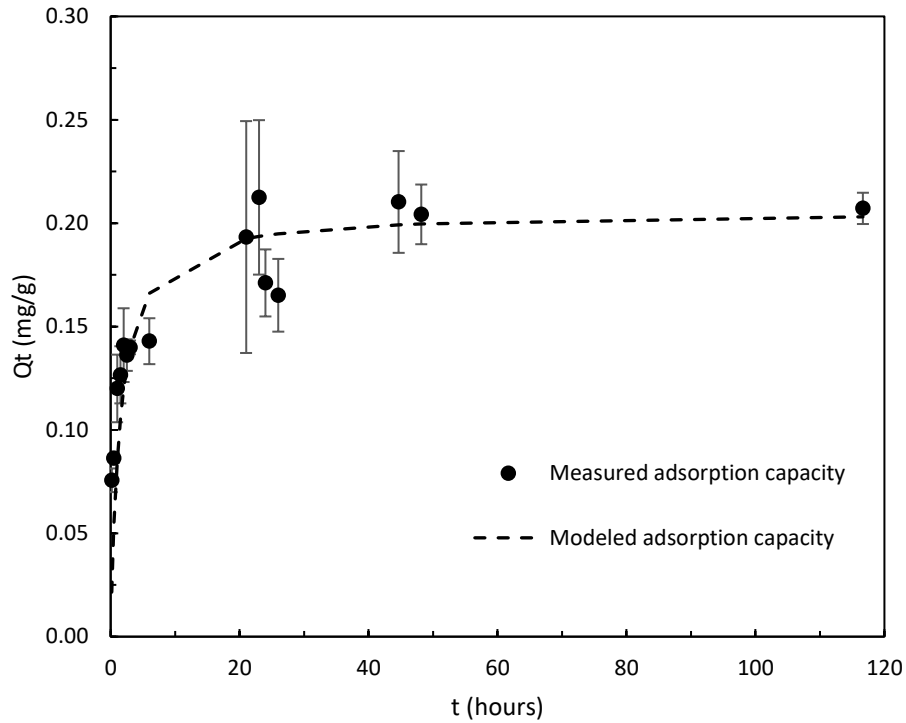


Figure 4.2. Effect of contact time on glyphosate adsorption capacity. Soil KG1.1 with air removed: 2 g, glyphosate initial concentration: 8 mg/L, KCl 0.1 M, 180 rpm, and 20°C.

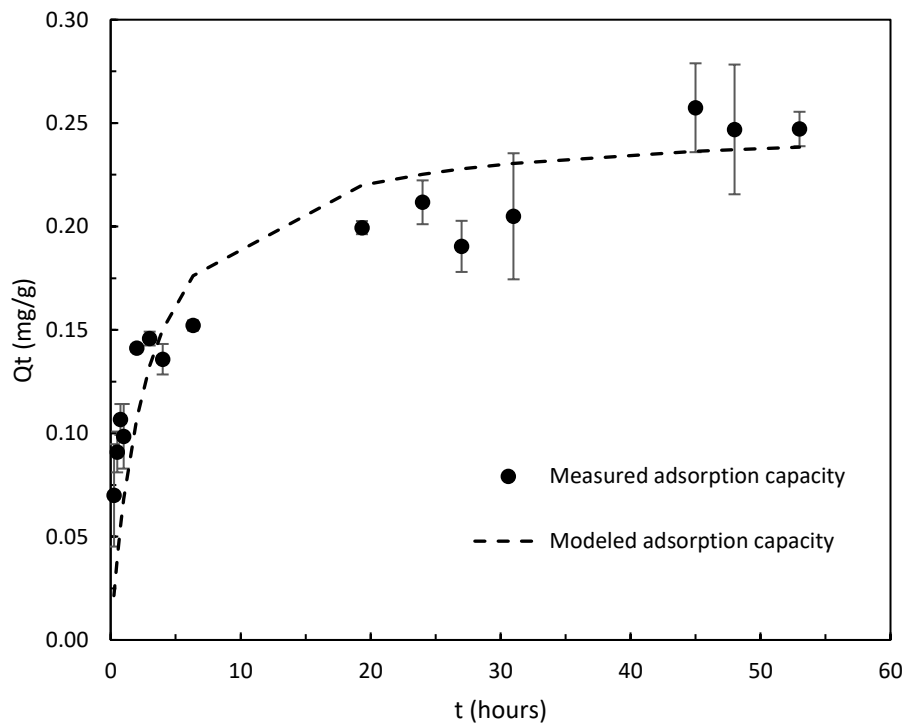


Figure 4.3. Effect of contact time on glyphosate adsorption capacity. Soil KG1.1 with air removed: 2 g, glyphosate initial concentration: 8 mg/L, artificial rainwater, 180 rpm, and 20°C.

Table 4.1. Parameters of pseudo-second order model.

	Experimental Q_t (mg/g)	Modeled Q_t (mg/g)	K_2 (g/mg h⁻¹)	R^2
KG1.1 moistened 24h and KCl 0.1 M	0.41 ± 0.04	0.39	1.79	0.99
KG1.1 with air removed and KCl 0.1 M	0.20 ± 0.01	0.20	3.46	0.99
KG1.1 with air removed and rainwater	0.25 ± 0.03	0.24	1.54	0.98

The chemisorption of glyphosate to the soils under investigation can be explained by several mechanisms. According to Dollinger et al. (2015), the primary sorption mechanism observed in the analyzed soils is the formation of complexes between the phosphonate groups of glyphosate and polyvalent cations present in the soil. This dominant mechanism implies that the presence of dissolved ions, including divalent cations like calcium and magnesium, in artificial rainwater can elevate the ionic strength of the solution. In the same context, Dollinger et al., point out that stronger interactions occur between the charged glyphosate molecules and the charged surfaces of soil minerals. Consequently, the adsorption capacity of the soil for glyphosate is enhanced.

Dollinger et al. (2015) proposed a mechanism that involves the formation of strong bonds, such as Fe-O-P(glyphosate) and Al-O-P(glyphosate), through ligand exchange between the phosphonate group of glyphosate and singly coordinated Al-OH and Fe-OH groups on the surfaces of soil minerals with varying charges. Dollinger et al. further explains that this sorption mechanism is believed to predominantly occur on the fractured edges of layer silicates, poorly ordered silicates, or iron- and aluminum oxides. Additionally, Dollinger et al. highlights that another sorption mechanism involves the binding of glyphosate to humic substances (HS) through hydrogen bonding at acidic or neutral pH, or the formation of HS-Me-glyphosate complexes, where Me represents a trivalent or divalent metal cation. This mechanism has been reported as a secondary sorption mechanism.

4.2 PH AND TEMPERATURE EFFECT

4.2.1 Effect of pH on glyphosate adsorption

In KG1.1 soil, it can be observed that within the pH range of 3 to 7, both adsorption capacity and percentage removal exhibit statistical equivalence, as they fall within the same range (Figure 4.4). However, from pH 8 it is noticeable a significant difference, giving as result a lower adsorption removal percentage and capacity. According to Ololade et al. (2019), except for pH 1 and 2, glyphosate carries a net negative charge that intensifies as the pH increases. The increased negative charge of glyphosate and soils leads to a decrease in the electrostatic attraction between the soil and glyphosate. Dollinger et al. (2015) and De Jonge & Wollesen De Jonge (1999) also corroborate these findings, reporting that an elevation in pH results in stronger electrostatic repulsion, thereby reducing the sorptive strength of glyphosate.

The behavior of the glyphosate molecule with the pH of point of zero charge (pH_{pzc}) of the potential components of soil can be examined by referring to Figure 2.3. In the case of silicate, the pH_{pzc} value is 2.0 (Worch, 2012). When silicate and glyphosate interact at a pH higher than 2.0, both of their negatively charged molecules will be present, resulting in a weak interaction. Comparing the pH_{pzc} of kaolinitite (clay), which is approximately 4 (Sawyer et al., 2003), reveals a similar situation. Glyphosate interacts differently with iron and aluminum hydroxides, for example, with pH_{pzc} values of 9.1 and 8.5 for $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, respectively (Worch, 2012). Thus, glyphosate will have a negative charge while aluminum and iron hydroxides will have a positive charge when interacting with glyphosate at pH values lower than their pH_{pzc} . As a result, there will be a stronger electrostatic attraction between the two, leading to more adsorption. This is supported by Figure 4.4, which shows a decline in glyphosate adsorption capacity and removal percentage at pH 8.

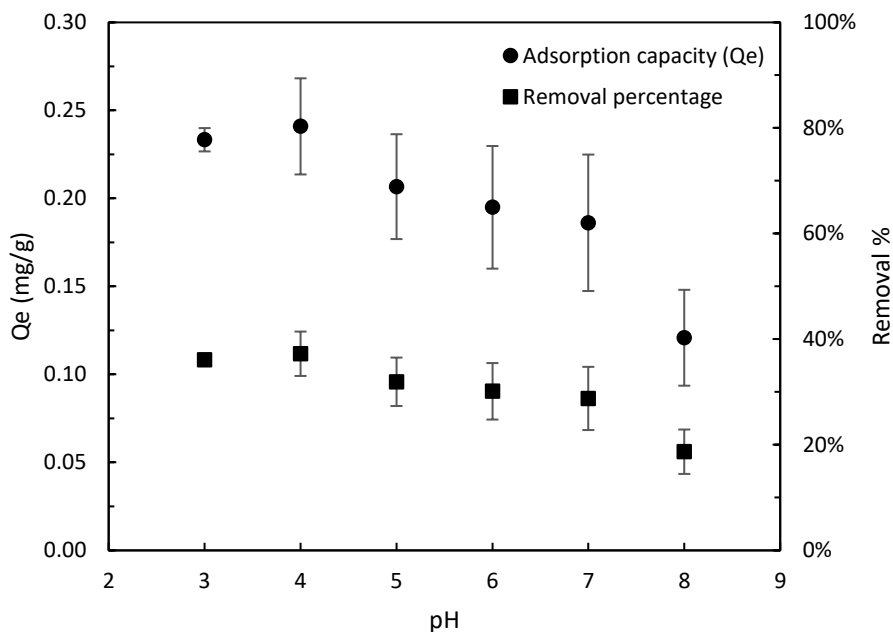


Figure 4.4. Adsorption capacity and removal percentage of soil KG1.1 on glyphosate at different pH.

4.2.2 Effect of temperature on glyphosate adsorption

The influence of temperature on the adsorption capacity and percentage removal of glyphosate in KG1.1 soil was found to be statistically similar. At a temperature of 10 °C, an adsorption capacity of 0.19 ± 0.02 mg/g and a percentage removal of 28.5 ± 3.0 % were observed. Similarly, at a temperature of 20 °C, the values were 0.17 ± 0.02 mg/g and 29.9 ± 2.8 % respectively. Although the influence of temperature is not statistically significant, a slight reduction in adsorption capacity is found with increasing temperature. These findings align with a study conducted by Kahihia (2021) which also examined temperatures, including 30 °C. Kahihia reported similar results with a slight reduction in adsorption capacity and percentage adsorption with increasing temperatures.

4.3 ADSORPTION ISOTHERMS

The adsorption isotherms of glyphosate in soil KG1.1, KG1.2, KG2 and fine material (ballast) using artificial rainwater were analyzed at its original pH without modifying it . The results revealed a non-linear isotherms (Figure 4.5). The measured average values of pH and EC for the respective solutions and soil samples are as follows: pH 4.12, 6.13, 7.61, and 7.97, and EC 39.4, 25.3, 41.3, and 59.7 μ S/cm for soils KG1.1, KG1.2, KG2, and the fine material,

respectively. These adsorbents demonstrated different adsorption capacities and adsorption removal percentages of glyphosate. An experimental Q_{\max} value of 0.22, 0.14, 0.06, and 0.27 mg/g, along with a experimental maximum removal percentage of 68.48, 11.95%, 7.85%, and 36.74% respectively, were obtained. According to Schwarzenbach et al. (2003), sorption isotherms involving charged organic sorbates and natural solids often exhibit non-linear behavior, indicating significant changes in the solid-water distribution ratio as a function of the sorbate's dissolved concentration.

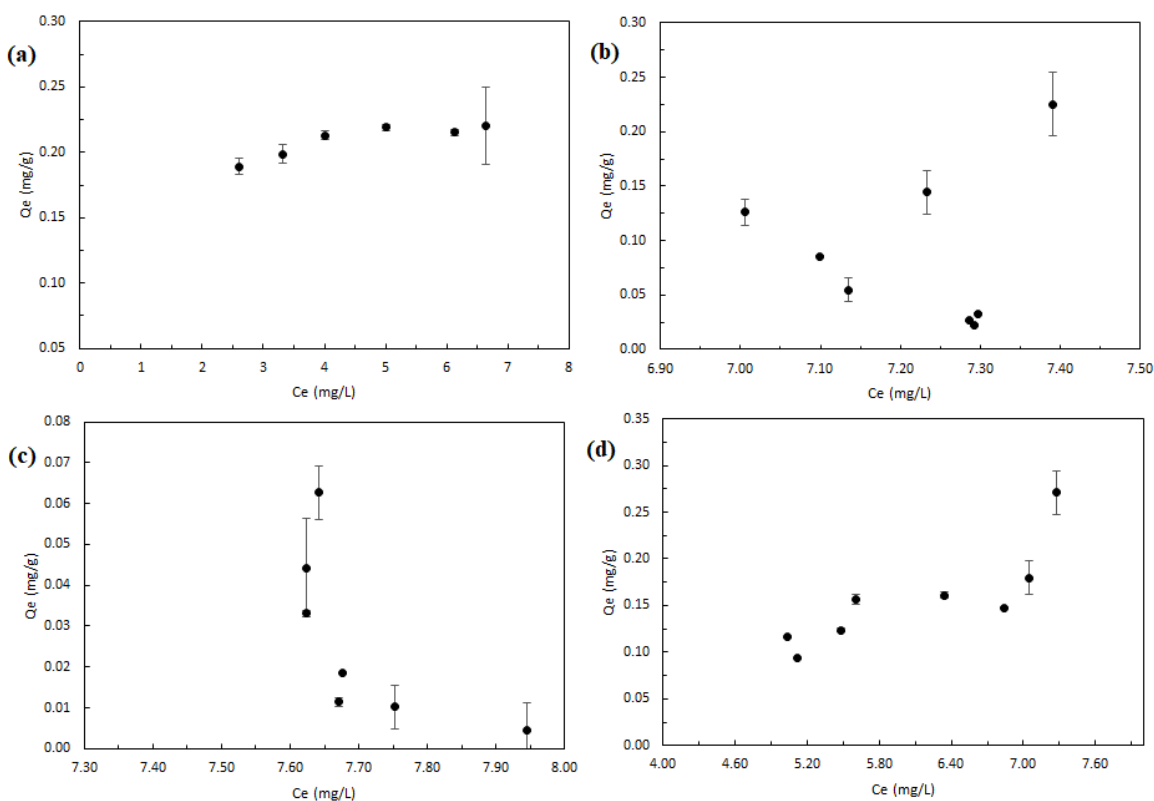


Figure 4.5. Glyphosate experimental adsorption isotherms: (a) KG1.1, (b) KG1.2 (c) KG2 and (d) Fine material (ballast). Dissolution with artificial rainwater; 180 rpm at 20° C. (a) humid with air removed; (b), (c) and (d) dry, without treatment.

The Langmuir and Freundlich models were utilized for analysis, obtaining the results shown in Table 4.2. In the case of KG1.1, considering the R^2 values, the Langmuir model demonstrated a superior fit to the data. The R_L value of 0.0882 obtained indicates a favorable adsorption. According to Langmuir's theory, adsorption occurs at specific active sites on a homogeneous and energetically uniform surface of the adsorbent (Rakić et al., 2013). In this

case, a monolayer of glyphosate particles adsorbs initially onto the KG1.1 soil surface, after which adsorption ceases due to the saturation of available active sites.

Regarding the KG1.2, KG2 and fine material, the Langmuir model exhibited a better fit to the data, as evidenced by its higher R^2 value compared to that of the Freundlich model. However, the negative Q_m values contradict the experimental Q_m , and the R_L suggests unfavorable adsorption. Consequently, the Freundlich model better represents the adsorption process of glyphosate in the fine material, indicating multi-layer processes occurring on heterogeneous surfaces (Carneiro et al., 2015). Notably, the obtained K_f value is exceptionally low compared to previous studies conducted by Glass (1987); De Jonge et al. (2000); (Padilla & Selim, 2019), and Gros et al. (2017), implying weaker adsorption of glyphosate.

Table 4.2. Adsorption isotherm Langmuir and Freundlich constants for glyphosate in soil KG1.1, KG1.2, KG2 and fine material from ballast.

Soil	Langmuir model			Freundlich model			
	Q_m (mg/g)	R_L	R^2	K_{ads} (L/mg)	K_f (mg/g)/(L/mg) ^{1/n}	1/n	R^2
KG1.1	0.2490	0.0882	0.9107	1.2463	0.1658	0.1564	0.8481
KG1.2	2.2640	-2.6045	0.0076	-0.1739	752315	-8.2191	0.0287
KG2	0.0005	-13.2129	0.4834	-0.1352	1.29E+17	-21.2960	0.3054
Fine material (ballast)	-0.1909	2.3275	0.7348	-0.0717	0.0056	1.8224	0.7193

The presence of organic matter is a potential factor contributing to the low soil capacity. Organic matter can indirectly affect glyphosate adsorption by covering the adsorption sites on amorphous oxides (Ololade et al., 2014). When utilizing KG1.1 soil, which exhibited better glyphosate capacity, this soil has been consistently used for analysis and research at the Faculty of Civil Engineering in HTWD. Consequently, the prolonged handling and processing of this soil may have led to the removal of a significant portion of organic matter and other interfering substances. On the other hand, soils KG1.2, KG2, and the fine material (ballast) have not been subjected to studies or modifications that could alter their original content. This discrepancy could explain a higher presence of organic matter or other interferents that reduce the adsorption capacity. However, it is important to note that

there is currently no concrete data to support this assumption. Data such as total organic carbon (TOC), SOM and others, which may support these assumptions, were not measured.

The findings presented by (Campos-Pereira et al., 2023) indicate a reduction in the concentration detected in the soil extracts, specifically in the soil with the lowest organic carbon (OC) content. This decrease can be attributed to the soil's limited retention capacity, which is likely a consequence of its low OC content and high proportion of sand. This particular condition is also observed in soils found in railway systems, which may explain the reduced capacity of these soils to retain glyphosate.

The presence of SOM is a crucial factor to consider in the context of glyphosate adsorption in soil. Its role in the sorption of glyphosate appears to be controversial and twofold. Firstly, SOM may hinder glyphosate sorption by obstructing sorption sites. Secondly, SOM may enhance glyphosate sorption because higher SOM content favors poorly ordered aluminum and iron oxides, which possess a high sorption capacity (Ololade et al., 2014). Unfortunately, there is a lack of data regarding the actual SOM content in the sampled soil, which hinders a more detailed analysis of its impact on glyphosate adsorption in KG1.1 soil. Additionally, it is essential to consider other factors such as the specific surface area, saturating cation, or isoelectric point of the soil (Dollinger et al., 2015).

The mineral composition of the sorbent plays a crucial role in determining the charge density, which is influenced by specific responses to the surrounding conditions. In the case of KG1.1, the main component is silica (SiO_2), which belongs to the group of inert minerals. Silica minerals are generally considered chemically inactive materials, having minimal impact on the physicochemical properties of soils. They primarily act as diluents to the more reactive clay and humic substances. The surface area of KG1.1 is relatively small, typically ranging from 2 to 3 m^2/g depending on particle shape. The surface charge of silica particles is also negligible or very low. Any limited cation and anion exchanges observed are more attributed to the Si-O broken bonds and Si-OH groups present on the particle edges (Tan, 2011).

To evaluate the impact of soil treatment, KG1.2, KG2, and the fine material were washed and treated to eliminate air trapped in the soil micropores, as detailed in section 3.4.1. A comparison was made between the adsorption capacity and glyphosate removal percentage before and after the treatment. Adsorption isotherms were not built after carrying out this

treatment to the soils. For this reason, only the data of the adsorption capacity and removal percentage in equilibrium conditions (48 hours) were compared. Unfortunately, no improvement in the results was observed, with little variation between the two conditions (Figure 4.6). It is important to note that while the removal of air from the micropores of the soil can enhance glyphosate adsorption, washing the soil may result in the loss of fine material and potential organic matter. Additionally, the use of a high temperature (105°C) for soil drying might alter the soil's composition.

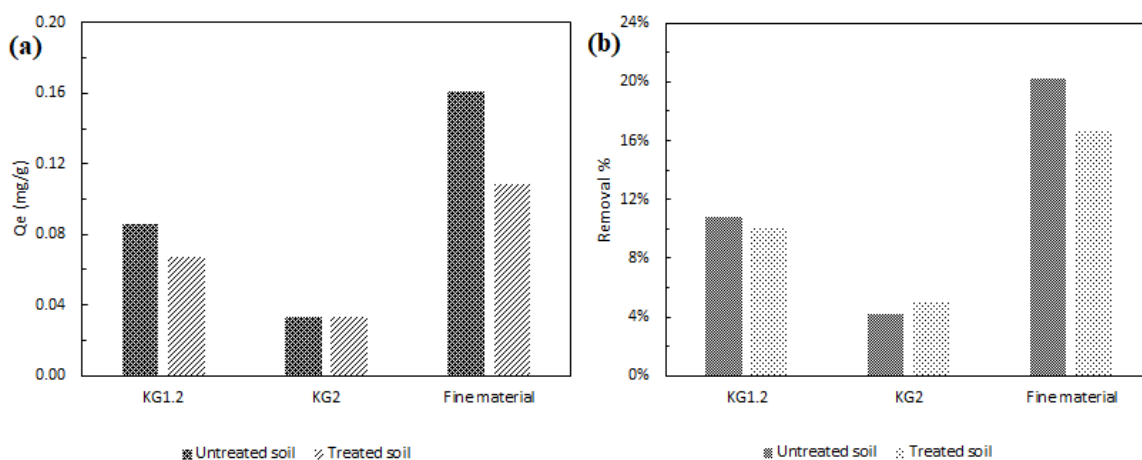


Figure 4.6. Comparison of glyphosate adsorption on KG1.2, KG2 soils and fine material before and after washing and micropore air removal treatment: (a) adsorption capacity and (b) percentage removal. 180 rpm at 20°C; using artificial rainwater.

As previously established, the adsorption of glyphosate tends to increase as the pH value decreases. This is attributed to the decreased solution pH, which reduces the negative charge of glyphosate molecules and allows for a greater extent of adsorption onto soils (Ololade et al., 2014). The relatively higher pH values observed in soils KG1.2, KG2, and the fine material could be a contributing factor to the low adsorption of glyphosate in these soils. Conversely, in the case of the fine material from the ballast, which exhibits better adsorption capacity, this could be attributed to a higher surface area, as observed by (Ololade et al. (2014), where increased surface area led to significantly enhanced glyphosate adsorption.

Furthermore, the adsorption of glyphosate can be influenced by the chemical composition of the soils. Certain factors, such as metals and phosphate, may either enhance or worsen the glyphosate adsorption in the soil. According to Dollinger et al. (2015), the

formation of complexes between the phosphonate groups of glyphosate and polyvalent cations present in the soil has been proposed as a mechanism for strong sorption of glyphosate. The same author concludes that the influence of soil-exchanged cations on glyphosate sorption follows the order: $\text{Na}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Zn}^{2+} < \text{Mn}^{2+} < \text{Fe}^{3+} < \text{Al}^{3+}$. Daily railway operations have been shown to impact soil quality along rail tracks and supporting infrastructures, resulting in elevated concentrations of pollutants such as metals in various railway locations (Vo et al., 2015). However, the presence of these metals may contribute to glyphosate adsorption. The polyprotic acidic nature of glyphosate likely contributes to its high affinity for mineral components, particularly those rich in trivalent cations such as Al^{3+} and Fe^{3+} (I. A. Ololade et al., 2014). This can be confirmed by Gimsing & Borggaard (2002) where from studying the adsorption of glyphosate in three types of soil, the soil with the largest amount of aluminum oxides and second highest amounts of iron oxides absorbs more glyphosate than the other two soils. In an ongoing investigation at HTWD, a tracer test using the KG1.1 soil has been conducted, and seepage water samples have revealed a concentration of 0.0057 ± 0.0031 mg/L of Fe ions and 0.0106 ± 0.0145 mg/L of Al ions. These findings suggest the possible presence of these metals in the KG1.1 soil. However, it is important to note that further comprehensive studies are necessary to accurately determine the actual concentration of Fe and Al ions in the soil.

5 CONCLUSIONS AND RECOMENDATIONS

5.1 CONCLUSIONS

The experimental results of adsorption kinetics fit better the pseudo-second order model. This finding indicates that glyphosate adsorption follows a chemisorption mechanism.

Lowering the pH values enhances the adsorption of glyphosate in the soil due to a reduction in the negative charge of glyphosate, resulting in an increased electrostatic attraction between the soil and glyphosate.

The use of rainwater resulted in a slightly higher glyphosate adsorption capacity, likely attributed to an improvement in the electrostatic interactions between the glyphosate and the soil.

Railway system soils demonstrate a relatively lower to moderate adsorption capacity for glyphosate when compared to other types of soils. The experimental results reveal that the glyphosate adsorption capacity in the studied soil layers followed the order of KG2 < KG1.2 < fine material < KG1.1, encompassing a removal percentage ranging from 7.9 to 68.5%.

Railway soils typically exhibit a lower SOM content compared to agricultural soils. Therefore, it becomes important to analyze this parameter, as it plays a dual role in glyphosate adsorption. On one hand, it may reduce glyphosate adsorption by blocking soil active sites, or it could facilitate herbicide biodegradation.

5.2 RECOMENDATIONS

It is recommended to expand the experiments using lower concentrations to get a more realistic view of glyphosate adsorption in railway systems since real conditions are predicted to have concentrations significantly lower than the one examined (8 mg/L).

To protect the integrity of the soil and guarantee reliable experimental results, it is suggested to take into account utilizing a lower temperature for the drying process.

Further investigations on glyphosate dynamics in railway system soils are recommended to gain a better understanding of its transport behavior and impact. Column tests can increase the understanding of how this herbicide behaves.

More comprehensive data on the soils used in railway systems are needed to accurately predict the behavior of glyphosate and other herbicides in the environment. Factors such as soil chemical and biological composition (SOM, TOC, metals content) should be considered.

It is recommended to explore the incorporation of different soils or materials, such as iron or aluminum oxides, into railway soils to enhance their adsorption capacity.

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APPENDICES

APPENDIX 1: GLYPHOSATE QUANTIFICATION

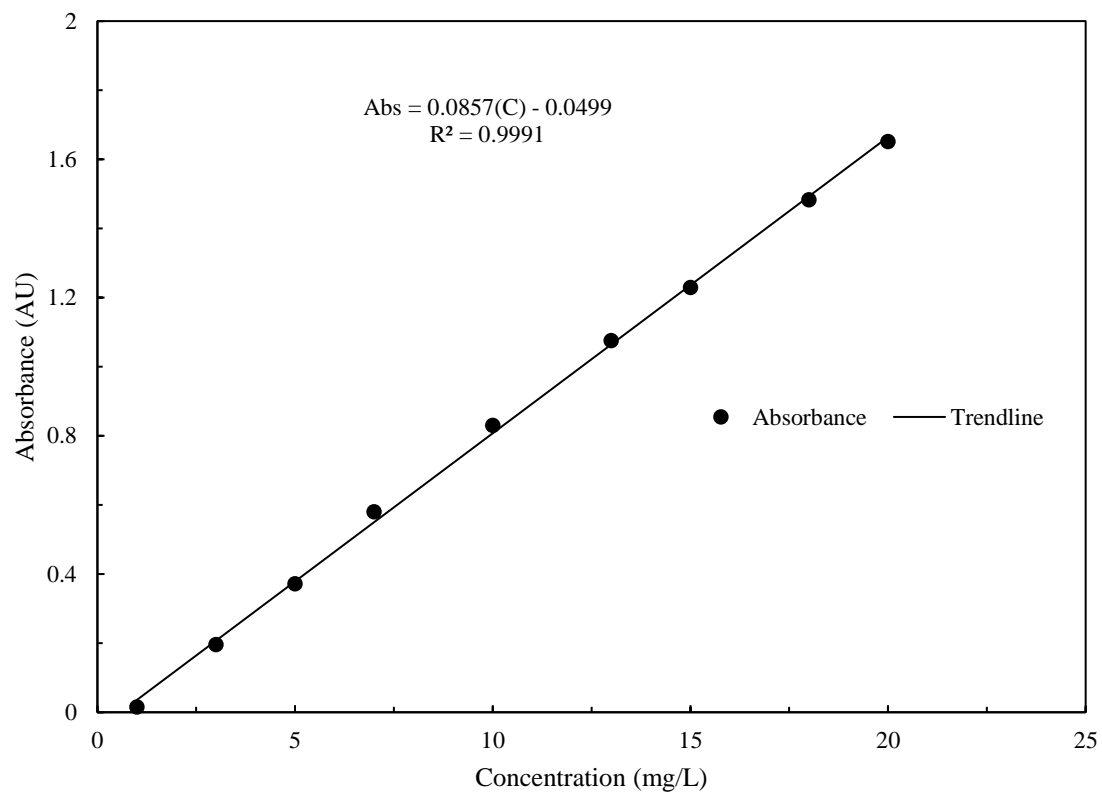


Figure A.1.1. Calibration curve for glyphosate quantification.

APPENDIX 2: GLYPHOSATE ADSORPTION KINETICS

Table A.2.1. Data used in the calculation of glyphosate adsorption kinetics using KCl 0.1 M, KG1.1.

Sample	Average final concentration (mg/L)	Time of contact (hours)	Mass (g)	Qt (mg/g)	STD Qt	Removal %	STD Removal
Kin-Gly-Blanco-01		0.3	2.0079	-		-	
Co	8.38	0.0	-	-		0.00%	
Kin-Gly-01.1	8.0560	0.1	2.0035	0.0324	0.0140	3.88%	0.0167
Kin-Gly-01.2	7.4551	0.3	2.0035	0.0924	0.0428	11.05%	0.0512
Kin-Gly-02.1	6.6091	0.5	2.0062	0.1766	0.0156	21.14%	0.0187
Kin-Gly-02.2	6.5916	0.8	2.0062	0.1784	0.0016	21.35%	0.0020
Kin-Gly-03.1	6.7375	1.0	2.0081	0.1637	0.0058	19.61%	0.0069
Kin-Gly-03.2	6.3816	1.5	2.0081	0.1991	0.0230	23.85%	0.0276
Kin-Gly-04.1	5.6289	2.0	2.0066	0.2743	0.0074	32.84%	0.0089
Kin-Gly-04.2	5.4539	2.5	2.0066	0.2917	0.0107	34.92%	0.0128
Kin-Gly-05.1	6.0432	3.0	2.0068	0.2330	0.0016	27.89%	0.0020
Kin-Gly-05.2	5.7981	3.5	2.0068	0.2574	0.0148	30.82%	0.0177
Kin-Gly-06.1	5.4364	4.0	2.0009	0.2943	0.0016	35.13%	0.0020
Kin-Gly-06.2	5.2264	6.5	2.0009	0.3153	0.0033	37.64%	0.0039
Kin-Gly-07.1	4.5904	22.3	2.0053	0.3780	0.0025	45.23%	0.0030
Kin-Gly-07.2	4.2754	24.3	2.0053	0.4095	0.0387	49%	0.0463
Kin-Gly-08.1	4.1645	32.7	2.0081	0.4199	0.0016	50.31%	0.0020

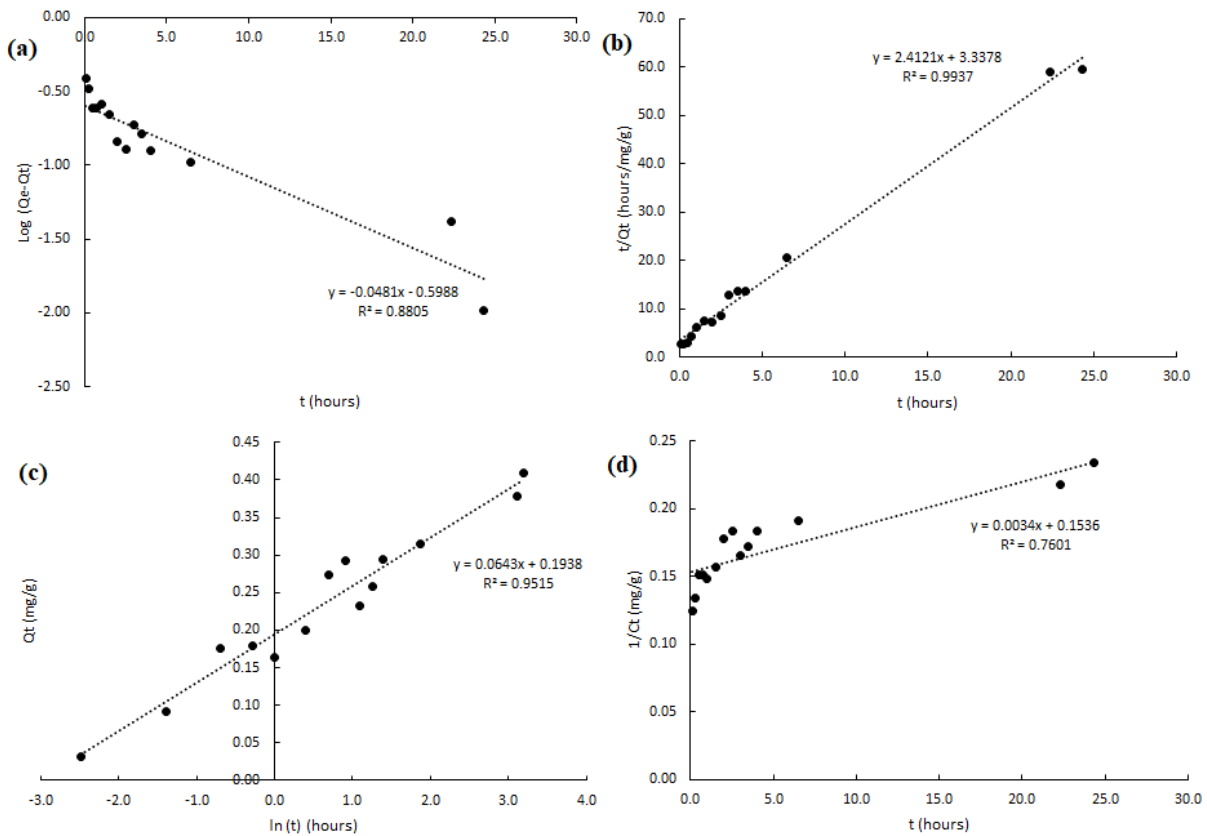


Figure A.2.1. Models of glyphosate adsorption kinetics in KG1.1 type soil: (a) pseudo-first order, (b) pseudo-second order, (c) Elovich and (d) second order. KCl 0.1 M, 20°C, 180 rpm.

Table A.2.2. Data used in the calculation of glyphosate adsorption kinetics using KCl 0.1 M, KG1.1 treated for air removal.

Sample	Average final concentration (mg/L)	Time of contact (hours)	Mass (g)	Qt (mg/g)	STD Qt	Removal %	STD Removal
Kin-Gly-Blank1		1.0	1.9495	-		-	
Kin-Gly-Blank2			1.9495				
Co	5.58	0.0	-	0.0000		0.00%	
Kin-Gly-01.1	4.8471	0.2	1.9492	0.0756	0.0057	13.20%	0.0103
Kin-Gly-01.2	4.7421	0.5	1.9492	0.0864	0.0023	15.08%	0.0044
Kin-Gly-02.1	4.4154	1.0	1.9471	0.1201	0.0163	20.93%	0.0281
Kin-Gly-02.2	4.3512	1.5	1.9471	0.1267	0.0138	22.08%	0.0236
Kin-Gly-03.1	4.2170	2.0	1.9394	0.1410	0.0178	24.48%	0.0310
Kin-Gly-03.2	4.2637	2.5	1.9394	0.1362	0.0076	23.65%	0.0133
Kin-Gly-04.1	4.2229	3.0	1.9461	0.1399	0.0033	24.38%	0.0059
Kin-Gly-04.2	4.1937	6.0	1.9461	0.1429	0.0111	24.90%	0.0192
Kin-Gly-05.1	3.7036	21.0	1.9460	0.1933	0.0561	33.68%	0.0990
Kin-Gly-05.2	3.5169	23.0	1.9460	0.2125	0.0373	37.02%	0.0665
Kin-Gly-06.1	3.9137	24.0	1.9529	0.1711	0.0162	29.92%	0.0281
Kin-Gly-06.2	3.9720	26.0	1.9529	0.1651	0.0176	28.87%	0.0310
Kin-Gly-07.1	3.5403	44.7	1.9443	0.2102	0.0246	36.60%	0.0428
Kin-Gly-07.2	3.5986	48.2	1.9443	0.2042	0.0144	35.56%	0.0251
Kin-Gly-08.1	3.5694	116.7	1.9453	0.2071	0.0076	36.08%	0.0148

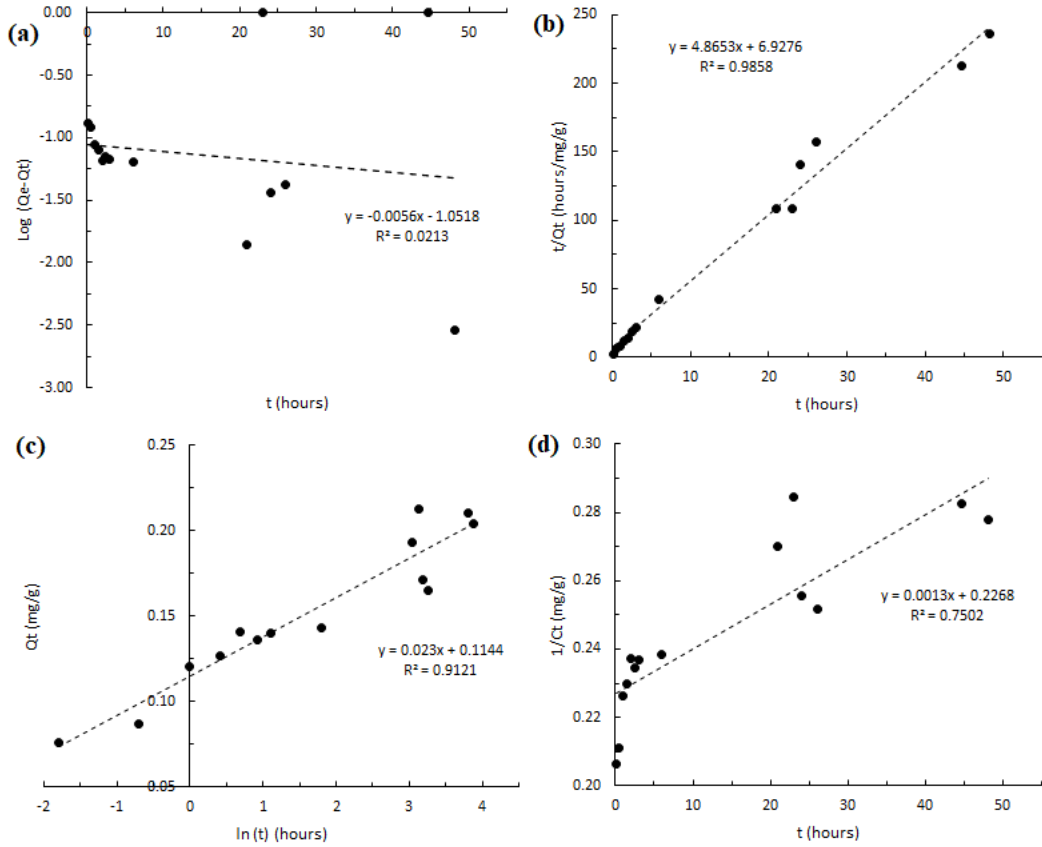


Figure A.2.2. Models of glyphosate adsorption kinetics in air removed KG1.1 type soil: (a) pseudo-first order, (b) pseudo-second order, (c) Elovich and (d) second order. KCl 0.1 M, 20°C, 180 rpm.

Table A.2.2. Data used in the calculation of glyphosate adsorption kinetics using artificial rainwater, KG1.1 treated for air removal.

Sample	Average final concentration (mg/L)	Time of contact (hours)	Mass (g)	Qt (mg/g)	STD Qt	Removal %	STD Removal
Rainwater	-	-	-	-	-	-	-
Rainwater-with-soil							
Co	6.29	0.0	-	-		0.00%	
Kin-Gly-01.1	5.5881	0.3	2.0022	0.0699	0.0248	11.13%	0.0394
Kin-Gly-01.2	5.3781	0.5	2.0018	0.0909	0.0099	14.47%	0.0157
Kin-Gly-02.1	5.2205	0.8	2.0022	0.1066	0.0075	16.98%	0.0118
Kin-Gly-02.2	5.3022	1.0	2.0018	0.0985	0.0156	15.68%	0.0249
Kin-Gly-03.1	4.8763	2.0	2.0009	0.1411	0.0017	22.45%	0.0026
Kin-Gly-03.2	4.8296	3.0	2.0009	0.1458	0.0033	23.20%	0.0052
Kin-Gly-04.1	4.9288	4.0	2.0022	0.1358	0.0074	21.62%	0.0118
Kin-Gly-04.2	4.7655	6.3	2.0022	0.1521	0.0024	24.22%	0.0039
Kin-Gly-05.1	4.2929	19.3	2.0008	0.1995	0.0032	31.73%	0.0052
Kin-Gly-05.2	4.1704	24.0	2.0008	0.2117	0.0106	33.68%	0.0171
Kin-Gly-06.1	4.3804	27.0	2.0043	0.1904	0.0124	30.34%	0.0197
Kin-Gly-06.2	4.2345	31.0	2.0043	0.2049	0.0305	32.66%	0.0262
Kin-Gly-07.1	3.7095	45.0	2.0035	0.2574	0.0215	41.01%	0.0341
Kin-Gly-07.2	3.8145	48.0	2.0035	0.2469	0.0314	39.34%	0.0499
Kin-Gly-08.1	3.8145	53.0	2.0019	0.2471	0.0083	39.34%	0.0849

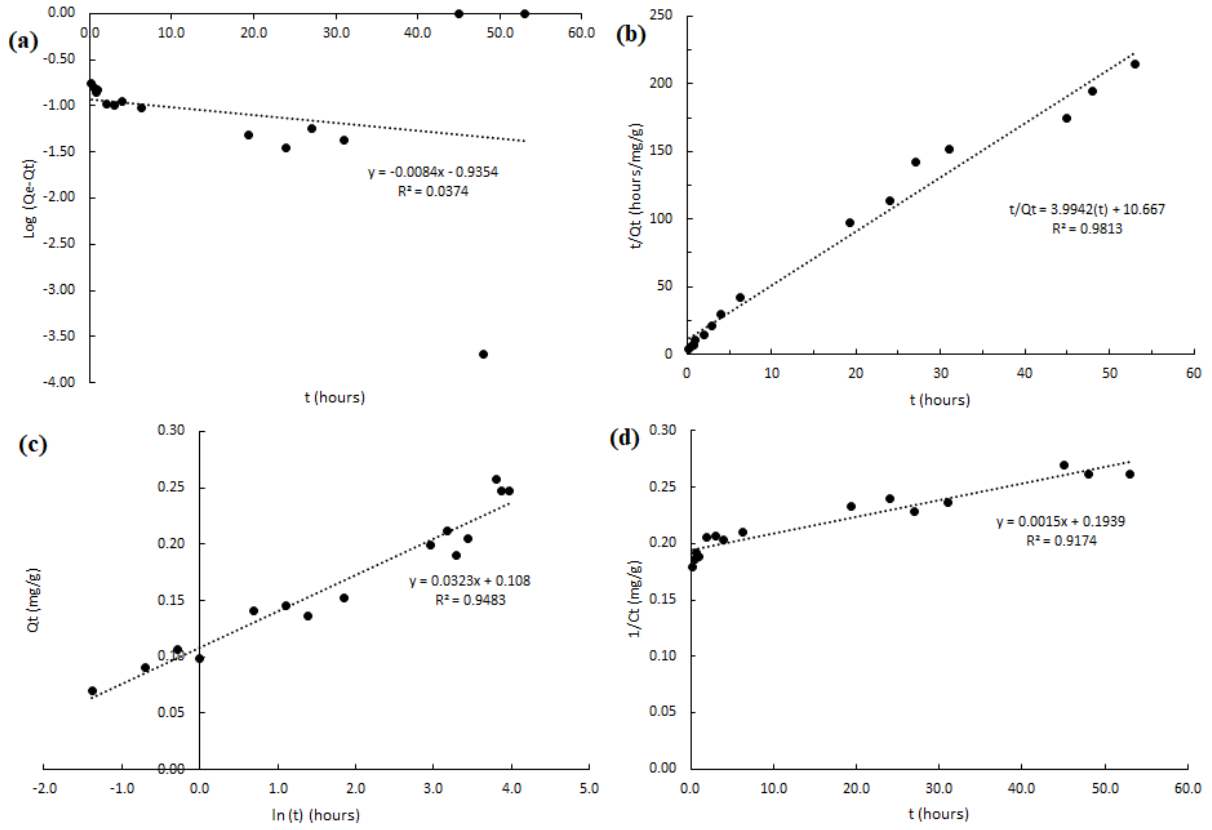


Figure A.2.2. Models of glyphosate adsorption kinetics in air removed KG1.1 type soil: (a) pseudo-first order, (b) pseudo-second order, (c) Elovich and (d) second order. Artificial rainwater, 20°C, 180 rpm.

APPENDIX 3: PH AND TEMPERATURE EFFECT

Table A.3.1. Data used in the calculation of the effect of pH in glyphosate adsorption using KCl 0.1 M, KG1.1 treated for air removal. 180 rpm at 20°C.

Sample	pH	Average final concentration (mg/L)	Time of contact (hours)	Mass (g)	Electrical Conductivity ($\mu\text{S/cm}$)	Qe (mg/g)	Removal %
Blank1_pH			0.0	2.0044	11.235	-	-
Blank2_pH				2.0044			
Co		8.52	24.0	-	-	-	0.00%
01_pH_original	4	6.0723	24.0	2.0030	10.71	0.2447	28.75%
02_pH_2	2	2.7585	24.0	2.0031	11.21	0.5755	67.63%
03_pH_5	5	5.9557	24.0	2.0002	10.62	0.2567	30.12%
04_pH_7	7	6.0665	24.0	2.0019	10.61	0.2454	28.82%
05_pH_10	10	7.2800	24.0	2.0025	10.62	0.1241	14.58%

Table A.3.2. Data used in the calculation of the effect of pH in glyphosate adsorption using artificial rainwater, KG1.1 treated for air removal. 180 rpm at 20°C.

Sample	pH	Electrical Conductivity ($\mu\text{S/cm}$)	Average final concentration (mg/L)	Time of contact (hours)	Qe (mg/g)	Removal %
Blank-With soil		23.30		0.0	-	-
Blank-Without soil		32.6			-	
Co	0		6.48	48.0	-	0.00%
01-pH 3	3.0	120.7	4.1412	48.0	0.2333	36.07%
02-pH 4	4.0	36.4	4.0653	48.0	0.2409	37.24%
03-pH 5	5.0	25.00	4.4096	48.0	0.2067	31.93%
04-pH 6	6.0	27.65	4.5263	48.0	0.1949	30.13%
05-pH 7	7.0	30.15	4.6138	48.0	0.1861	28.78%
06-pH 8	8.0	56.65	5.2672	48.0	0.1208	18.69%

Table A.3.3. Data used in the calculation of the effect of temperature in glyphosate adsorption using KCl 0.1 M, KG1.1 treated for air removal. 180 rpm at 10°C.

Sample	Average final concentration (mg/L)	Time of contact (hours)	Mass (g)	Qe (mg/g)	Removal %
Blank1_pH		0.0	2.0044	-	-
Blank2_pH			2.0044		
Co	6.82	24.0	-	-	0.00%
01_T10	4.8121	24.0	2.0030	0.2010	29.49%
02_T10	4.7188	24.0	2.0031	0.2103	30.86%
03_T10	5.1097	24.0	2.0002	0.1715	25.13%

APPENDIX 4: ADSORPTION ISOTHERMS

Table A.4.1. Data used in the calculation of glyphosate adsorption isotherm using artificial rainwater and KG1.1 treated for air removal. 180 rpm at 20°C.

Sample	Ce (mg/L)	Time of contact (hours)	Mass (g)	Initial pH	Final pH	Initial EC (μS/cm)	Final EC (μS/cm)	Qe (mg/g)
Blank-glyphosate	-	48.0	-	4.208	4.265	25.9	24.0	-
Rainwater		48.0	-	5.872	5.670	19.5	19.5	
Co	8.29	48.0	-	4.208	-	25.9	-	-
01-0.5g	7.9102	48.0	0.5041	4.208	4.171	25.9	27.6	0.1504
02-1g	7.2567	48.0	1.0033	4.208	4.171	25.9	31.2	0.2059
03-1.5g	6.6324	48.0	1.5038	4.208	4.156	25.9	33.3	0.2204
04-2g	6.1307	48.0	2.0047	4.208	4.130	25.9	36.1	0.2154
05-3g	4.9988	48.0	3.0040	4.208	4.105	25.9	40.4	0.2191
06-4g	4.0187	48.0	4.0072	4.208	4.085	25.9	46.4	0.2132
07-5g	3.3186	48.0	5.0036	4.208	4.088	25.9	48.3	0.1987
08-6g	2.6126	48.0	6.0034	4.208	4.064	25.9	51.9	0.1891

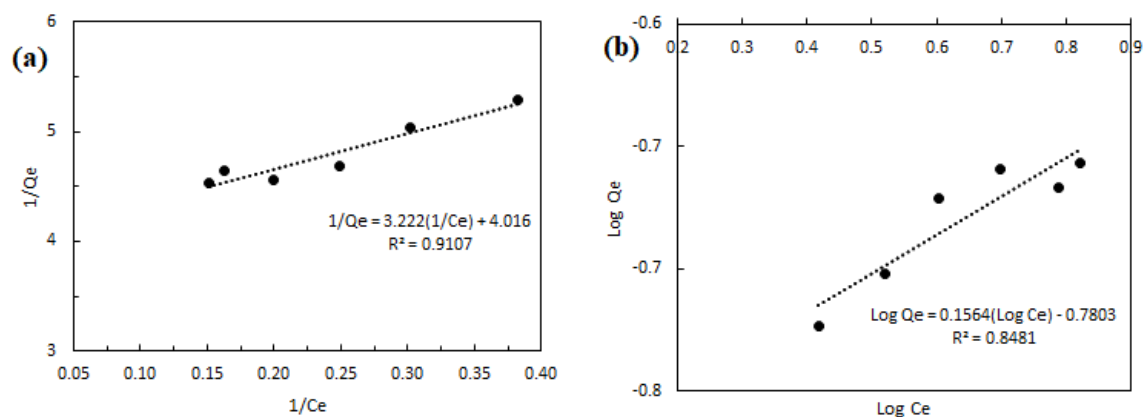


Figure A.4.1. Glyphosate adsorption isotherm models in KG1.1 soil in artificial rainwater: (a) Langmuir model and (b) Freundlich model.

Table A.4.2. Data used in the calculation of glyphosate adsorption isotherm using artificial rainwater and KG1.2 without washing. 180 rpm at 20°C.

Sample	Ce (mg/L)	Time of contact (hours)	Mass (g)	Initial pH	Final pH	Initial EC (μS/cm)	Final EC (μS/cm)	Removal %
Blank-glyphosate	-	48.0	-	4.155	4.344	25.7	27.1	-
Rainwater		48.0	-	5.767	5.916	13.3	56.9	
Co	7.96	48.0	-	4.155	-	25.7	-	0.00%
01-0.5g	7.3909	48.0	0.5026	4.155	5.575	25.7	46.9	7.11%
02-1g	7.2334	48.0	1.0020	4.155	5.794	25.7	17.9	9.09%
03-1.5g	7.0058	48.0	1.5062	4.155	6.033	25.7	20.5	11.95%
04-2g	7.0992	48.0	2.0075	4.155	6.002	25.7	23.0	10.78%
05-3g	7.1342	48.0	3.0025	4.155	6.410	25.7	23.1	10.34%
06-4g	7.2975	48.0	4.0076	4.155	6.231	25.7	23.6	8.29%
07-5g	7.2859	48.0	5.0066	4.155	6.600	25.7	22.7	8.43%
08-6g	7.2917	48.0	6.0025	4.155	6.422	25.7	24.3	8.36%

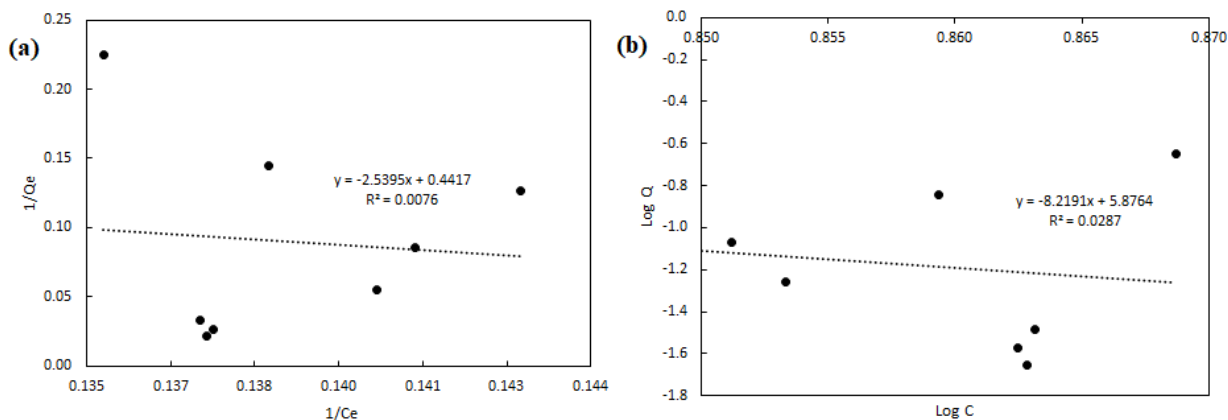


Figure A.4.2. Glyphosate adsorption isotherm models in KG1.2 soil in artificial rainwater: (a) Langmuir model and (b) Freundlich model.

Table A.4.2. Data used in the calculation of glyphosate adsorption isotherm using artificial rainwater and KG2 without washing. 180 rpm at 20°C.

Sample	Ce (mg/L)	Time of contact (hours)	Mass (g)	Initial pH	Final pH	Initial EC (μS/cm)	Final EC (μS/cm)	Removal %
Blank-glyphosate	-	48.0	-	4.155	4.344	25.7	27.1	-
Rainwater	-	48.0	-	5.767	5.736	13.3	21.8	-
Co	7.96	48.0	-	4.155	-	25.7	-	0.00%
01-0.5g	7.9452	48.0	0.5070	4.155	7.053	25.7	31.9	0.15%
02-1g	7.6418	48.0	1.0042	4.155	6.948	25.7	34.7	3.96%
03-1.5g	7.6243	48.0	1.5026	4.155	7.575	25.7	36.2	4.18%
04-2g	7.6243	48.0	2.0079	4.155	7.178	25.7	43.1	4.18%
05-3g	7.6768	48.0	3.0024	4.155	8.237	25.7	43.3	3.52%
06-4g	7.7526	48.0	4.0076	4.155	7.798	25.7	46.6	2.57%
07-5g	7.6709	48.0	5.0052	4.155	8.182	25.7	47.0	3.59%
08-6g	7.3326	48.0	6.0076	4.155	7.866	25.7	49.3	7.85%

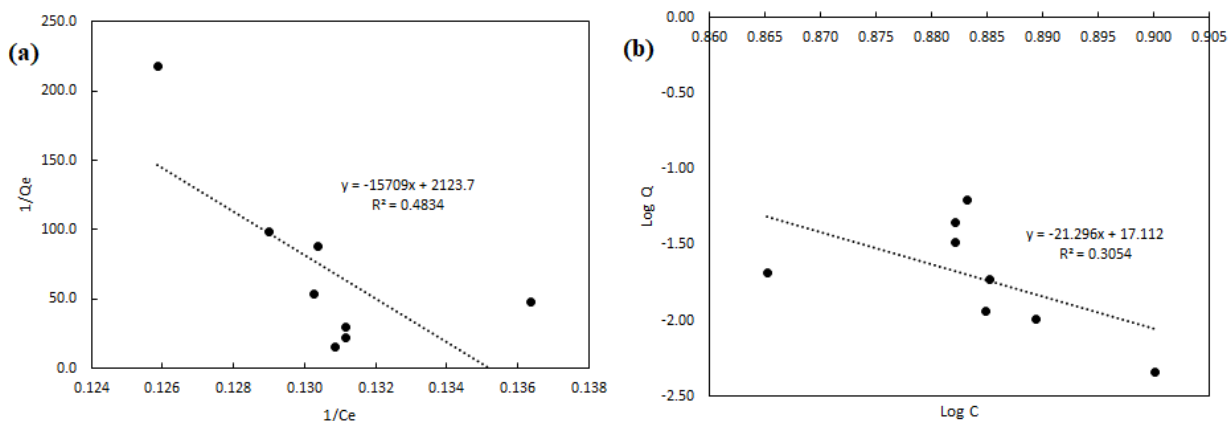


Figure A.4.3. Glyphosate adsorption isotherm models in KG2 soil in artificial rainwater: (a) Langmuir model and (b) Freundlich model.

Table A.4.2. Data used in the calculation of glyphosate adsorption isotherm using artificial rainwater and fine material (ballast) without washing. 180 rpm at 20°C.

Sample	Ce (mg/L)	Time of contact (hours)	Mass (g)	Initial pH	Final pH	Initial EC (μS/cm)	Final EC (μS/cm)	Removal %
Blank-glyphosate	-	48.0	-	4.155	4.244	25.7	27.1	-
Rainwater		48.0	-	5.767	5.736	13.3	21.8	
Co	7.96	48.0	-	4.155	-	25.7	-	0.00%
01-0.5g	7.2742	48.0	0.5041	4.155	7.811	25.7	31.6	8.58%
02-1g	7.0525	48.0	1.0052	4.155	7.942	25.7	42.6	11.37%
03-1.5g	6.8425	48.0	1.5070	4.155	8.022	25.7	47.2	14.00%
04-2g	6.3466	48.0	2.0029	4.155	7.879	25.7	55.4	20.24%
05-3g	5.6056	48.0	3.0055	4.155	8.137	25.7	64.6	29.55%
06-4g	5.4772	48.0	4.0065	4.155	8.000	25.7	71.8	31.16%
07-5g	5.0338	48.0	5.0057	4.155	8.134	25.7	80.3	36.74%
08-6g	5.1214	48.0	6.0050	4.155	7.816	25.7	83.7	35.64%

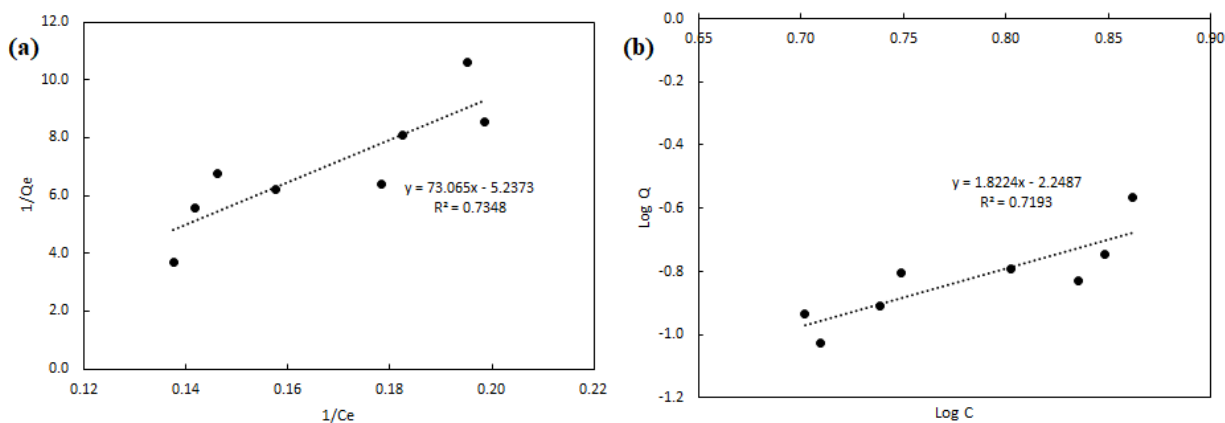


Figure A.4.4. Glyphosate adsorption isotherm models in fine material from ballast in artificial rainwater: (a) Langmuir model and (b) Freundlich model.

APPENDIX 5: ARTIFICIAL RAINWATER

Table A.5.1. Data used in the formulation of artificial rainwater.

Ion	Concentration in natural rainwater (mg/L)	STD Concentration (mg/L)	Concentration stock solution X100 (mg/L)	MM (g/mol)	Final concentration (mg/L)
Cl ⁻	0,6707	0,2482	67,0732	35,453	0,6707
K ⁺	0,2039	0,2023	20,3880	39,0983	0,2039
Na ⁺	0,2457	0,1371	24,5703	22,9898	0,2457
Mg ²⁺	0,1239	0,1593	12,3867	24,305	0,1239
Ca ²⁺	0,3780	0,2035	37,7953	40,078	0,3791
NO ₃ ⁻	2,0443	0,8101	204,4272	62,0049	2,1740
SO ₄ ²⁻	1,1935	0,2944	119,3478	96,06	1,0029
NH ₄ ⁺	0,5385	0,4288	53,8453	18,04	0,5385

ANNEXES

ANNEX 1: DATA OF RAINWATER SAXONY

In the attached Excel document named “Inhaltsstoffe_Regenwasser_2022” is found the data of the natural rainwater of Saxony in Germany, used for the formulation of the artificial rainwater.

ANNEX 2: DATA OF SOILS KG1.1, KG1.2, KG2 AND BALLAST

In the attached documents named “Siebschlammung KG 1 Material 01.09.22”, “1391-400-BER_Zwischenbericht_Anhang 30_47_Neuwied_Labor_GEO”, “1391-200-BER_Zwischenbericht_Anhang 13_Ingolstadt_Labor_Geotechnik_GEPRO”, and “Schurfprofile_Bf Ludwigslust” is found the data of the characteristics of the soils KG1.1, KG1.2, KG2 and ballast, respectively.