Decontamination of water contaminated by the herbicide glyphosate through adsorption technology: a critical review

Descontaminación de agua contaminada por el herbicida glifosato mediante tecnología de adsorción: una revisión crítica

Descontaminação de águas contaminadas pelo herbicida glifosato através de tecnologia de adsorção: uma revisão crítica

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Abstract

One of the biggest problems facing today's society is the rampant use of herbicides, as agricultural overproduction increasingly relies on these chemicals. Despite having a targeted application, their release into soil particles and water resources is inevitable, leading to damage at environmental and social levels. Therefore, adsorption technology presents itself as an alternative to decontaminating wastewater, presenting a high advantage in the removal and cost-benefit of the process. This study provides a qualitative exploratory analysis, where the understanding of the topic is achieved based on a thorough bibliographical survey focused on the removal of glyphosate using different adsorbent materials. Work-related to glyphosate adsorption analyzes several parameters such as pH, adsorbent dosage and adsorbate concentration, process kinetics, and temperature effect. It was observed that when the herbicide concentration was increased, the adsorption capacity also increased, whereas removal showed the opposite behavior, decreasing with increasing concentration. The ideal pH value depends largely on the characteristics of the adsorbent such as surface area, and functional groups present on the surface, among others. The kinetic studies showed a better fit to the Pseudo-second order model, while the adsorption equilibrium studies showed a better fit to the Freundlich and Langmuir model. Nonetheless, current literature shows that several materials can be used as alternative sources of adsorbents for the remediation of glyphosate present in water. In a global view, the use of pesticides has intensified, as it increases the final productivity of the product. Due to a lack of control, such as non-existent guidelines, especially in low-income countries, or poorly supervised legislation, its entry into the environment has grown steadily. This corroborates the need to develop and improve remediation technologies.

Keywords: Wastewater Treatment, Global scale, Contaminants, Biosorbents, Adsorption Process.

Resumen

Uno de los mayores problemas que enfrenta la sociedad actual es el uso desenfrenado de herbicidas, ya que la sobreproducción agrícola depende cada vez más de estos químicos. A pesar de tener una aplicación específica, su liberación en partículas del suelo y recursos hídricos es inevitable, lo que provoca daños a nivel ambiental y social. Por lo tanto, la tecnología de adsorción se presenta como una alternativa para descontaminar aguas residuales, presentando una alta ventaja en remoción y costo-beneficio del proceso. Este estudio proporciona un análisis exploratorio cualitativo, donde la comprensión del tema se logra a partir de un exhaustivo levantamiento bibliográfico centrado en la eliminación de glifosato utilizando diferentes materiales adsorbentes. El trabajo relacionado con la adsorción de glifosato analiza varios parámetros como el pH, la dosis de adsorbente y la concentración de adsorbato, la cinética del proceso y el efecto de la temperatura. Se observó que al aumentar la concentración del herbicida también aumentó la capacidad de adsorción, mientras que la capacidad de remoción mostró el comportamiento contrario, disminuyendo al aumentar la concentración. El valor de pH ideal depende en gran medida de las características del adsorbente como área superficial, grupos funcionales presentes en la superficie, entre otras. Los estudios cinéticos mostraron un mejor ajuste al modelo de pseudosegundo orden, mientras que los estudios de equilibrio de adsorción mostraron un mejor ajuste al modelo de Freundlich y Langmuir. Por lo tanto, la literatura actual muestra que se pueden utilizar varios materiales como fuentes alternativas de adsorbentes para la remediación del glifosato presente en el agua. A nivel global, el uso de pesticidas se ha intensificado, ya que aumenta la productividad final del producto. Debido a la falta de control, como directrices inexistentes, especialmente en países de bajos ingresos, o una legislación mal supervisada, su entrada al medio ambiente ha crecido de manera constante. Esto corrobora la necesidad de desarrollar y mejorar tecnologías de remediación.

Palabras clave: Tratamiento de Aguas Residuales, Escala global, Contaminantes, Biosorbents, Proceso de adsorción.

Resumo

Um dos grandes problemas que a sociedade atual enfrenta é o desenfreado uso de herbicidas, visto que a superprodução agrícola apresenta cada vez mais dependência nesses produtos químicos. Apesar de apresentarem uma aplicação direcionada a sua liberação em partículas de solos e recursos hídricos é inevitável levando a prejuízos a níveis ambientais e sociais. Com isso a tecnologia da adsorção apresenta-se como uma alternativa para descontaminar as águas residuais, apresentando uma alta vantagem na remoção e no custo benefício do processo. Este estudo fornece uma análise exploratória qualitativa, onde a compreensão da temática é realizada a partir de um minucioso levantamento bibliográfico direcionado na remoção do glifosato mediante diferentes materiais adsorventes. Os trabalhos relacionados a adsorção do glifosato analisam vários parâmetros como pH, a dosagem do adsorvente e a concentração do adsorbato, cinética do processo e afeito da temperatura. Foi observado que ao elevar a concentração do herbicida a capacidade de adsorção também se elevou, já a remoção apresenta comportamento contrário diminuindo com a elevação da concentração. O valor do pH ideal depende muito das características do adsorvente como área superficial, grupos funcionais presentes na superfície entre outros. Os estudos cinéticos apresentaram melhor juste ao modelo de Pseudo-segunda ordem, já os estudos de

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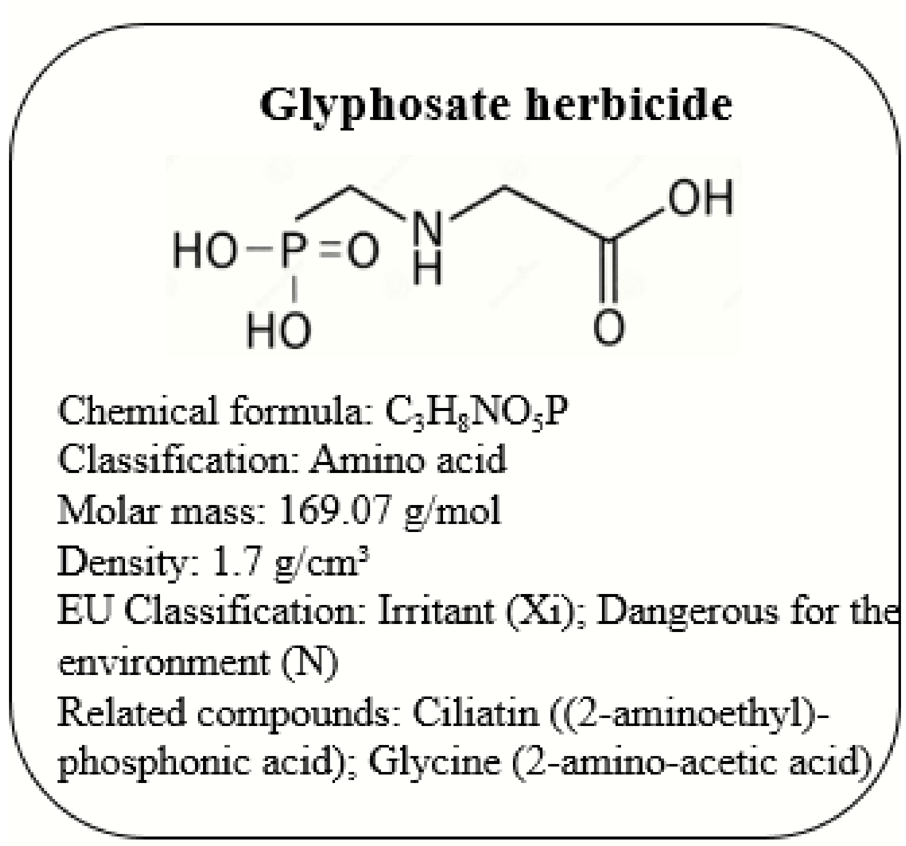
equilíbrio de adsorção apresentaram melhor ajuste ao modelo de Freundlich e Langmuir. Com isso a literatura atual evidencia que vários materiais podem ser usados como fontes alternativas de adsorventes da remediação do glifosato presente na água. Em uma visão global o uso de pesticidas tem se intensificado, pois, o mesmo eleva a produtividade final do produto. Devido à falta de controle, como diretrizes inexistentes principalmente em países de baixa renda, ou por legislações pouco fiscalizadas a sua entrada no meio ambiente tem crescido constantemente. Isso corrobora com a necessidade de se desenvolver e aprimorar tecnologias de remediação.

Palavras-chave: Tratamento de Águas Residuais, Escala global, Contaminantes, Biossorventes, Processo de adsorção.

1. Introduction

Due to the low rotation of different agricultural culture, which corroborates the practice of monoculture, agricultural species are increasingly dependent on agricultural pesticides (Foo and Hameed, 2010). Over the years, discharges of these products into the environment have increased, which are initially aimed at combating pests, but when they enter the food chain they end up affecting the entire ecosystem (Franco et al., 2022a). According to Vanessa et al. (2018), they state that the rapid distribution of pesticides in the soil and water resources is linked to good porosity and runoff into rivers and lakes, contaminating the chain as a whole. In the literature, it is possible to observe a series of studies that indicate the imbalance of the ecosystem with the presence of these chemicals, which affects the air, water, and soil entering the system of terrestrial and aquatic living organisms (Bastos Gonçalves et al., 2020; Gill et al., 2018; Sen et al., 2019; Torretta et al., 2018). Glyphosate is a molecule with specific chemical characteristics as shown in Figure 1. It is also defined as a non-selective, post-emergent, and systemic herbicide. Its continuous and intense use is due to its high efficiency in combating dicotyledonous weeds and monocotyledons. Since these undesirable plants are found in several agricultural crops, glyphosate is now used in the cultivation of oats, wheat, rice, corn, sorghum, soybeans, coffee, pastures, and sugar cane (Noori et al., 2020; Silvia et al., 2020).

Figure 1. Chemical information of the glyphosate herbicide molecule.



Several agricultural additives are sold in Brazil, among them glyphosate is highly consumed, for example, in the period from 2015 to 2021 it was the most sold product, corresponding to 35% of total pesticide sales, which corresponds to approximately 966,340.83 tons (Correa et al., 2023). However, its use also corresponds to a global scale where it was launched worldwide in 1974 and has since been commercialized (Vithanage et al., 2016). Globally, it is the second most used chemical compound in genetically altered crops, in this sense over 1.6 billion kilograms have already been consumed in the United States alone (Peillex and Pelletier, 2020). This data is alarming, as it corresponds to almost 20% of total world consumption (Singh et al., 2019) Bacillus subtilis, and Rhizobium leguminosarum. In Africa, consumption has also increased, and in the period from 2008 to 2012, it went from 12 to 20 million liters (Chen et al., 2019; Lerbs et al., 1990). This is highly concerning given its damage to both aquatic species and several amphibian species, being most affected when concentrations exceed 400 µg L^{-1} (Bai and Ogbourne, 2016). Once present in soil particles, the herbicide can also exist in the form of its metabolites, which are aminomethylphosphonic acid and sarcosine (Noori et al., 2020), in addition to its degradation product, methylphosphonic acid (Feng et al., 2020).

Water treatment plants (WTPs) do not have a high glyphosate removal efficiency, since conventional treatments do not correspond to 100% efficiency, so other processes complementary to the treatment of WTPs are highly necessary (Georgin et al., 2023, 2022a). Other possibilities include ultraviolet radiation (UV) (Ng'etich and Martincigh, 2021), ion exchange, Advanced Oxidative Processes (AOPs) (Chang et al., 2022), and adsorption (L. Jiang et al., 2018; Liao et al., 2018; Serra-Clusellas et al., 2019; Valle et al., 2019). Each of these processes has its respective positive and negative points in addition to involving limitations regarding operational costs and efficiencies. In this case, adsorption is widely used as it is easy to operate, highly flexible, and efficient, in addition to allowing the use of different adsorbents (Ahmad et al., 2023; De Araújo et al., 2016; Dehmani et al., 2023a; Kausar et al., 2018; Narayanan et al., 2023).

In the adsorption process, one or more chemical compounds, also known as adsorbates, are transferred. These are generally found in the fluid phase and begin to aggregate on the surface of the adsorbent, which corresponds to the solid phase. Attraction can occur through interactions of a chemical or physical nature, in these cases characteristics such as functional groups, surface area, porosity, and pore diameter are fundamental for good efficiency (Bouzidi et al., 2023; Yanan et al., 2023). The materials used as adsorbents are solid particles on their surface and the herbicide species begin to occupy the pores until saturation (Kausar et al., 2018). This study provides a review of the removal of the herbicide glyphosate in an aqueous medium through the adsorption process, as well as presents experimental conditions such as temperature, pH, adsorption kinetics and equilibrium, thermodynamics, and adsorption capacity, as well as other results. Glyphosate-based formulations represent one of the most used herbicides worldwide. Its toxic impacts range from animals (endocrine disruptors to humans (cancer), due to this the World Health Organization classified it as a highly dangerous product. In addition to this, the physical characteristics make the producer highly soluble in water, which corroborates its leaching in water compartments. All these aspects highlight the importance of studies on a global scale regarding the remediation of herbicides from the environment.

2. Materials and methods

The development of this study is supported by qualitative research, as it is based on the dynamic relationship between the object and subjectivity. The objective is achieved through exploratory research, where the understanding of the topic studied is carried out through a bibliographic review based on databases such as *Web of Science*, *Elsevier,* and Google Scholar. All selected articles correspond to the period from 2010 to 2023, which analyzed the remediation of water compounds through the use of adsorption technology. Several groups of adsorbent materials have been used and developed. The most relevant information such as adsorbent characteristics, adsorbate concentration, isothermal and kinetic analyses, and thermodynamic parameters are covered in this review article. The words used in the search include glyphosate, adsorption, contamination, environment, adsorbent, toxicology, and remediation.

3. Materials and methods

Table 1 provides different adsorbents and their respective glyphosate adsorption capacity. At first, it is clear that very different performances were achieved, this indicates that adsorption is directly affected by the textural properties, in addition to this the pH and temperature conditions, in addition to the herbicide concentration and contact time must also be analyzed.

Table 1. Maximum adsorption capacities of the herbicide glyphosate through different adsorbents.

Adsorbent material	Maximum adsorption capacity in (mg g^{-1})	Reference
D151 preloaded with Fe^{3+}	481.8	(Guo et al., 2020)
D301 Resin	833.3	(Chen and Zhou, 2016)
Carboxymethylchitosan graphene aerogels	578.0	(Ding et al., 2018)
Mesoporous silica coated with manganese oxides	300.0	(Ambiental et al., 2023)
Hydrated iron oxide particles	140.0	(E. A. O. Pereira et al., 2019)
Modified Nano-$CuFe_2O_4$	269.4	(Jia et al., 2020)
Forest soil	161.3	(Sen et al., 2017)
Microporous cornstarch	138.9	(Dong et al., 2021)
Zeolite 4A	112.7	(Zavareh et al., 2018)
Resin modified with nanometric copper hydroxide	140.0	(Zhou et al., 2017)
Rice husk	123.0	(Vithanage et al., 2016)
Palm loaded with nano-zero-valent iron	80.0	(X. Jiang et al., 2018)
$MnFe_2O_4$ activated carbon	93.5	(Chen et al., 2019)
Water treatment waste (sludge)	85.9	(Hu et al., 2011)
Activated carbon modified with orthophosphoric acid prepared from the bark of *Eucalyptus camaldulensis* (EBAC)	66.7	(Sen et al., 2019)
Multi-metal biosorbent	6.0	(Ramrakhiani et al., 2019)
Solid ferrihydrite	54.9	(R. C. Pereira et al., 2019)
Graphene oxide functionalized with $MnFe_2O_4$	6.8	(Marin et al., 2019)
Newspaper waste	48.4	(Nourouzi et al., 2010)
Pequi shell	8.6	(Borba et al., 2019)
Graphene oxide (GO) functionalized by magnetic iron oxide nanoparticles	46.8	(Santos et al., 2019)
Granular coal loaded with 0.5% manganese and 1% iron	9.2	(Yamaguchi et al., 2019)
Woody biochar	44.0	(Mayakaduwa et al., 2016)
Biopolymer membranes	10.9	(Carneiro et al., 2015)
$MnFe_2O_4$-graphene	39.0	(Yamaguchi et al., 2016)
Functionalized dendrimers	14.0	(Guo et al., 2019)
Chitosan	35.0	(Rissouli et al., 2017)
Chitin	14.0	(Rissouli et al., 2017)

Some materials showed high adsorption capacity, such as D301 resin (833.33 mg g^{-1}) (Chen and Zhou, 2016), D151 preloaded with Fe^{3+} (481.85 mg g^{-1}) (Xiao and Meng, 2020), carboxymethylchitosan-graphene (578 mg g^{-1}) (Ding et al., 2018), modified Nano-$CuFe_2O_4$ (269.4 mg g^{-1}) (Xiao and Meng, 2020), forest soil (161.29 mg g^{-1}) (Sen et al., 2017), microporous corn starch (138.89 mg g^{-1}) (Dong et al., 2021), Resin modified with nanometric copper hydroxide and hydrated iron oxide particles (140 mg g^{-1}) (Yamaguchi et al., 2016; Zhou et al., 2017) and rice husk (123.03 mg g^{-1}) (Herath et al., 2016). Zhou et al. (2019) in order to remove glyphosate from an aqueous solution, used a resin modified with nanometric copper hydroxide (D201Cu). In this study, the interference of temperature, contact time, concentration of NaCl, humic acid, pH, and fulvic acid was analyzed. After synthesizing and characterizing the resin, the authors observed that the presence of fulvic and humic acid interfered with the adsorption capacity of glyphosate, reducing the efficiency of the process. The pH parameter also showed that in the range of 4 to 10, D201Cu resins presented excellent removal performance with a maximum capacity of 140 mg g^{-1}.

The study by Yamaguchi et al. (2019) used granular charcoal loaded with 0.5% manganese and 1% iron (GAG/Mn/Fe) as a glyphosate adsorbent. The authors highlighted that the system's equilibrium was only reached after 24 hours of process, reaching a maximum capacity of 9.19 mg g^{-1}, at a temperature of 45°C and adsorbent dosage of 20 mg L^{-1}. The natural glyphosate solution had an acidity of 3.8 where after the addition of the adsorbent, no pH adjustment was carried out. In this aspect, the authors highlight that the toxic effects of each acid-base form of glyphosate are unknown. The study by Sen et al. (2019) analyzed the performance of an activated carbon modified with orthophosphoric acid. The residual biomass used corresponds to the bark of *Eucalyptus camaldulensis* (EBAC). The developed adsorbent obtained operational parameters optimized by using the Box-Behnken model, the best conditions were achieved at pH 10, herbicide concentration of 20.28 mg $L^{-1,}$ and an adsorbent dosage of 199.92 mg L^{-1} added in 50 mL of solution. The removal achieved was 98%, and as the glyphosate concentration increased, the capacity also increased. The isothermal studies obtained a maximum capacity of 66.76 mg g^{-1}, the best-fitting model was the Langmuir monolayer (Langmuir, 1918), which presented a K_L of 0.178 (adsorbent/adsorbate interaction constant or Langmuir affinity constant). As a result, both adsorbents developed can be used efficiently in the remediation of aqueous solutions containing glyphosate, as they have high removal capacities, which are more recommended than those with lower capacities, such as *pequi* peel with a capacity of 8.59 mg g^{-1} (Borba et al., 2019).

4. Factors influencing the adsorption process

An important parameter in investigating the adsorption process is the pH of the medium, which can influence the surface charge of the adsorbent and the dissociation of glyphosate species. Another aspect of the adsorbent is the Zero Charge Point (pH_{PCZ})(Drumm et al., 2021; Georgin et al., 2021)acid red 97 (AR97, this is related to the pH value, at this point the solid particles have a zero charge, the discovery of this point is important to analyze the surface phenomena that involve adsorption. With this, new information can be obtained regarding the charges on the surface of the adsorbent as the pH of the medium is modified, this elucidates why adsorption is more efficient at certain pH points (Guiza, 2017). When the pH used in the adsorption process is equal to pH_{pcz}, the surface of the adsorbent material is neutral. When pH > pH_{pcz}, in this case, it indicates that the surface of the adsorbent material is mostly negatively charged, meaning that cations tend to be more adsorbed. The adsorption of anions tends to be more favorable at pH levels lower than pH_{pcz}, this occurs because the surface of the adsorbent has positive charges, resulting in electrostatic attraction (Dehmani et al., 2023a, 2023b; Georgin et al., 2022b). Mayakaduwa et al., 2016 used wood residues for the production of biochar and subsequent use in the removal of glyphosate, where the pH parameter of the medium had a strong influence on the efficiency of the process. When increasing from 5 to 6 the capacity went from 11.03 to 21.6 mg g^{-1}, respectively, this behavior is related to the degree of ionization of the glyphosate.

In the study by Zhou et al. (2017), the pH of the medium varied from 3 to 12, initially from 3 to 5, and the adsorption capacity using resin went from 50.1 mg g^{-1} to 179.1 mg g^{-1}, where it was concluded that in the range of 4 to 10, the adsorbent proved to be stable with a good adsorption capacity close to 140 mg g^{-1}, demonstrating the good adsorption capacity for a wide pH range. The study by Borba et al. (2019) prepared activated carbon from *pequi* peel carbonized in a muffle furnace under a limited oxygen atmosphere and with temperature and carbonization time adaptations of 380°C and 15 minutes, respectively. The pH parameter of the solution was analyzed at values of 5.5, 7, and 8, and the adsorption capacity increased with its increase, going from 1.05 ± 0.22 to 4.04 ± 0.34. The zero charge point of the adsorbent was 6.6, corroborating the maximum capacity values at pH 8, which presents a negative surface charge density. When using pure granular carbon (GAC) Yamaguchi et al. (2019), showed that the material presents a negative charge in acidic conditions, as does the herbicide, in these conditions adsorption is unfavorable. To solve this behavior, the authors used granular carbon loaded with 0.5% manganese and 1% iron (GAC/Mn/Fe), thus, in acidic conditions (pH=3.8) the adsorbent is positive, favoring the adsorption of carbon molecules negatively charged glyphosate. In contrast, when using hydrated iron oxide particles (E. A. O. Pereira et al., 2019), the authors observed that as the pH of the medium was raised to 7, glyphosate adsorption reduced from 140 to 20 mg g^{-1} at a pH of 2, as a result, the medium becomes negative when the pH is raised, with no electrostatic attractions between the adsorbent and the herbicide.

The herbicide concentration was also varied in several studies, as was the adsorbent dosage, so the removal efficiency is highly dependent on the concentration relationship and the number of sites available on the adsorbent surface (Zhou et al., 2019). In general, increasing the concentration shows a reduction in the concentration percentage, this is related to the saturation of the adsorption sites on the surface of the adsorbent. On the other hand, when the herbicide concentration is increased, the adsorption capacity is also increased. Most of the studies analyzed, the capacity increased with the increase in concentration, increasing the driving force in the mass transfer process (Sen et al., 2019). When varying the glyphosate concentration from 5 to 30 mg L^{-1} (Sen et al., 2019), at a constant pH of 7 and contact time of 30 min, the authors observed that the adsorption capacity showed linear behavior. The adsorbent dosage also favored adsorption, increasing removal from 71 to 77% with an increase from 5 to 100 mg of adsorbent. Above 100 mg, adsorption was not high, which corroborates the greater availability of active sites, which support binding to glyphosate. With this dose of 150 mg/50 mL, no additional increase in adsorption occurred. Very high dosages can corroborate the occurrence of overlapping sites, which prevents the accommodation of glyphosate molecules (Sen et al., 2019).

Therefore, it can be observed that the strong dependence between the concentration of glyphosate, the adsorption capacity, and the dosage of the adsorbent, this information is important both for experimental analysis and for economic viability studies, these studies avoid future waste and increase the efficiency of the process. (Vitória et al., 2021). Studying the time required for the adsorbent to reach saturation is also necessary (Sen et al., 2019) since the adsorption rate can interact with the adsorbent and adsorbate molecules, that is, this factor indicates the kinetic behavior of adsorption for a given adsorbent at a given initial concentration of the adsorbate (Franco et al., 2022b). When using a carbonaceous material as an adsorbent (Sen et al., 2019) the authors observed that the maximum removal of 89% was achieved in 120 min of operation. During the process, after 120 min, the repulsion increases, and due to this, after saturation, an increase in adsorption capacity is no longer observed.

5. Kinetic, isothermal and thermodynamic adsorption studies

Carrying out kinetic analyses makes it possible to analyze the use of an adsorbent by obtaining the speed, through different concentrations and the process time, which can be in hours, minutes, or days. This determines the rate of adsorbate removal from the fluid phase to the adsorbent or the time involved in the mass transfer of one or more components contained in a liquid to the adsorbent (Grassi et al., 2023; Lazarotto et al., 2022). With experimental data, several kinetic models can be tested, such as Pseudo-second order (Azizian, 2004), Elovich (Elovich and Larionov, 1962), Pseudo-first order (Ho and McKay, 1999), and the intraparticle diffusion model (Naeem et al., 2018), according to Table 2

Table 2 Commonly employed adsorption kinetic models.

Model name	Equation	Parameters	
Pseudo-first order	$q_t=q_1\,(1\text{-exp}(\text{-}k_1t))$	k_1 pseudo-first order rate constant (min^{-1}); q_1 pseudo-first order adsorption capacity ($mg\ g^{-1}$);	(1)
Pseudo-second order	$q_t=\frac{t}{\left(\frac{1}{k_2q_2^2}\right)+\left(\frac{t}{q_2}\right)}$	k_2 pseudo-second order rate constant ($g\ mg^{-1}\ min^{-1}$); q_2 pseudo-second order adsorption capacity ($mg\ g^{-1}$);	(2)
Elovich	$q_t=\frac{1}{a}\ln(1+abt)$	a is the Elovich rate constant ($mg\ g^{-1}\ min^{-1}$); b is the desorption constant of Elovich model ($g\ mg^{-1}$);	(3)
Intraparticle diffusion model	$q_t = k\sqrt{t}$ $k = 6q_e\sqrt{\frac{D_e}{\pi r}}$	k is the intraparticle diffusion model ($mg\ g^{-1}$)($min^{-1/2}$); q_e is the adsorption capacity ($mg\ g^{-1}$); D_e is the effective diffusion ($cm\ s^{-1}$); R is the radius of the adsorbent (cm);	(4)

In parallel to the kinetic studies, the articles also mostly provide isothermal studies, varying the concentration of the herbicide depending on the adsorption capacity and often using different temperatures. New information regarding the viability and possibility of using the material, as well as the estimation of maximum adsorption capacities using isothermal models (Zhou et al., 2019). Among the various isotherm equations, we can mention Freundlich (Suzuki & Kawazoe, 1974), Toth (Terzyk et al., 2003)"mendeley":{"formattedCitation":"(Terzyk et al., 2003, Langmuir (Langmuir, 1918), Sips (Sips, 1948) and Redlich-Peterson (Redlich and Peterson, 1959) isotherms as given in Table 3

Table 3 Commonly employed adsorption isotherm models.

Model name	Equation	Paramters	
Freundlich	$q_e=K_FC_e^{1/n_F}$	K_F is the Freundlich constant ((mg g^{-1}) (mg $L^{-1})^{-1/n}$); n_F is the Freundlich heterogeneity factor (dimensionless);	(5)
Langmuir	$q_e=q_L\frac{K_LC_e}{1+K_LC_e}$	q_L is the maximum adsorption capacity of Langmuir model ($mg\ g^{-1}$); K_L is the Langmuir constant ($L\ mg^{-1}$);	(6)
Sips	$q_e=q_S\frac{K_SC_e^{ns}}{1+K_SC_e^{ns}}$	q_S is the maximum adsorption capacity of the Sips model ($mg\ g^{-1}$); K_S is the Sips constant	(7)
Toth	$q_e=q_T\frac{K_TC_e}{\sqrt[n_T]{1+(K_TC_e)^{n_T}}}$	q_T is the maximum adsorption capacity of the Tóth model ($mg\ g^{-1}$); K_T is the Tóth constant ($L\ mg^{-1}$); n_T is the Tóth exponent (dimensionless);	(8)
Redlich Peterson	$q_e=q_{RP}\frac{K_{RP}C_e}{1+a_{RP}C_e^{n_{RP}}{}_e}$	K_{RP} is the first Redlich-Peterson constant ($L\ kg^{-1}$); a_{RP} is the second Redlich-Peterson constant ; n_{RP} is the Redlich-Peterson exponent (dimensionless);	(9)

The results of the isothermal studies of the articles used in this study are listed in Table 4, where it is observed that the Langmuir homogeneous surface and Freundlich heterogeneous surface isothermal models were the ones that best fit the experimental data. Regarding the kinetic studies, it was observed that the Pseudo-first order model followed by the Pseudo-first order model and Elovich were the ones that best fit the kinetic data

Table 4. Kinetic, isothermal, and thermodynamic studies of glyphosate adsorption using different.

Adsorbent	Kinetic model	Isotherm model	Type of thermodynamic process	Reference
Palm loaded with nano-zero-valent iron	Pseudo-second order	Langmuir	x	(Bhattacharya et al., 2017)
Activated carbon prepared from the bark of *Eucalyptus camaldulens*	Pseudo-second order	Freundlich	Spontaneous ($\Delta G° < 0$) and endothermic	(Sen et al., 2019)
Pequi shell	Pseudo-first order	Langmuir	x	(Borba et al., 2019)
Modified Nano-$CuFe_2O_4$	Pseudo-second order	Freundlich and Langmuir	x	(Jia et al., 2020)
Carboxymethylchitosan - graphene aerogels	Pseudo-second order	Langmuir	x	(Ding et al., 2018)
D301 Resin	Pseudo-second order	Langmuir	Spontaneous ($\Delta G° < 0$) and exothermic	(Chen and Zhou, 2016)
Zeolite 4A	Pseudo-second order and pseudo-first order	Langmuir	x	(Zavareh et al., 2018)
Microporous cornstarch	Pseudo-second order	Langmuir	Spontaneous ($\Delta G° < 0$) and exothermic	(Dong et al., 2021)
Solid ferrihydrite	Pseudo-second order	Langmuir	x	(R. C. Pereira et al., 2019)
Forest soil	Pseudo-second order	Langmuir	Spontaneous ($\Delta G°<0$) and exothermic	(Sen et al., 2017)
$MnFe_2O_4$ activated carbon	Pseudo-second order	Freundlich	x	(Chen et al., 2019)
Multi-metal biosorbent	Pseudo-second order	Langmuir	x	(Hu et al., 2011)
$MnFe_2O_4$.graphene	Pseudo-second order	Freundlich	Spontaneous, Exothermic, and viable in the range of 5-45°C	(Yamaguchi et al., 2016)
Granular coal loaded with 0.5% manganese and 1% iron	Pseudo-second order	Freundlich	Spontaneous ($\Delta G° < 0$) and endothermic	(Yamaguchi et al., 2019)
Graphene oxide (GO) functionalized by magnetic iron oxide nanoparticles	Pseudo-second order	Langmuir	Spontaneous, exothermic, and favorable at a temperature of 15-45 °C	(Santos et al., 2019)
Functionalized dendrimers	Pseudo-second order	Langmuir	x	(Guo et al., 2019)

The Langmuir monolayer model is related to the adsorption of a given adsorbate through a set of well-defined active sites, in which each site is responsible for retaining a single adsorbent species that do not interact with each other. According to Morse et al. (2011), the equation proposed by Langmuir (1918) presents an assumption of the existence of a defined number of sites, once adsorbed the herbicide molecules do not interact with each other, indicating an energetic equivalence of the sites. This implies the formation of a monolayer; this behavior is contrary to that indicated by the Freundlich model. In this case, it is suggested that the adsorption process occurs in the form of multilayers. In addition to the application of models, isothermal studies generally involve the use of different temperatures, which is generally a significant physicochemical parameter in the efficiency of the process and can influence the capacity of the adsorbent (Bikash et al., 2016). Another aspect is that using different temperatures makes it possible to estimate thermodynamic parameters, which are essential for evaluating the adsorption process by informing about the inherent energetic changes. If the process is favorable to an increase in temperature in the system, the process generally has an endothermic nature, on the contrary, if an increase in temperature does not favor the process, the system tends to be exothermic in nature, which is more favorable to large-scale application as it consumes less energy reducing operational costs (Vitória et al., 2021).

The study by Rissouli et al. (2017), analyzed the adsorption of glyphosate through the use of chitosan and chitin, both adsorbents showed a better fit to the Langmuir isotherm, and the maximum capacities were 35.08 and 14.04 mg g^{-1}, respectively. The values of the equilibrium parameter (R_L) for both adsorbents are between 0 and 1, showing favorable adsorption in both systems, being 0.86-0.93 (chitosan) and 0.170-0.860 (chitin). The study by Mayakaduwa et al. (2016) showed that using biochar as an adsorbent, the isothermal curves showed a better fit to the Freundlich and Temkin model. In this study, the Freundlich exponent *n* (equation 1) indicates favorability of adsorption. This corroborates with a value lower than 1 being 0.406, with this the authors indicate that the herbicide is adsorbed to a more heterogeneous surface corresponding to the biochar surface. Some articles suggest that a good fit to the Temkin isotherm (Temkin and Pyzhev, 1939) may indicate a process governed by chemisorption, however, for such a statement it is necessary to estimate the thermodynamic adsorption parameters. In this same study, the R_L values obtained were between 0.15 and 0.88, confirming the favorable sorption according to the assumptions of the Freundlich model (Gray and Do, 1989).

Analyzed the adsorption of the herbicide through biochar produced from the residual biomass of sugarcane bagasse, the authors reported that the kinetic studies correspond to the Pseudo-second order model, in which it was observed a constant of 0.8428 g mg^{-1} min^{-1} (Ambiental et al. 2023). Because of this, the authors state that the process can be governed by forces of a chemical nature, however, kinetic models as well as isothermal models cannot be used to state the adsorption mechanism that involves the adsorbate molecules with the surface of the adsorbent. In this same study, the authors observed that the Langmuir isotherm was well used to represent the equilibrium data, obtaining a maximum capacity of 3.68 mg g^{-1}. Quickly in the first two minutes of the process, around 30% of the herbicide had already been adsorbed, totaling 40% after 13 minutes of operation. Despite the low adsorption capacity obtained compared to other studies in the literature, it is worth noting that this material was used at a much lower dosage and with a highly low herbicide concentration compared to other studies. The K_L value was 0.056, being less than 1, corroborating a favorable process ($K_L < 1$) (Ambiental et al. 2023).

Zavareh et al. (2018) analyzed the adsorption of glyphosate through the use of zeolite as an adsorbent, the authors highlighted a selective process in pH conditions close to 7. The isothermal data were fitted to non-linear models, in which the isotherm of Langmuir presented an excellent fit with a maximum capacity of 112.7 mg g^{-1}. The kinetic data correspond to the highly fast equilibrium time with excellent fit to the Pseudo-second order and Pseudo-first order models. When using modified Nano-$CuFe_2O_4$ as an adsorbent, the authors (Jia et al., 2020) an effective method for the removal of aqueous glyphosate is developed by employing nano-CuFe2O4 modified biochar (BC observed that the Freundlich and Langmuir isotherms presented excellent adjustments, however, the authors state that the process may involve physical and chemical forces, where again it is reaffirmed that such interaction can only be asserted through the use of the estimate of thermodynamic parameters. In this same study, the kinetic data were well adjusted to the Pseudo-second order model, where again, mistakenly, the authors reaffirmed the process of a chemical nature. With the use of modified Nano-$CuFe_2O_4$, the maximum capacity of the herbicide reached 269.4 mg g^{-1} with a relatively fast equilibrium time of 240 min, which was obtained at room temperature (298 K), for a concentration of 600 mg L^{-1} in acidic conditions (pH = 4).

Finally, Yamaguchi et al. (2016) reported the adsorption of the herbicide on $MnFe_2O_4$. Isothermal studies were conducted at five temperatures. When this parameter was raised, the adsorption of glyphosate decreased, indicating an exothermic process. $MnFe_2O_4$ obtained a maximum capacity of 39 mg g^{-1}, which was reached at the lowest temperature studied. When using isothermal models, it was observed that the curves presented a better fit to the Freundlich model, suggesting the formation of multilayers with electrostatic interactions. The R_L values varied in the range of 0.054 to 0.998, indicating that the $MnFe_2O_4$ compound presents a favorable adsorption of glyphosate. The kinetic data presented a good fit to the Pseudo-second order model for all different concentrations, however, the authors claim that there are interactions of a chemical nature, which is unfavorable to the desorption process (Yamaguchi et al., 2016).

Of the few studies that analyzed thermodynamic parameters, the study with the microporous corn starch adsorbent indicated a highly viable and spontaneity process, showing an increase in negative values of the standard Gibbs free energy ($\Delta G°$) as the temperature increased. The exothermic nature can only be confirmed with the negative value of the standard enthalpy change (ΔH) (Lima et al., 2019, 2015). The possible reason for the decrease in the adsorption capacity of the exothermic process is that the increase in temperature decreases the adsorptive forces between the glyphosate molecules and the active sites of the adsorbent, thus resulting in the decrease of the adsorption capacity (Zhou et al., 2019). When preparing charcoal from the bark of *Eucalyptus camaldulensis* (EBAC), the authors observed negative values in the standard entropy (ΔS), as a result of which the herbicide molecules lost randomness at the solid/liquid interface during the adsorption process, negative values of the standard Gibbs free energy, minus for the lowest temperature analyzed, which indicates the spontaneity of the process. Finally, the adsorption of the herbicide on GAC/Mn/Fe was endothermic in nature as the ΔH presented a positive value, thus the increase in temperature favored the mobility of the herbicide molecules, contributing to their accommodation and arrival at the sites present on the surface of the adsorbent (Sen et al., 2019).

6. Future perspectives

The first aspect to be analyzed is that the pH parameters and adsorbent dosage were not always analyzed in the studies, where the authors only informed, or in many cases, this was not even mentioned. This makes it difficult to optimize the process on a large scale. Optimizing the dosage is necessary to enable and scale its application in large quantities, thus avoiding the use of an overdose for possible small removals, which would be wasteful. Another point to be analyzed is that not all studies estimated the kinetic and isothermal parameters in a non-linear way, so linear formulas were used, this allows overestimated capacity values, which are above the real values. As a result, the data loses its reliability and can lead to economic losses in real water treatment situations. Another point is that when carrying out the isothermal study it is recommended to use different temperatures, as this is the only way to estimate the thermodynamic parameters. Many studies carried out experiments only at one temperature, which makes it impossible to estimate thermodynamic parameters and not obtain further information about the nature of the process and the interactions that govern it. Thus, the next studies on glyphosate adsorption must carry out a study on the variation of both the adsorbent dosage and the pH variation. Other knowledge gaps still need to be filled, such as the application of physical statistical analyses together with mass transfer models. Once present in the environment, glyphosate is found with other chemical compounds such as atrazine, paraquat, 2,4-D, and diuron, which leads to the interference of these molecules during the adsorption process must also be analyzed, strengthening further studies regarding the competitive adsorption during the process.

One possibility when it comes to large-scale wastewater treatment is application in a fixed bed, being that more studies analyzing the behavior of these adsorbents in a column are necessary. Proper modeling must also be carried out along with column experiments. Generally, these tests require a greater amount of adsorbent, this factor generates the necessity of economic feasibility before large-scale application. It is worth noting that the remediation of contaminated areas in a real environment often does not allow controlling certain conditions such as pH, temperature, and the existence of other chemical compounds, which is why, for the process to be efficient, it often requires the use of other technologies, such as degradation. advanced types of Fenton (Andreozzi et al., 1999) or photocatalytic (Suo et al., 2019) corncob and corn starch was prepared through one-step pyrolysis. The biochar was characterized, and the capacity for triazine pesticide (TRZ. Electrochemical degradation (Ben Hafaiedh et al., 2020), co-precipitation (Sharifpour et al., 2020), catalytic oxidation (Corma et al., 1997), and phytoremediation (Gavrilescu, 2020) the biomass feedstock is a central part of the smart economy, to produce food, energy, chemicals, and protect the environment. This chapter discusses some basic aspects and recent advances in biomass usage, processing and analysis from two perspectives. The first addresses the application of biomass in environmental remediation (phytoremediation, biosorption and bioaccumulation, and carbon dioxide sequestration can also be used. More studies using adsorption in conjunction with another complementary process need to be carried out. No analyses were observed with the application of fuzzy inference systems to model and optimize the remediation process nor the use of neural networks. With these new perspectives described, new horizons can be directed to the scientific community.

Conclusion

This study sought to provide a wide range of relevant information about the removal of glyphosate in an aqueous medium using different adsorbents such as Resin D301, mesoporous silica coated with manganese oxides, graphene, among other materials. The adsorption capacity of the adsorbent was analyzed under different experimental conditions, such as the effect of the initial concentration of glyphosate, and the effect of pH, in addition to kinetic, equilibrium, and thermodynamic studies. The herbicide adsorption process presents a certain dependence on the pH values of the medium, generally increasing the herbicide concentration leads to a decrease in removal and an increase in adsorption capacity. Increasing the dosage increases the adsorption capacity and decreases removal. The experimental parameters control the efficiency of the adsorbent, which can make its application on a real scale difficult. One solution is to apply other technologies together to improve efficiency. The Langmuir and Freundlich isotherm models are those that best fit the experimental data from the articles analyzed. The kinetic data were well represented by the Pseudo-second order model. Finally, the studies reveal that there are already developed adsorbents that can be successfully applied in the remediation of water contaminated with glyphosate, however, more studies must be conducted in order to break the existing barrier between the scientific community and society, only then can community and the planet as a whole will be able to benefit from scientific advances made in this area.

Declaration of competence of interests

The authors have nothing to declare.

Authors contributions

Jordana Georgin – Writing, Dison S. P. Franco - Reviewing, Lucas Meili - Reviewing.

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