



Ecotoxicology of glyphosate and recent advances in its mitigation by adsorption

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Abstract

Glyphosate (*N*-[phosphonomethyl]glycine) is one of the most popular herbicides now used in agricultural practice. The aim of this paper was to discuss the research progress and innovations in recent years on the mitigation of glyphosate (GLY) from aqueous media by adsorption. The ecotoxicology of GLY was discussed in the domain of its chronic and sub-chronic toxicity, genotoxicity, reproductive toxicity, and carcinogenicity, and potential risks of food contamination were discussed. It was observed that polymers and resins are the best class of adsorbents for GLY adsorption from aqueous media. GLY adsorption was best fit to either Freundlich or Langmuir isotherm depending on the nature of the adsorbent. The pseudo-second-order kinetics was also the best fit for modelling the kinetics of GLY adsorption. A review of the thermodynamics revealed that GLY adsorption was usually spontaneous and exothermic. Research trends and knowledge gaps are in the area of chemical mobility in environmental systems (especially in the presence of other chemical species), the use of heavy metal-laden adsorbent and molecular modelling. Furthermore, it was observed that the ecotoxicology of GLY still has some contentious areas where there is no conclusive stance.

Keywords Adsorption · Ecotoxicology · Environment · Glyphosate · Water pollution

Introduction

Due to urbanisation and industrialisation, water pollution is now one of the major environmental challenges of the twenty-first century (Ighalo and Adeniyi 2020). There is now the release of a diversity of emerging pollutants in the aqueous environment (Jeirani et al. 2017). These pollutants are toxic to humans, animals, and plants (Bai and Ogbourne 2016; Cherik et al. 2015; Jaishankar et al. 2014). Herbicides and pesticides

are a class of emerging pollutants now used due to the mechanisation of agriculture (Hoppin et al. 2006). One of the most popular types is glyphosate (Richmond 2018). Glyphosate (*N*-[phosphonomethyl]glycine) is a white crystalline powder with a molar mass of 169.07 g/mol. More details of the basic description of the compound are given in Table 1.

Glyphosate (GLY) is a highly effective, anionic, non-selective herbicide popularly utilised in agricultural practice (Zhou et al. 2017). It was introduced into the global market

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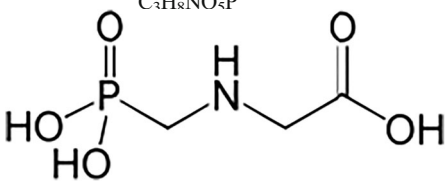
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Table 1 Basic properties of GLY (PubChem 2020; Sharma et al. 2012; Struger et al. 2008)

Property	Values
CAS number	1071-83-6
IUPAC name	2-(Phosphonomethylamino)acetic acid
Chemical formula	C ₂ H ₈ NO ₅ P
Chemical structure	
Molar mass	169.07 g/mol
Specific gravity (at 20 °C)	1.704
Solubility in water (at 20 °C)	10.5 g/l
pKa	2.0, 2.6, 5.6, 10.6
Melting point	230 °C
Flashpoint	Non-flammable
Groundwater ubiquity score value	< 1.8
Half-life in water	7–10 weeks
Half-life in soil	60 days

around 1974 (Herath et al. 2015). It is now the second most frequently utilised herbicide in the cultivation of genetically modified crops (Xu et al. 2016). Since the year 1974, over 1.6 billion kilograms of GLY has been utilised in the USA (about 19% of the estimated 8.6 billion kilograms of global use) (Benbrook 2016). Two-thirds of the total GLY used in the USA from 1974 to 2014 has been applied in just the past 10 years (Benbrook 2016). GLY usage in Africa has been on the increase every year, and it was reported to have increased from 12 to 20 million litres between 2008 and 2012 (Richmond 2018). GLY has serious negative effects on amphibians and aquatic species at concentrations above 400 µg/l (Bai and Ogbourne 2016). In the soil, it can also exist as its metabolites (sarcosine and aminomethylphosphonic acid) (Gimsing et al. 2004) and its degradation product (methylphosphonic acid) (Flores et al. 2018).

GLY is of the class of organophosphorus herbicides (specifically a phosphonate) and is used to kill wooden plants, broadleaf weeds, and grasses (Barja and dos Santos Afonso 1998). It can accumulate in soil with a long half-life because it is strongly adsorbed on soil minerals (Sheals et al. 2002; Yang et al. 2018). It, however, can be leached from the soil into the aqueous environment despite its ability to get immobilised in soil minerals (Barja and dos Santos Afonso 2005). Though previously considered as an eco-friendly herbicide, its environmental safety has been questioned (Hagner et al. 2013; Solomon and Thompson 2003). According to the US Environmental Protection Agency (EPA), the maximum contaminant level GLY is 700 µg/l in drinking water

(Ramrakhiani et al. 2019). It can lead to death by deliberate overdose of the compound. Besides, the toxicology in humans at lower doses is mutagenic, carcinogenic, and genotoxic (Lin and Garry 2000; Manas et al. 2009).

Adsorption is an extensively investigated technique for removing pollutants from aqueous solutions using materials from organic (Eletta et al. 2020b; Ighalo and Eletta 2020a) and inorganic sources (Gupta and Bhattacharyya 2011; Kausar et al. 2018). Numerous studies have considered that adsorption of GLY from aqueous media both in recent times and from classical studies (Glass 1987; McConnell and Hossner 1985). Studies have investigated the use of inorganic-based materials like goethite (Xu et al. 2016; Yang et al. 2018), magnetite (Yang et al. 2018), organic-based materials like graphene (Undabeytia et al. 1996), polymers like polystyrene resins (Xiao and Wen 2016), and a host of others.

Within the scope of the authors' exhaustive search, there are no systematic reviews on GLY adsorption from aqueous media. This paper aims to discuss the ecotoxicology of GLY and evaluate the research progress and innovations made in recent years on the mitigation of GLY from the aqueous environment by adsorption. The review will help evaluate knowledge gaps and elucidate future perspectives in the research area. Studies like these are important as they help keep track of covered ground, guide researchers to potential innovations, and shape the direction of research. In light of the drive for environmental sustainability, critical reviews such as these are justified.

Ecotoxicology of glyphosate

In the last three decades, GLY has been widely used for the control of weed (herbicide) in agriculture. The Environmental Protection Agency (EPA) in the USA classified GLY as a non-toxic herbicide based on its toxicity data and its unique action mode through a biochemical pathway. Many scientific articles also confirmed the recommendation. However, in recent times, there are been several reports that GLY and its metabolite aminomethylphosphonic acid (AMPA) being potentially toxic due to their residues accumulation in the food chain (Bai and Ogbourne 2016). The Food and Agriculture Organization (FAO) also reports that GLY and AMPA dietary risk can be caused when ingested with over 1 mg/kg body weight (FAO 2005). Furthermore, it has been established by researchers that GLY can persist in the environment, and its assessment associated with health risks is complicated compared with data. This section discusses the ecotoxicological effects of GLY.

Acute poisoning

There have been several cases of high exposure to GLY and its metabolites. Williams et al. (2000) reported that 125 µg/kg and 5 µg/kg daily of GLY and AMPA, respectively, are exposed to adult humans causing acute poisoning. Roberts et al. (2010) reported its cardiorespiratory toxicity effect which caused 3.2% fatality cases with an average time of 20 h to death in adults with acute self-poisoning. Greim et al. (2015) also reported that the lethal dose-effect through oral and dermal of GLY on animals (i.e. rat) is much higher at > 5000 mg/kg body weight or > 2000 mg/kg body weight. The difference in the reported values is caused due to different formulations of GLY (i.e. most commercial formulation contains surfactants to increase its efficiency through high penetration of active ingredient). As a result, there is a need to focus more on the effect of the formulation rather than the active ingredient (Currie et al. 2015). In vitro, it was observed that the toxicity effect of neat GLY (~ 2 g/l) is lower than that of Roundup® 400 and 450 (~ 0.001 g/l) (Gasnier et al. 2009). Though it was also observed that the presence of GLY without any surfactant affected the vertebrate embryos morphogenesis formation (Paganelli et al. 2010). Therefore, it is important to estimate the parameter using both the formulation and GLY only.

Chronic and sub-chronic toxicity

In the study by Greim et al. (2015), a no-observed-adverse-effect level (NOAEL) for chronic toxicity was suggested as 560 mg/kg body weight. Williams et al. (2000) also concluded in their research work that rodent tolerant level can withstand

20,000 mg/kg body weight of GLY uptake daily. However, Cox (1995) observed that daily consumption of GLY ranging from 60 to 2500 mg/kg daily for 90 days in mice and rat will damage their liver, increase the acidity level of their bile, cause inflammation of the kidneys, reduce their body weight, and increase the potassium and phosphorous levels in the blood. Benedetti et al. (2004) observed that irreversible damage of hepatocytes occurs on rats when exposed to GLY at the rate of 5 to 490 mg/kg body weight for 2 days to 75 days, and this suggests irreversible damage in mammals in a lower rate. Liver damage has also been reported by Çağlar and Kolankaya (2008) which occurs in rats after the occurrences of exposures of 56 and 560 mg/kg of GLY for between 35 and 90 days. It has also been observed that one exposure of GLY (low concentration) is enough to cause cytotoxicity and change in cell function, for example, in case of disruption of human endocrine at 0.5 ppm and cytotoxicity of in vitro at 10 ppm (Gasnier et al. 2009).

Genotoxicity

The effect of GLY which results in genotoxicity has been regularly questioned and always rejected (Greim et al. 2015), but some other studies often reported damage of DNA which results from the use of high doses of GLY. Koller et al. (2012) also reported that GLY has been observed to damage DNA cells of humans through sub-agricultural doses. He further explained that this damage occurs between the concentration of 10 and 20 mg/l. Kier and Kirkland (2013) suggested that GLY was not genotoxic but rather its cytotoxicity that is responsible for the DNA damage. Therefore, whatever the causes either directly or indirectly, recent facts suggested that damage to DNA may result from exposure to GLY.

Reproductive toxicity

Glyphosate (GLY) has not been a hundred percent confirmed to cause toxicity in reproduction. Therefore, it is still a potential reproductive toxicant (Williams et al. 2000), but Greim et al. (2015) reported that the NOAEL between 50 and 300 mg/kg day whilst Romano et al. (2012) suggested that exposure to GLY at NOAEL concentration may cause adverse effects on the reproduction function of offspring. They further reported exposure of female rats in pregnancy at 50 mg/kg body weight led to reproductive toxicity in the male offspring by causing change to the offspring behaviour and reproduction parameters. Given these findings, Dallegrave et al. (2007) suggested the needs to improved our knowledge of the effect of GLY on reproduction system on mammalian animals.

Carcinogenicity

Several works of literature have debated whether GLY is carcinogenic or not but Kier and Kirkland (2013) reported that it is not possible for a mutation to cause carcinogenicity. Chruscielska et al. (2000) reported that, when the rat was feed with water containing GLY within NOAEL for 2 years, carcinogenicity was not observed from the results. Despite these studies, the possibility of GLY not inducing carcinogenicity has been questioned. Other researchers have opined that further research is needed to prove the carcinogenic potential of GLY. George et al. (2010) reported that there are potential carcinogenic cases in various parts of the mouse system such as thyroid tissues, intestine, liver, kidney, skin, and breast. Furthermore, Thongprakaisang et al. (2013) also discussed the possibility of promoting tumour in the skin cell and proliferation in the breast cells in vivo mouse and in vivo human, respectively. Guyton et al. (2015) also reported that GLY has been observed in some agricultural workers through multiple tests on their blood and urine, and there was an indication that they were ingested through adsorption. Microbes can degrade GLY to aminomethyl phosphoric acid (AMPA) and on the detection of AMPA in the blood suggesting intestinal microbial metabolism in humans. Guyton et al. (2015) further reported the classification of GLY as “probably carcinogenic” (group 2A) by the International Agency for Research on Cancer (IARC). IARC research team reviews the studies of US EPA on GLY before arrived at this conclusion. Gillezeau et al. (2019) recommended evaluation across geographic regions and sources of exposure (food residues, household use, and occupational). Therefore, there is a need for further studies to investigate and fully understand the carcinogenic effect of GLY.

Possible risks of glyphosate to human health via food contamination

The residues of GLY and its metabolite (AMPA) in the consumption of food by humans are of great concern in toxicological potential when its level is above acceptable daily intake (FAO 2005). Bernal et al. (2012) reported that the residues are present in different food sources intake of both plant and animal materials. In 2015, the European Food Safety Authority has reviewed GLY maximum residue limit ranges from 0.025 to 2 mg/kg per any food source (EFSA EFSA 2015). However, for some cereal such as wheat, oat, and barley, the maximum residue limit of less than or equal to 30 mg/kg was recommended whilst for fish tissue consumption, no maximum residue limit has been established (McQueen et al. 2012) since there is no legal testing requirement of GLY bioconcentration. The likelihood of a human experience side effect of this toxicant after a long period of consumption of contaminated food is very high. McQueen et al. (2012)

reported on 40 expecting mothers assessed for the residue of GLY after the residue was observed at 75% of the food items studied; the concentration is not up to 0.4% of the acceptable daily intake. Though less than the average of the crop sample contains a high level of the residue, processing of the food would further reduce its level (Williams et al. 2000). It was furthermore observed by McQueen et al. (2012) that the assessment of food residue was proved to be lower than the expected daily intake.

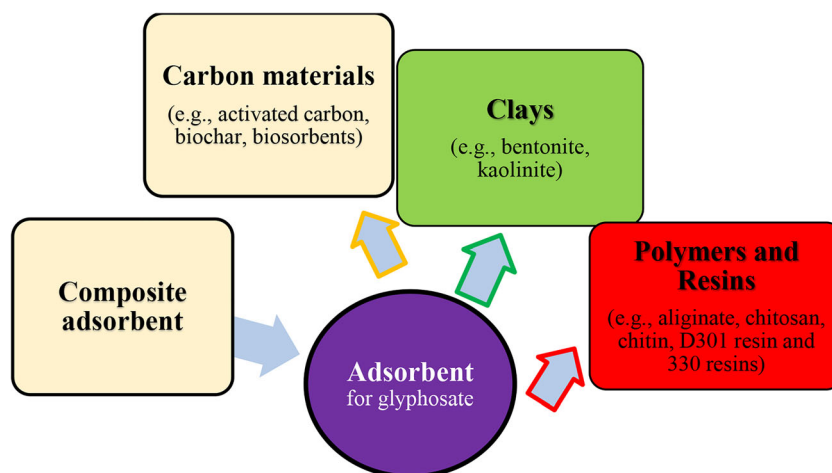
However, in the case of crops that are genetically modified against GLY, the residues of the concentration are very high compared with non-genetically modified crops possibly due to different application practices (Swanson et al. 2014). Though after the modification of the active ingredient, change in application also increases the chances of contamination of crops. Therefore, it becomes a greater concern as such crops are more widely used. Niemann et al. (2015) reported that, in a human urine sample, GLY was observed in increasing measure (a suggestion of dietary exposure). They suggested that the specific report is insufficient to be a conclusion for human health risk. But Mesnage et al. (2015) suggested that the low concentration of the GLY may also result in risks for humans since it is not an edible chemical; therefore, further research should be considered before the conclusion on the risk of human health.

Adsorption media and surface interactions

Various methods have been explored to remove GLY as a contaminant from water systems such as run-off and underground water system; such methods are photo-catalysis, photo-electrocatalysis (Yang et al. 2018) oxidation (Rubi-Juarez et al. 2016), and adsorption (Mayakaduwa et al. 2016). Among several of these methods, adsorption has been most interesting to many researchers due to its convenience, environmentally friendly operation, low cost, and availability of material of adsorbents (Mayakaduwa et al. 2016). There are many adsorbents reported for the adsorption of GLY which includes activated carbon (AC), carbon-based materials, clays, polymers, organic, and synthetic resin. However, adsorption effects of these known adsorbents were unsatisfactory. Consequently, it is necessary to review these adsorbents and various factors influencing the adsorption process of GLY. In the section, we discuss the adsorption media and their associated interactions. The adsorbents for GLY uptake are classed into four as shown in Fig. 1.

To generalise the surface interactions, we examine the report of Herath et al. (2016). Herath et al. (2016) conducted mechanistic modelling of the adsorption of GLY onto biochar derived from rice husk. Generally, physical adsorption is majorly caused by the forces of molecular interactions, and these include induced dipole interactions, van der Waals dispersion

Fig. 1 Broad classification of adsorption media for glyphosate

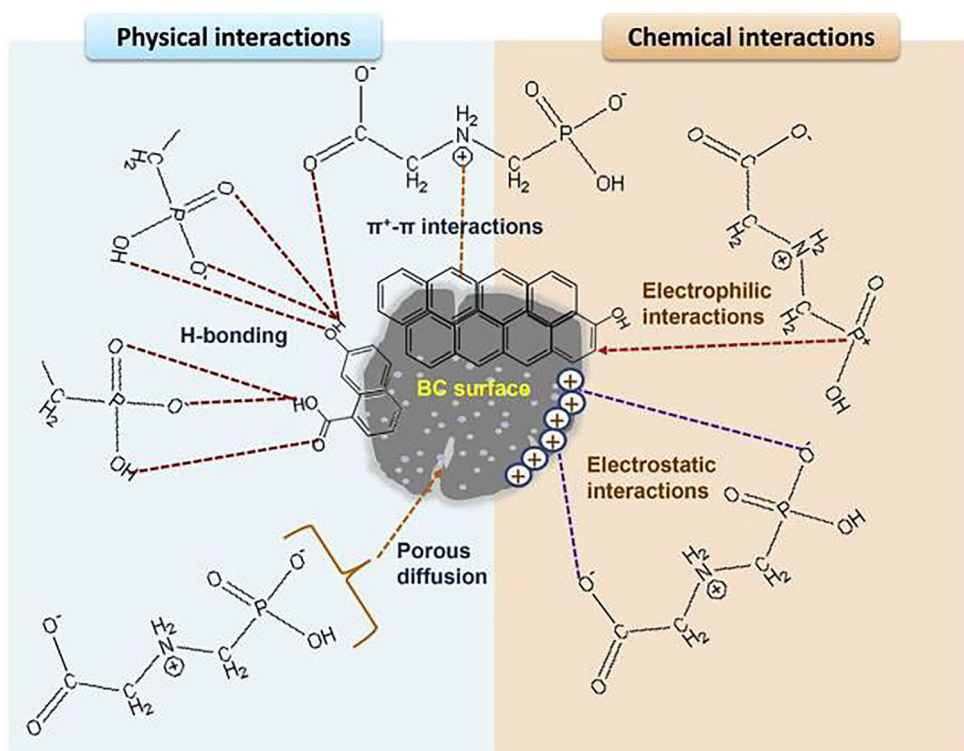


forces, π - π interactions, and hydrogen-bonding interactions (Essandoh et al. 2015). The possible physical mechanisms of GLY adsorption onto biomass biochar are summarised. At low pH, the phosphate group of the GLY tends to be readily protonated hence making it capable of acting as a strong electrophile. This protonated phosphate can interact with the ortho- and parapositions of any aromatics on the adsorbent (see Fig. 2) hence adsorb the molecule by chemisorption. Furthermore, GLY can be adsorbed by electrostatic interactions between an adsorbent with a net positive surface charge. Above the point of zero charges, this could end up being repulsion (thereby reduced sorption capacity) as the adsorbent surface then possesses a negative charge.

Adsorption Process through Carbon Materials

Biomass, coal, and lignite are the most common sources of the available commercially activated carbon (CAC), but any carbonaceous materials can also be used in the preparation of adsorbents of carbon (Chen et al. 2019) due to their low cost and availability. Coal is a mixture which contained minerals and carbonaceous materials. Due to its carbonaceous nature, it is one of the most commonly used precursors in the production of activated carbon. The nature of original vegetation influences the sorption properties of each activated carbon produced from it, and the extent of the physical and chemical properties occurs after deposition. However, since coal is a

Fig. 2 Possible mechanisms of GLY adsorption onto biochar (Herath et al. 2016)



mixture (impure material), it has different surface properties and also different sorption properties. Other waste materials can also offer cheap activated carbon such as biomass and so on. These waste materials often cause environmental pollution since they have little or no economic value. So, to control pollution, there is a need to convert them to activated carbon to make them have economic value and most importantly provide alternative means to the existing activated carbon (Igwegbe et al. 2020). However, a wide variety of carbons have been produced from wastes such as rice husk (AbdulHalim et al. 2011), coconut shell (Ignatowicz 2011), sunflower (Eletta et al. 2020a), and a host of others (Adeniyi and Ighalo 2019).

Adsorption process through clays

Clay is a good adsorbent use in the purification of wastewater over many decades. Clay has a high surface area which is responsible for its high adsorption capacity in the removal of the various adsorbate. However, herbicides were not left out among all these adsorbates. Nwosu et al. (2019) and Ajala et al. (2018) reported the use of kaolinite and bentonite clays, respectively, in herbicide adsorption. GLY adsorption using clays was reported by Flores et al. (2018). He discussed that montmorillonite clay belongs to the family of smectites (2:1 layered silicate) and is also called bentonite clay. It has a very high specific surface area and a surface charge of negative with at least interlayer and outer layer surface sites (Flores et al. 2018). These make montmorillonite clay quite suitable for the studies on GLY adsorption. Ren et al. (2014) reported that GLY and its metabolites always form inner-sphere complexes, glyphosate-montmorillonite system surface complexation aluminol and/or silanol groups of the external surface, and the charge on the amino attracted by the negative surfaces of the interlayer space. This suggested the accumulation of GLY in the soil which questions the sustainability of the glyphosate-montmorillonite system. The magnitude of the impacts depends on the rates and frequency of the GLY application (Mamy et al. 2010).

Adsorption process through polymers and resins

Polymeric adsorbents have many features that attract their usage in recovering organic pollutants from aqueous media. The following features are stable framework, good mechanical strength, good adsorption capacity, and feasible regeneration for repeated usage (Carneiro et al. 2015). These features have increased the demand for its usage in the recovery of organic pollutants. The solubility of GLY is very high in aqueous solution. GLY can interact with both alkali and acid because of the presence of NH , COOH , and H_2PO_3 functional groups. Therefore, it is difficult for polymeric adsorbents to remove GLY under the condition of a coexisting high

concentration of salinity. Up till now, there is no report on the successful adsorption of GLY using polymeric adsorbent under the condition of a coexisting high concentration of salinity. The use of biopolymeric membranes (prepared with alginate, chitosan, and alginate/chitosan combination) for the adsorption of GLY in aqueous samples was investigated (Carneiro et al. 2015). The characterisation of the membrane was based on the membrane solubility, swelling, and mechanical, chemical, and morphological properties. The report showed that chitosan membranes and certain biopolymers in extension can adsorb GLY and can be used to treat a water sample contaminated with GLY successfully. Therefore, biopolymers have good potential for the treatment of agricultural chemicals present in the water system.

Adsorption of GLY using organic or synthetic resin was suggested to be an effective medium of treatment of GLY contaminant or pollutant in wastewater, but much work is still left undone in recent times especially in alkali medium. Xiao and Wen (2016) have examined the adsorption of GLY from aqueous solution acidic medium (pH 2.51) using 2-aminopyridine modified polystyrene resin, D301 resin, and 330 resins and studied the influencing factors, salinity resistance, and mechanism, and it was observed that the maximum adsorption capacity of GLY onto the three resins was observed at pH of 2.51, and GLY was adsorbed in the form of $\text{HO-PO}_2^- - \text{CH}_2 - \text{NH}_2^+ - \text{CH}_2 - \text{COOH}$ and $\text{HO-PO}_2^- - \text{CH}_2 - \text{NH}_2^+ - \text{CH}_2 - \text{COO}^-$. The three resins exhibited the adsorption capacity of the GLY in the following order: modified polystyrene resin, < D301 resin, and < 330 resin, based on their total exchange capability. Modified polystyrene resin exhibited excellent resistance of salinity which resulted from the bonding of hydrogen for GLY adsorption whilst others showed a single adsorption mechanism. Though, GLY can interact with both acid and alkali based on their three functional groups. It is advised to further observe resins in the removal of GLY in an alkali pH medium.

Mitigation of glyphosate pollution by adsorption

Recent advances in glyphosate adsorption

In this section, some of the more interesting and novel studies on GLY adsorption are discussed, and a special focus was on papers published in the past 5 years. Arroyave et al. (2016) investigated the mobility of GLY in environmental systems. In their study, the effect of humic acid on the adsorption/desorption behaviour of GLY onto hydrous ferric oxide surfaces (in this case goethite) was investigated. Humic acid is found in a soil environment whilst goethite is a clay. Humic acid will affect the process because it can form complexes with Fe(II) at the surfaces. It was observed that GLY sorption

was impeded by the presence of humic acid. Based on the observations of Arroyave et al. (2016), the adsorbed humic acid induces electrostatic repulsion at the sites with the GLY thereby reducing the amount of the latter adsorbed. Carneiro et al. (2015) studied the sorption of GLY unto biopolymeric membranes such as chitosan and alginate. Alginate is a water-soluble linear polysaccharide whilst chitosan is obtained from the deacetylation of chitin. The key finding of the paper is the higher adsorption of 10.88 mg/g of chitosan membrane in comparison with 8.70 mg/g of the chitosan-alginate bilayer. Interestingly, alginate did not show any adsorption capacity for GLY. In the domain of other polymeric materials, the result of this study is not as promising when compared with adsorption capacities of 98.5 mg/g for deprotonated granular polyaniline (Milojevic-Rakic et al. 2013), 59.9 mg/g for protonated nanostructured polyaniline (Milojevic-Rakic et al. 2013), and 131.58–169.49 mg/g for resin D301 (Chen et al. 2016).

Chen et al. (2019) studied the adsorption of GLY by activated carbon obtained from cellulose and immobilised with MnFe_2O_4 in a one-pot solvothermal process. The nanoparticles alone were observed to have an adsorption capacity of 93.48 mg/g, and the activated carbon alone had an adsorption capacity of 61.44 mg/g. A synergistic effect was observed from the immobilisation as the adsorption capacity of the cellulose-activated carbon with immobilised MnFe_2O_4 nanoparticles having a sorption capacity for GLY of 167.2 mg/g. This is being even greater than the sum of the individual components. MnFe_2O_4 -activated carbon hybrid exhibited a charge of positive within acidic region below pH 6 and showed good dispersion stability and magnetic properties. Chemisorption dominated the adsorption process, and the new bonds were formed between MnFe_2O_4 and GLY by simulations. They formed bonds that were suggested to be bonding between electrons in the p orbital of the adsorbent and the electron in the d orbital of the adsorbate. The idea of the study was to develop an adsorbent with a positive net surface charge (even at low pH) that would have an affinity for the negatively charged GLY (as with other organophosphorus pesticides).

Yang et al. (2018) compared the adsorption and photo-degradation of GLY onto goethite and magnetite. Goethite had a higher adsorption capacity of 7.9 mg/g in comparison with magnetite (6.7 mg/g). Goethite had a higher point of zero charges than magnetite. The stronger interaction between the more positively charged surface of goethite and the negatively charged GLY is responsible for its higher sorption capacity. On the other hand, the photo-degradation of GLY was higher with magnetite than with goethite. This was due to a greater release of iron from the magnetite which assisted the generation of reactive oxygen species in the magnetite/UV system. This study was conducted so as an integrated insight of GLY fate in the environment can be obtained. Waiman et al. (2016) studied the competitive adsorption of GLY and phosphate

onto goethite. The study revealed that the adsorption maximum for phosphate was higher than for GLY though they coexist at the goethite surface. Spectroscopic evidence revealed that the nature of GLY bonding to goethite is also not affected by phosphate.

Ramrakhiani et al. (2019) studied the sorption of GLY using adsorbents reclaimed from the sorption of heavy metals. The study was quite interesting because the adsorbents still had heavy metals in them whilst being used for GLY sorption. The adsorbent from the tannery was initially loaded with Ni(II), Co(II), Zn(II), and Cd(II). The removal efficiency of > 90% was observed for GLY in aqueous media. This raises the concern of metal desorption during the adsorption of GLY. By evaluating the biosorbent stability, they observed that desorption only occurred at extreme (high or low) pH within human regulatory limits. In a similar work, Rivoira et al. (2016) used SBA-15 impregnated with iron nanoparticles. Therein, it was established that, in such form, the adsorbent can adequately remove GLY. Further, they showed that 12.5 mM of NaOH would effectively desorb GLY from the SBA-15 matrix and regenerate it for subsequent reuse.

Molecular modelling has been an important aspect of the computational investigations of GLY uptake (Khouri et al. 2010). De Oliveira et al. (2017) studied the adsorptive interaction between $\text{B}_{12}\text{N}_{12}$ nanocage using a theoretical approach known as density functional theory (DFT). The study was able to reveal the structural stability of the nanocage after complexation with GLY. A typical GLY- $\text{B}_{12}\text{N}_{12}$ complex predicted by DFT is shown in Fig. 3. Furthermore, the thermodynamic analysis predicted an exothermic chemisorption process. The highest occupied molecular orbital and the lowest unoccupied molecular orbital energies were located in the GLY which implied that the molecule can be removed by chemical

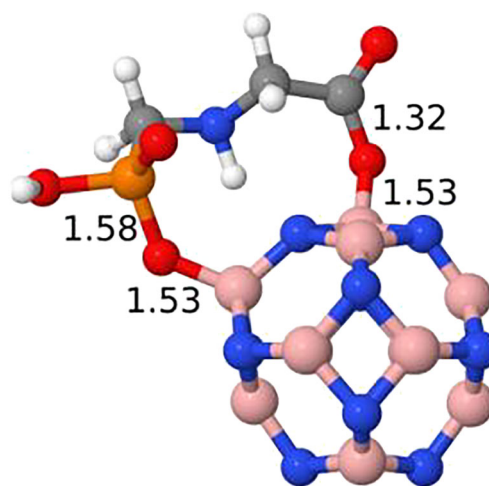


Fig. 3 Typical GLY- $\text{B}_{12}\text{N}_{12}$ complex optimised with density functional theory. Intramolecular distances are in Å

reaction (chemisorption). The study was able to theoretically determine the suitability of $B_{12}N_{12}$ nanocage for the intended application.

A few other research studies in recent times have conducted a variety of novel adsorption investigations for GLY. Orcelli et al. (2018) studied the adsorptive interaction of GLY onto goethite in a typical environmental system. From the behaviour of desorption and adsorption under a variety of factors, it was observed that, in soils with high goethite content, groundwater would be more easily contaminated by GLY. The study observed the formation of inner and outer-sphere complexes and an adsorptive process that is consequent on a variety of mechanisms. A molecular theory has been applied to study the equilibrium conditions of GLY adsorption from aqueous solutions to hydrogel films of cross-linked poly(allylamine) (Perez-Chavez et al. 2018) and surface-grafted poly(allylamine) (Pérez-Chávez et al. 2019). Zhang et al. (2019) evaluated the degradation of GLY using combinations of visible light, goethite, and oxalate. From the study, tetracycline (an antibiotic) and diethyl phthalate (a plasticizer) were well degraded whilst a major proportion of GLY remains adsorbed on goethite. The study explained that there might be a possible underestimation of GLY levels and toxicity in previous studies as it may be further desorbed from minerals and reenter aquatic and biological media.

Table 2 summarises the adsorption capacities (to four significant figures) of various adsorption media onto GLY and sorted in decreasing order. It is quite conspicuous that polymers and resins have the highest sorption capacities for GLY. Polymeric resins and natural polymers have a high internal surface area, a controlled pore-size distribution, and a relatively high porosity. Furthermore, the pores are big enough to allow molecules into the gaps. Polymeric resins possess numerous functional groups besides the conventional carbon bonds which assist in a variety of chemical interactions with GLY.

Equilibrium isotherm and kinetic modelling

Other studies in recent times have conducted equilibrium isotherm modelling, kinetic modelling, and thermodynamic analysis. Table 3 summarises the equilibrium and kinetic modelling results. In most cases, the best-fit isotherm model was either Langmuir (mono-layer) or Freundlich (multi-layer). The nature of the adsorbent plays a major role in determining whether the adsorption is mono or multi-layer. Xiao and Wen (2016) observed that the adsorption of GLY to several resins was the best fit for the Freundlich isotherm. Also, biochar from rice husk (Herath et al. 2016), coconut shell (Herath et al. 2019), quickstick (Mayakaduwa et al. 2016), and

eucalyptus bark (Sen et al. 2019) have shown adsorption in multi-layer. This informs that these adsorbents likely have a heterogeneous energetic distribution of active sites (Freundlich 1906). Furthermore, it can be seen from Table 3 that the kinetics of GLY adsorption is predominantly a pseudo-second order. This is an indicator that GLY adsorption is dependent on the number of metal ions present in the solution as well as the free sites on the adsorbent surface (Ho et al. 2000).

Thermodynamic modelling

A few other recent studies have considered the thermodynamics of GLY adsorption. Besides the study of Chen et al. (2016), the other studies in Table 4 reported negative values of ΔG^0 which indicates spontaneity of adsorption. For the investigation of Chen et al. (2016), it was explained that the positive value of ΔG^0 led to entropy playing a leading role in the process. This means that the driving force of the adsorption process is more dominant than the chemical bonding force. The negative values of the enthalpy change (ΔH^0) indicate that GLY adsorption is exothermic. The values of $\Delta H^0 > 30$ kJ/mol is suggestive of chemisorption whilst those < 10 kJ/mol is suggestive of physisorption by van der Waal's interaction (Chen et al. 2016). Furthermore, the exothermic nature of adsorption means more GLY will be adsorbed at lower temperatures and vice versa. In most cases, a negative value of ΔS^0 was observed for the uptake of GLY except for forest soil (Sen et al. 2017). Negative value of ΔS^0 reveals that there is a decrease in the degree of disorderliness and randomness at the solid-liquid interface during adsorption (Hevira et al. 2020; Ighalo and Eletta 2020b).

Research trends and knowledge gaps

Based on this review, some trends have been observed in the literature. These research trends have been discussed alongside observed gaps in knowledge as this could help serve as a foundation for other investigations by other authors.

- i. Recent studies have evaluated the mobility of GLY in environmental systems by studying the adsorption of the compound itself and its metabolites onto natural clays such as montmorillonite (Flores et al. 2018), goethite (Arroyave et al. 2016; Orcelli et al. 2018), and magnetite (Yang et al. 2018). This is an important aspect of contaminant hydrology in from classical times (Gimsing and Borggaard 2007). In the future, more investigations are likely to emerge using other types of soil sample.
- ii. Other studies have now progressed to examining the effect of other chemical species in the GLY-clay adsorption system. These include phosphates, fulvic acid, and humic

Table 2 Sorption capacities of different adsorption media for GLY

Adsorbent	Adsorption capacity (mg/g)	Method of determination	Reference
Resin D330	724.6	Langmuir	Xiao and Wen (2016)
Cross-linked amino-starch	610.0	Sips	Guo et al. (2018)
Resin D301	480.8	Langmuir	Xiao and Wen (2016)
Resin GQ-08	380.2	Langmuir	Xiao and Wen (2016)
Resin D301	330.4	Experiments	Zhou et al. (2017)
Amine-functionalised polymer	229.0	Langmuir	Samuel et al. (2017)
Cellulose AC with immobilised MnFe_2O_4	167.2	Experiments	Chen et al. (2019)
Forest soil	161.3	Langmuir	Sen et al. (2017)
Rice husk biochar	123.1	Langmuir	Herath et al. (2016)
MnFe_2O_4 nanoparticles	93.48	Experiments	Chen et al. (2019)
Palm biochar loaded with nanozero-valent iron	80.00	Langmuir	Jiang et al. (2018)
Magnetically modified graphene oxide	70.10	Langmuir	Li et al. (2018)
Eucalyptus bark AC	66.78	Langmuir	Sen et al. (2019)
Cr-based MOF	64.25	Experiments	Feng and Xia (2018)
Cellulose-activated carbon	61.44	Experiments	Chen et al. (2019)
Ferrihydrite	54.88	Langmuir	Pereira et al. (2019)
Quickstick biochar	44.00	Langmuir	Mayakaduwa et al. (2016)
Palm biochar	40.49	Langmuir	Jiang et al. (2018)
MnFe_2O_4 -graphene oxide	39.00	Experiments	Yamaguchi et al. (2016)
Chitosan	35.10	Langmuir	Rissouli et al. (2017)
Chitin	14.10	Langmuir	Rissouli et al. (2017)
Chitosan membrane	10.88	Experiments	Carneiro et al. (2015)
Chitosan/alginate membrane	8.700	Experiments	Carneiro et al. (2015)
Goethite	7.900	Langmuir	Yang et al. (2018)
MnFe_2O_4 -graphene oxide	6.800	Langmuir	Marin et al. (2019)
Magnetite	6.700	Langmuir	Yang et al. (2018)
Wood biochar	0.057	Experiments	Herath et al. (2019)
Coconut shell-activated carbon	0.017	Experiments	Herath et al. (2019)

acid (Arroyave et al. 2016). Competitive adsorption systems such as this help to show the adsorbent affinity for the specific adsorbate in the presence of other competing species (Ighalo et al. 2020). It is also investigated as the effects of background electrolytes (Gimsing and Borggaard 2001).

- iii. This review has also observed that polymers and resins are the best class of adsorbents for GLY adsorption. Numerous other resins have not been investigated in this

domain, and this represents a very viable area of investigation for future studies.

- iv. The use of adsorbents laden with heavy metals has also been considered in a recent study for GLY adsorption. It is imperative that future investigations examine the stability of the heavy metals within the adsorbent matrix to avoid the leaching and/or desorption of these species during the removal of GLY (or below regulatory limits at least).

Table 3 Summary of equilibrium isotherm and kinetic modelling

Adsorbent	Isotherm		Kinetics		Reference
	Best fit	R^2	Best fit	R^2	
Chitosan membrane	Freundlich	0.998	Pseudo-second order	0.996	Carneiro et al. (2015)
Chitosan/alginate membrane	Freundlich	0.990	Pseudo-second order	0.993	Carneiro et al. (2015)
Resin D301	Langmuir	> 0.93	Pseudo-second order	> 0.98	Chen et al. (2016)
Cr-based MOF	Langmuir	-	Pseudo-second order	-	Feng and Xia (2018)
Cross-linked amino-starch	Sips	> 0.98	Pseudo-second order	> 0.99	Guo et al. (2018)
Rice husk biochar	Freundlich	0.983	Pseudo-first order	0.972	Herath et al. (2016)
Wood biochar	Freundlich	0.957	Pseudo-second order	0.999	Herath et al. (2019)
Coconut shell-activated carbon	Freundlich	0.811	Pseudo-second order	0.997	Herath et al. (2019)
Palm biochar loaded with nanozero-valent iron	Langmuir	> 0.96	Pseudo-second order	> 0.99	Jiang et al. (2018)
Modified graphene oxide	Langmuir	> 0.98	Pseudo-second order	0.983	Li et al. (2018)
Quickstick biochar	Freundlich	0.960	Pseudo-second order	0.983	Mayakaduwa et al. (2016)
Goethite	Langmuir	> 0.98	Pseudo-second order	0.997	Orcelli et al. (2018)
Heavy metal-laden biosorbent	Langmuir	> 0.97	Pseudo-second order	0.997	Ramrakhiani et al. (2019)
Chitin	Langmuir	0.990	-	-	Rissouli et al. (2017)
Chitosan	Langmuir	0.930	-	-	Rissouli et al. (2017)
Functionalized star-shaped polymeric particles	-	-	Pseudo-second order	0.999	Samuel et al. (2017)
Activated carbon	-	-	Pseudo-second order	0.993	Samuel et al. (2017)
Forest soil	Langmuir	0.808	Pseudo-second order	0.983	Sen et al. (2017)s
Eucalyptus bark AC	Freundlich	0.988	Pseudo-second order	1.000	Sen et al. (2019)
MnFe ₂ O ₄ -graphene oxide	Freundlich	> 0.97	Pseudo-second order	0.999	Yamaguchi et al. (2016)
Resin D330	Freundlich	> 0.99	-	-	Xiao and Wen (2016)
Resin D301	Freundlich	> 0.99	-	-	Xiao and Wen (2016)
Resin GQ-08	Freundlich	> 0.99	-	-	Xiao and Wen (2016)
Resin D301	-	-	Pseudo-second order	> 0.99	Zhou et al. (2017)

v. There have also been studies conducted on the molecular modelling of GLY adsorption onto some very intricately synthesised adsorbent species in the in silico domain. Such theoretical investigations are important as they help deduce the suitability of these novel adsorbents for GLY before any further experimental work.

vi. Soil pH varies from acidic to sometimes alkaline depending on the region. Though the effect of pH is usually evaluated across the pH spectrum, little interest is paid to the solution chemistry of the adsorption at high pH. This was observed in this review especially for resins. Since resins have been observed to be one of the most effective classes of adsorbents for GLY removal, it is

Table 4 Summary of adsorption thermodynamics

Adsorbent	Thermodynamics				Reference
	Temp (°C)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)	
Resin D301	40	26.20	- 92.64	- 379.5	Chen et al. (2016)
Cross-linked amino-starch	20	- 28.78	- 82.47	- 183.24	Guo et al. (2018)
Forest soil	20	- 16.58	- 16.12	0.038	Sen et al. (2017)
Eucalyptus bark AC	30	- 1.167	- 0.0204	- 5.281	Sen et al. (2019)
MnFe ₂ O ₄ -graphene oxide	25	- 4.789	- 5.764	- 3.593	Yamaguchi et al. (2016)

expedient that further detailed studies be carried out on the solution chemistry across the pH spectrum.

- vii. On a final note, the ecotoxicology of GLY still has some contentious areas. There is still no conclusive stance on its genotoxicity, reproductive toxicity, and carcinogenicity. Though outside the research spectrum of traditional engineers and environmental chemists, these are key areas that still require exploration for researchers in the sciences.

Conclusion

In this review, the ecotoxicology of GLY was first examined. Certain aspects such as its chronic and sub-chronic toxicity, genotoxicity, reproductive toxicity, carcinogenicity, and potential risk of food contamination were discussed. The potentials of carbon materials, clays, polymers, and resins as an adsorbent for GLY sorption were discussed. It was observed that polymers and resins are the best class of adsorbents for GLY adsorption from aqueous media. GLY adsorption is usually best fit to either Freundlich or Langmuir isotherm depending on the nature of the adsorbent. The pseudo-second-order kinetics was also the best fit for modelling the kinetics of GLY adsorption. This is an indicator that GLY adsorption is dependent on the number of metal ions present in the solution as well as the free sites on the adsorbent surface. A review of the thermodynamics revealed that GLY adsorption is usually spontaneous and exothermic. The exothermic nature of adsorption means more GLY will be adsorbed at lower temperatures and vice versa. Research trends and knowledge gaps are in the area of chemical mobility in environmental systems (especially in the presence of other chemical species), the use of heavy metal-laden adsorbent, and molecular modelling. It can be surmised that great progress has been in the research domain in recent times, and positive results have been obtained.

Author contributions JOI: conceptualization, formal analysis, validation, writing—original draft, review and editing. OJA: investigation, formal analysis, writing—original draft, review and editing. AGA: administration of project, validation, supervision, writing—review and editing. EOE: data curation, formal analysis, investigation. MAA: supervision, validation, writing—review and editing.

Data availability Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

Compliance with ethical standards

Ethics approval and consent to participate This article does not contain any studies involving human or animal subjects.

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