Adsorption-desorption of glyphosate in tropical sandy soil exposed to burning or applied with agricultural waste

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Abstract

The present study investigated glyphosate adsorption-desorption in Malaysian sandy soil exposed to burning or applied with cow dung or rice husk ash (RHA). One gram each of the adsorbents (control, burnt soil, soil + cow dung, soil + RHA) was separately and in replicate mixed with solution of 20 mL of glyphosate at different initial concentrations (0, 25, 50, 100, 150, 200, 250 and 300 mg L^{-1}), shaken for 24 hours, centrifuged at 10, 000 rpm for 10 minutes and later the decanted supernatants were collected. Desorption study follow immediately through addition of 20 mL of 0.01 M $CaCl_2$ solution and then treated like adsorption study. Glyphosate analysis was done using high performance liquid chromatography with fluorescence detector and isotherm data was fitted to linear, Freundlich, Langmuir and Temkin models. Freundlich best fits the adsorption of glyphosate and application of cow dung or RHA enhanced the soil affinity for glyphosate. Freundlich isotherm constant (K_F) for soils treated with RHA and cow dung were 9.768 mg g^{-1} and 6. 751 mg g^{-1}, respectively as compared to 3.189 mg g^{-1} for the control soil. However, the greatest K_F value (387.238 mg g^{-1}) was recorded by burnt Benta soil. Glyphosate adsorption by both control and treated soils was favourable (0.044 < R_L < 0.3). This study suggests that adsorption occurred through physical processes involving diffusion, complexation or ligand exchange. Glyphosate desorption from soils treated with cow dung and RHA was either hysteretic or reversible. Burning this soil should be discouraged due to its effect on increasing glyphosate mobility and possible groundwater contamination. Meanwhile, agricultural waste can be applied to this soil even though it might lead to an increased glyphosate mobility but because of its potential positive effect on the soil's biological functions, the glyphosate ions are bound to be degraded.

1. Introduction

Open-field burning and application of organic manure are widely practiced worldwide. As part of land clearing, Malaysian paddy farmers routinely burn their rice straws *in situ* before mechanized land preparations [1]. There are two seasons of rice cultivation in Malaysia; off-season (mid-March to mid-August) and main season (mid-September to mid-January). Therefore, once harvesting is completed during the off-season farmers are left with a very limited time—around a month and a half— to prepare for the main season [1-2]. This makes open-field burning the easiest way to dispose these straws and save time for field management for the next cropping season. It is also done to destroy sources of

pests and diseases [3]. Open burning can result in ash deposits due to oxidation of the rice straws and native soil organic matter which can lead to an increase in pH, addition of Na^+ and K^+, changes in soil minerals and exchangeable cations [4]. However, the burning practice causes severe environmental pollution and land degradation because it contributes to the emission of greenhouse gases such as carbon monoxide, methane and nitrous oxide [3].

To overcome the menace of open burning of soil and agricultural waste a popular waste management approach known as zero waste and zero burning is being advocated [1]. This approach employs direct incorporation of these waste or their compost into the soil as organic fertilizers [1,3,5,6]. Another alternative

includes using these waste for animal feeds, industrial raw materials, biofuel and off-site soil and water quality improvement [1,3,6]. Cow dung and rice husk ash are other agricultural waste abundantly found in Malaysia. An annual estimate of cow dung in Malaysia is 640, 650 tonnes (FAOSTAT, 2017) while annual production of rice husk ash is 1, 200 metric tonnes mill^{-1} [7]. These waste as mentioned earlier are used as industrial raw materials for energy source, production of biochar and/or applied to the soil as organic fertilizers. The advantages of applying organic fertilizers to soils include (i) increase soil biological action which enhances nutrient mobilization and decomposition of toxic substances; (ii) increase soil organic matter which improve exchange and retention capacities of nutrients and toxic substances; and (iii) increase soil aggregate stability and buffering capacity which promote root growth, P supply and increasing soil water retention [5].

Advocating for organic farming formed part of the plans in the Third National Agriculture Policy (NAP3) of Malaysia [5,8]. It involves refraining farmers from the use of chemical fertilizers, pesticide and pharmaceutical, and encouraging them to use organic input such as organic fertilizers and biological pest control for sustained productivity. This campaign was facilitated by launching of Malaysian organic certification program or *Sijil Organic Malaysia* (SOM) in 2003 [5] which helps in increasing attractiveness of Malaysian organic produce in both local and foreign markets. This is through their certification base on prerequisites of the Malaysian standard MS1529. A number of farmers adapted to this practice, however, Tiraieyari et al. [8] reported that majority are not practicing the method and the reason for this includes issues of temporary occupation licenses

(TOLs) of lands, expensive and long certification process and inadequate financial support from the government [9]. Alternatively, they apply chemicals as the best solution or employed an integrated approach involving the use of organic and inorganic input. The common basic agrochemicals used in Malaysia are fertilizers, fungicides, insecticides and herbicides. Raja Abdul [10] reported that in Malaysia weed problems are being solve by using herbicide without damage crops and increasing affordable cost. Glyphosate {N (phosphonomethyl) glycine} is among the common herbicides used in weed control on crops and open area. Glyphosate is a post-emergence weed killer consisting of three functional groups-phosphonic, carboxylic amines (Figure 1) and is capable of inhibiting protein synthesis in plant. Glyphosate physico- chemical properties are shown in Table 1. It is water soluble but insoluble in other solvent, odourless with average half-life of 47 days. Furthermore, it has low molecular weight, high surface tension, polarity and affinity as a result, it is non-volatile. It is applied on foliage, therefore, becomes non-active in soil due to its strong affinity soil and organic matter and oxides minerals [11]. Nonetheless, residues of glyphosate were discovered in surface [12,13] and underground water [14], which indicated the influence of soil properties and composition on adsorption and mobility of glyphosate. The main metabolic pathway of glyphosate in soil is its fast degradation to aminomethylphosphonic acid (AMPA), as a result, it is considered less toxic [15]. However, it was recently classified as probably carcinogenic to humans [16]. This makes the experts on pesticide residues in food and environment to re-consider glyphosate and AMPA for toxicological interest.
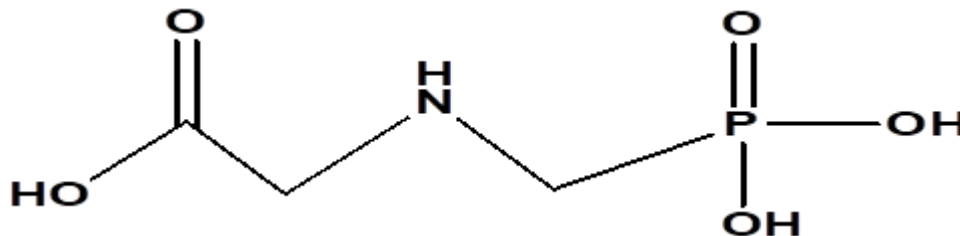

Figure 1. Chemical structure of glyphosate.

Table 1. Physical and chemical properties of glyphosate.

Common name	Glyphosate
Synonyms	N-(Phosphonomethyl) glycine
Chemical formula	$C_3 H_8 NO_5 P$
Molecular weight	169.09
Physical state and color	Crystalline powder, white
Density	1.704 (25°C)
Melting point	200-230°C
Boiling point	Decomposes at 187°C
Water solubility	10,000-15,700 mg L^{-1} at 25°C
Half life	1-174 days
Mobility potential	Very low
Toxicity class	III

In this study, two soil management scenarios were created in the laboratory to imitate open-field burning and application of agricultural waste. They are burning the soil to remove the biota and adding cow dung or rice husk ash to the Malaysian sandy soil. It should be noted that as far as we know the only two papers [4,17] on

glyphosate adsorption in soil after heating or removal of organic matter were on temperate soils. Furthermore, both papers did not give an account on the effect of additional organic matter on glyphosate sorption much less its mobility. Therefore, a similar study on tropical soils and taken into account the effect of additional

organic waste will help in increasing the knowledge of adsorption and mobility of glyphosate in soils. The aim of this study was to investigate the adsorption-desorption and potential mobility of glyphosate herbicide in soils exposed to burning or treated with either cow dung or rice husk ash (RHA).

2. Method

2.1 Sampling and chemicals

The present study used Benta soil series which sampled from Sementa Hulu (Lat. 3.841663 ^{0}N, Long. 101.947251 ^{0}E), located at Raub district, Malaysia. The soil was classified as Ultic Hapludalf based on the USDA soil taxonomy [18]. The soil sampling involves random collection of surface soils (0-20 cm) from five different sports which were later bulked to one composite sample. Cow dung was sampled from the animal section of the experimental farm (lat 2° 59′ 28.7″ N, long 101° 42′ 52.9″ E), Faculty of Agriculture, Universiti Putra Malaysia. Conversely, the rice husk ash (RHA) was collected from BERNAS Rice Mill Selangor, Malaysia (Lat. 3°40'32.4"N, Long. 100°59'42.5"E). Both the soil samples and that of agricultural waste were air dried, ground and sieved (2-mm sieve for the soil sample while 1-mm sieve for the cow dung and rice husk ash) then kept in a plastic container before analysis and further studies.

All solutions used in the present study were prepared using Millipore® Direct UV-Q water. Glyphosate (99.7% purity) and 9-flourenylmethlylchloroformate chloride (FMOC-Cl) of 97% purity were purchased from Sigma Aldrich® (Seelze, Germany) whereas acetonitrile was purchased from QREC®, Malaysia. Analytical grades of $CaCl_2$ and $HgCl_2$ were procured from Emsure® Germany and Sigma Aldrich® (India) respectively. The stock solution (500 mg L^{-1}) of glyphosate was prepared by dissolving 25 mg of its analytical grade powder into 50 mL Millipore® Direct UV-Q water. Working solutions for batch equilibrium sorption study were prepared by diluting appropriate stock solutions with Millipore® Direct UV-Q water.

2.2 Soil characterization, burning and application of agricultural waste

Details of soil characterization and its mineralogical determination has been previously `described in Garba et al. [19]. The burnt Benta soil was prepared according to the method described by [17] whereby about 15 grams of the soil sample was weighed into a porcelain crucible then ignited into a F62700 muffle furnace (Electrothermal Engineering, Essex, UK) at 550^{0}C for 2 hours and later allowed to cool at room temperature. The cow dung and RHA were applied at a rate of 10 tonnes ha^{-1} by mixing 1 g of the soil with 0.1 g of cow dung or RHA in a centrifuge tube. For homogeneity, the mixture was incubated for 1 week by maintaining its moisture content at field capacity throughout. After which the soil mixture was kept at room temperature to dry up prior to sorption study.

2.3 Batch equilibrium sorption experiment

Four set of soils in three replicates were used for this experiment and they are 1) the untreated Benta soil as control, 2) burnt Benta soil, 3) Benta soil applied with cow dung and 4) Benta soil amended with RHA. The sorption experiment was done according to the method described by Piccolo et al. [20] with some changes. Briefly, 1 g each of the soil samples were added into 50 mL centrifuge tubes and then a solution of 20 mL of glyphosate at different initial concentrations (0, 25, 50, 100, 150, 200, 250 and 300 mg L^{-1}) were added. The glyphosate solution was prepared in 0.01 M $CaCl_2$ solution consist of 200 mg L^{-1} $HgCl_2$ stand-in as a bioinhibitor. The centrifuge tubes containing the soil mixture and glyphosate solutions were putting into a rotary shaker and shaken for 24 hours at 100 rpm under room temperature. Afterward, the tubes were centrifuged at 10,000 rpm for 10 minutes using a Sartoruis 4–16 centrifugal machine (Sartoruis, Góttingen, Germany). Then, the supernatants were decanted and passed through a 0.45 µm P0377 HmbG syringe filter (Johchem, Malaysia) before analysis. Desorption study follows immediately after decantation of supernatants of the adsorption study. Thus, 20 mL of the background solution (0.01M $CaCl_2$ and 200 mgL^{-1} $HgCl_2$) was put into each of the centrifuge tubes and then treated like adsorption study. The glyphosate analysis in both adsorption and desorption samples was done using a high performance liquid chromatography with fluorescence detector (HPLC-FLD) method previously described by Garba et al. [21]. In brief, the filtered supernatant containing glyphosate was derivatized with 9-flourenylmethlylchloroformate chloride (FMOC-Cl). The glyphosate-FMOC derivatives were then analysed by HPLC-FLD using C18 Agilent® Zorbax Eclipse plus column (4.6 × 150 mm, 5 µm). The mobile phase consists a mixture of acetonitrile and a solution of 0.05 M KH_2PO_4 (30:70; v/v). The flow rate was 0.7 mL min^{-1} using an isocratic mode and injection volume of 20 µL at 40 °C column temperature. The method's excitation and emission wavelengths were 270 nm and 315 nm, respectively. Likewise, the method's lowest limits of detection and quantification were 0.021 mg kg^{-1} and 0.064 mg kg^{-1}, respectively.

2.4 Adsorption-desorption isotherms

The equilibrium concentration of glyphosate [q_e (mg/g)] was calculated using the Equation 1.

$$q_e = \frac{(C_i - C_e) \, x \, V}{W} \qquad (1)$$

Likewise, the glyphosate removal efficiency was calculated using the Equation 2.

$$Effeciency \, (\%) = \frac{(C_i - C_e)}{C_i} \, x \, 100 \qquad (2)$$

Where C_i and C_e are respective initial and equilibrium glyphosate concentrations (mg/L). While, V

is the volume of the solution (L) and W is the weight (g) of the soil used.

The adsorption behaviour of the adsorbate on the adsorbent was studied by fitting the isotherm data into the linear, Freundlich, Langmuir and Temkin isotherm models. The Table 2 shows both non-linear and linear equations of these isotherm models.

Table 2. Isotherm models and definition of their constants.

Model	Non-linear equation	Linear equation	plot	Constants and their definition
Linear		$q_e = K_d C_e + m$	q_e vs C_e	K_d: partitioning coefficient m: constant related to improved capability
Freundlich	$q_e = K_f C_e^{1/n}$	$\log q_e = \log K_f + \dfrac{1}{n}\log C_e$	$\log q_e$ vs $\log C_e$	K_F: adsorption affinity $1/n$: adsorption intensity
Langmuir	$q_e = \dfrac{Q_{max} b C_e}{1 + b C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{Q_{max}} C_e + \dfrac{1}{Q_{max} b}$	$\dfrac{c_e}{q_e}$ vs C_e	Q_{max}: constant related monolayer coverage b : constant related to adsorption affinity
Temkin	$q_e = \dfrac{RT}{b}\ln(A C_e)$	$q_e = \dfrac{RT}{b}\ln A + \dfrac{RT}{b}\ln C_e$	q_e vs $\ln C_e$	A: constant related to binding energy b: constant related to heat of adsorption

The most suitable isotherm model to represent the experimental data was determined using Marquardt's percent standard deviation (MPSD) (Equation 3):

$$MPSD = \sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{(q_{e,exp} - q_{e,calc})}{q_{e,exp}}\right)^2_i} \qquad (3)$$

Where n denote the number of data points, p denote the number of parameters for a given model, $q_{e,exp}$ and $q_{e,calc}$ are the experimental and calculated concentrations of the adsorbate at equilibrium (mg/g), respectively.

The hysteresis index (HI) which describes the nature of adsorption and desorption processes was determined from the values of constant n of Freundlich model for adsorption and desorption of glyphosate (Equation 4):

$$HI = \frac{n\ desorption}{n\ adsorption} \qquad (4)$$

The separation factor (R_L) was calculated from the constant of the Langmuir isotherm model and it describes the favorability of the glyphosate adsorption by the soil samples, thus (Equation 5):

$$R_L = \frac{1}{1 + bCo} \qquad (5)$$

The mobility of glyphosate was predicted using ground water ubiquity score (GUS) Equation 6.

$$GUS = log_{10}(t_{1/2} soil)\ x\ (4 - log_{10}(k_{oc})) \qquad (6)$$

Where $t_{1/2}$ is the glyphosate half-life in soil and K_{oc} stand for organic carbon normalized adsorption coefficient. The K_{oc} was determined from the partitioning coefficient (K_d constant) of the linear isotherm model by using the Equation 7.

$$K_{oc} = \frac{K_d}{\%\ soil\ organic\ carbon} \qquad (7)$$

Gustafson [22] reported that, GUS values are universal accepted indices for estimating mobility and persistence of pesticide in soil.

3. Results and discussion

3.1 Soil characteristics

The physicochemical properties of the soil are shown in Table 3. The soil texture was sandy as it had a high sand content (74.17%) but low in silt (5.83%) and clay (20%). The soil had 45% porosity and a bulk density of 1.45 g cm^{-1}, meanwhile it has 23. 88 % moisture content at field capacity. The EC value of the soil was 0.024 dS cm^{-1} and the pH was near neutral (6.73). The organic matter content was 5.23% and the soil cation exchange capacity (CEC) of the soil was 12.677 cmol$_{(+)}$ kg^{-1}. The values of percent free and amorphous oxides of Fe are 0.473 and 0.218, respectively while respective values of free and amorphous oxides of Al are 0.476% and 0.262%. The X-Ray diffractogram (Figure 2) revealed that the soil minerals were dominated by smectite (1.582 nm), mica (1.029 nm), kaolinite (0.720 nm, 0.358 nm), quartz (0.334 nm) and magnetite (0.201nm).

Benta soil was reported to have developed from andesite and rhyolite [23], thus, containing high amount of kaolinite and quartz leading to high sand fraction. The authors further reported that due to intense rainfall and high temperature in Malaysia, chemical weathering dominated the soil forming processes. Therefore, considering the land's undulating topography, erosion occurs at unstable slope leading to surface soil removal and this exposed its parent materials, hence, releasing basic cations [24] which resulted into higher soil pH, EC and base saturation as compared to the ultisols and oxisols soil orders in Malaysia. The low exchangeable Al (0.333 cmol$_{(+)}$ kg^{-1}) led to low Al saturation in the soil. At near neutral pH, most of the Al precipitated as Al(OH)$_3$ and therefore the exchange sites were dominated by the basic cations.

The author also attributed the low available P and higher Fe and Mn content to the soil parent materials. A ratio of amorphous/free iron oxides of > 0.05 (0.46 for the present study) shows that the soil is very active and low in crystallinity which was confirmed by the presence of mica and smectite. A soil bulk density of >1 g cm^{-3} is an indication of the presence of argillic horizon hence, according the USDA soil taxonomy classification this soil was classified as Alfisols [18].
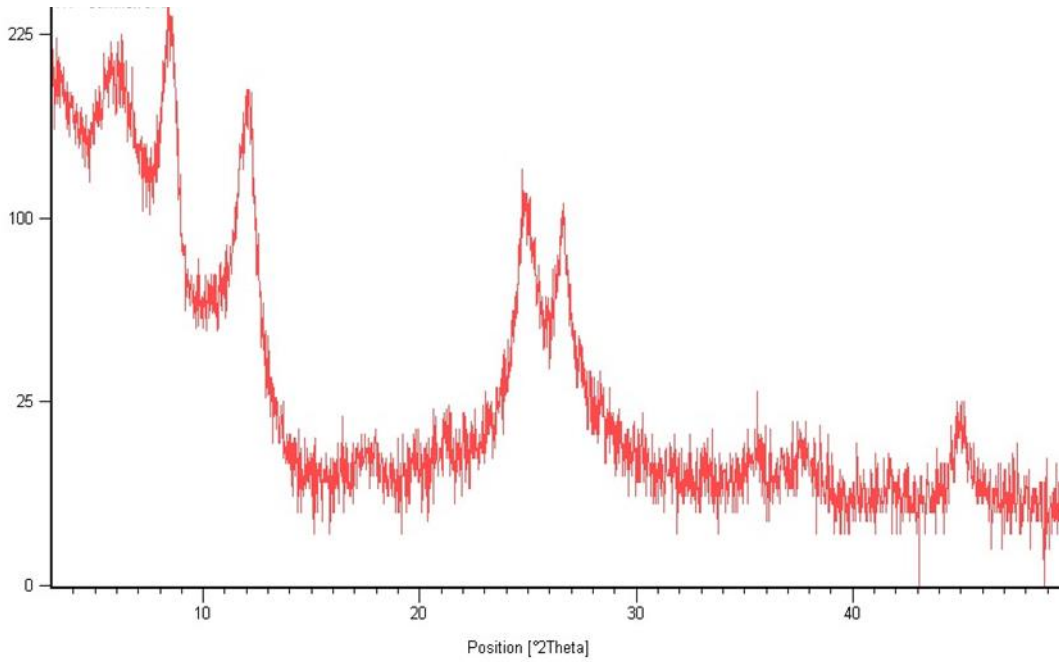
Figure 2. X-ray diffractogram of the soil used in the present study.

Table 3. Properties of the soil used in the present study.

Parameter	Result
Sand (%)	74.17 ± 0.83
Silt (%)	5.83 ± 0.83
Clay (%)	20.00 ± 1.43
Soil type	Sandy soil
Moisture content (%)	23.88 ± 0.89
D_b (g cm^{-3})	1.45 ± 0.14
Porosity (%)	45.00 ± 0.33
pH	6.73 ± 0.03
Ec (dS cm^{-1})	0.024 ± 0.001
Exchangeable Al (cmol$_{(+)}$ kg^{-1})	0.333 ± 0.07
Exchangeable H (cmol$_{(+)}$ kg^{-1})	0.333 ± 0.13
SOM (%)	5.23 ± 0.12
C (%)	1.665 ± 0.00
N (%)	0.164 ± 0.00
P (mg kg^{-1})	6.953 ± 0.16
S (mg kg^{-1})	60.100 ± 1.01
Exchangeable bases (cmol$_{(+)}$ kg^{-1})	
Ca	5.334 ± 0.64
K	0.331 ± 0.02
Mg	1.332 ± 0.07
Na	0.065 ± 0.00
CEC (cmol$_{(+)}$ kg^{-1})	12.667 ± 0.67
Micronutrients (mg kg^{-1})	
Cu	5.600 ± 0.10
Fe	13529 ± 22.94
Mn	547.700 ± 4.22
Zn	87.000 ± 2.16
Free FeO (%)	0.473 ± 0.01
Amorphous FeO (%)	0.218 ± 0.02
Free AlO (%)	0.476 ± 0.01
Amorphous AlO (%)	0.262 ± 0.09

3.2 Glyphosate removal efficiency

The result of glyphosate removal efficiency from the aqueous solution by the various adsorbent is shown in Table 4. It generally shows that, control and soils amended with the agricultural residues had greater removal efficiencies than burnt soil. Furthermore, an increasing removal efficiency was observed from all the absorbents due to increasing glyphosate initial concentration, even though, the low percent glyphosate removal (28.933%) was observed from burnt soil at 300 mg L^{-1}. By taken the concentration as a whole, high percent removal (89.516%) was obtained from the soil applied with rice husk ash. This was followed by the soil amended with cow dung (86.516%) and control (86.045%), while it was less in the burnt soil (76.304%).

Therefore, burning this soil resulted into 9.746% decreased in glyphosate removal compared to the control soil. Meanwhile, amending this soil with cow dung or rice husk ash led to 0.568% and 3.471% increase of glyphosate removal, respectively.

The present result indicates the influence of organic matter on glyphosate adsorption by this soil. Therefore, open burning with aimed of land clearing can lead to oxidation of its organic matter content. The consequence of this is decreasing glyphosate adsorption capacity and its more desorption from this soil which can results to its mobility and possible ground water contamination.

Equally, incorporation/external supplement of organic residues can increase the soil adsorption surfaces, thus, enhanced its glyphosate adsorption capacity. Soil sorption is a complex process because its total adsorption capacity is a function of the summation of individual sorption capacities of various soil components and properties [25]. These components are clay, organic matter and soil minerals content, while the profound soil properties affecting its adsorption are texture, CEC and pH. Therefore, anything affecting these components or properties is expected to affect soil sorption capacity.

Table 4. Glyphosate removal efficiency by the control and amended soils.

Initial concentration (mg l^{-1})	Glyphosate removal efficiency (%)			
	Control	Burnt soil	Soil with cow dung	Soil with rice husk ash
0	0	0	0	0
25	73.915	68.868	71.758	81.678
50	79.839	77.702	85.302	84.957
100	86.208	85.967	87.477	89.445
150	88.544	89.063	88.681	91.033
200	90.462	91.628	90.366	92.549
250	91.242	91.965	90.614	93.105
300	92.103	28.933	92.094	93.843
Mean	86.045	76.304	86.613	89.516

Fire intensity is generally described using fire temperature, therefore, low, medium and high fire intensities had a respective fire temperature of ≤ 200°C, ≤ 400°C and > 675°C [26]. Soil heating to as low as < 250 affect soil biological and chemical properties but the severity prevails more at temperature > 500°C [27,28]. Heating a sandy soil at a temperature above 450°C decreases it aggregate strength [28] which can resulted to a sharp increase in sand particles but decrease in silt and clay. Similarly, the authors reported total loss of soil organic matter, a decrease in kaolinite and resultant increase in pH. The trio significantly affect glyphosate adsorption and mobility in soil, thus, any change on them results in changing soil glyphosate adsorption capacity. The heating temperature in present study is 550°C which falls within the temperatures used by Araya et al [28], suggesting the total loss of organic matter, sharp increase in sand particle, decrease in CEC, dehydration of clay minerals and resultant pH increased due to K$^+$ and Na$^+$ ions from organic matter oxidation. The effect of these were suggested to result in low glyphosate removal efficiency by the burnt soil. Meanwhile applying cow dung or rice husk ash can to result to increasing organic matter content of this soil, and so, upsurge its surface charges and enhances adsorption strength [17,29], hence, greater glyphosate removal efficiency. Our previous study on the same soil showed an increased in adsorptive removal of aminomethylphosphonic acid (AMPA) - a metabolite of glyphosate and having the same soil adsorption site- due to amendment with cow dung or rice husk ash [30].

3.3 Glyphosate adsorption isotherms

The adsorption isotherms for glyphosate on different adsorbents were present in Figure 3. The isotherms obtained for all adsorbents were of "C" curve, thus, indicating a constant partitioning of glyphosate amongst the interfacial region of surfaces of the adsorbent and bulk solution. The C-curve isotherm is characterized by an initial slope of adsorptive concentration that remains independently until the maximum adsorption is achieved [31]. From the present result it can be hypnotized that, even with soil burning or application of organic manure glyphosate can be adsorb by the soil of the present study through entrapment in the intra and inter surfaces, therefore, no any binding energy between these surfaces and glyphosate ions.

The glyphosate adsorption isotherm data for both adsorbent were fitted to the four different models listed in Table 2 and the results of these model constant were shown in Table 5. Of all the models, control soil best fitted to Freundlich (r^2= 0.997) which followed by linear (r^2= 0.964), Langmuir (r^2= 0.905) and Temkin (r^2= 0.871). The soil applied with rice husk ash also followed a similar trend, however, the soil + cow dung has the trend of linear > Freundlich > Temkin > Langmuir. Meanwhile, the isotherm data for glyphosate adsorption on the burnt soil very poorly fitted to all models except Langmuir (r^2= 0.959). The soil applied with rice husk ash (178.386 mg g^{-1}) and control (151.325 mg g^{-1}) had higher values of K$_d$ constant of the linear model compared to soil + cow dung (127.983 mg g^{-1}) and burnt soil (0.888 mg g^{-1}). The K$_F$ constant of Freundlich isotherm model was higher in the burnt soil (387.238 mg g^{-1}), then soil amended with rice husk ash (9.768 mg g^{-1}), soil amended with cow dung (6.751 mg g^{-1}) and control was the least (3.187 mg g^{-1}). Meanwhile, the values of 1/n constant of the model showed the trend of control > soil + rice husk ash > soil + cow dung > burnt soil. The burnt soil had higher Q$_{max}$ (233.739 mg g^{-1}) of the Langmuir model. This followed by the soil applied with rice husk ash (36.649 mg g^{-1}), then soil + cow dung (27.937 mg g^{-1}) and control (24.374 mg g^{-1}). The values of b constant have the following trend soil

+ cow dung < control < soil + rice husk ash < burnt soil. The calculated Langmuir separation factor (R_L) for both adsorbents is < 1 and so, ranged from 0.194 to 0.447. The Temkin isotherm constant A for the adsorbents had the following trend burnt soil > soil + rice husk ash > soil + cow dung > control soil. Similar pattern was observed from the b constant which had ranged of 1.275 to 26.585 j mole^{-1}. The result of the calculated MPSD revealed that, linear model had values range of 0.040 to 8.377, Freundlich; 0341 to 0.430, Langmuir; 0.447 and Temkin; 5.663 to 95.310.

It is obvious, the best fitting relationship that measure the distribution of the adsorbate is describe by the correlation coefficient (r^2). It is also used in the corroboration of the consistency of the isotherm models, hence, describe the association between the experimental isotherm data and linear form of the adsorption isotherm model. The major defect of r^2 is that, it does not take into account the changes in error that occur during transformation of the isotherm models into linearized form. This makes it necessary to use an error function analysis to find out the model with best description of the experimental isotherm data. The MPSD is one of the error function use to determine the suitability of the isotherm model to describe experimental data [32]. Therefore, any model having less MPSD values fits the experimental isotherm data best. The order of Freundlich > Langmuir > linear > Temkin was emanated from MPSD values of the present study.
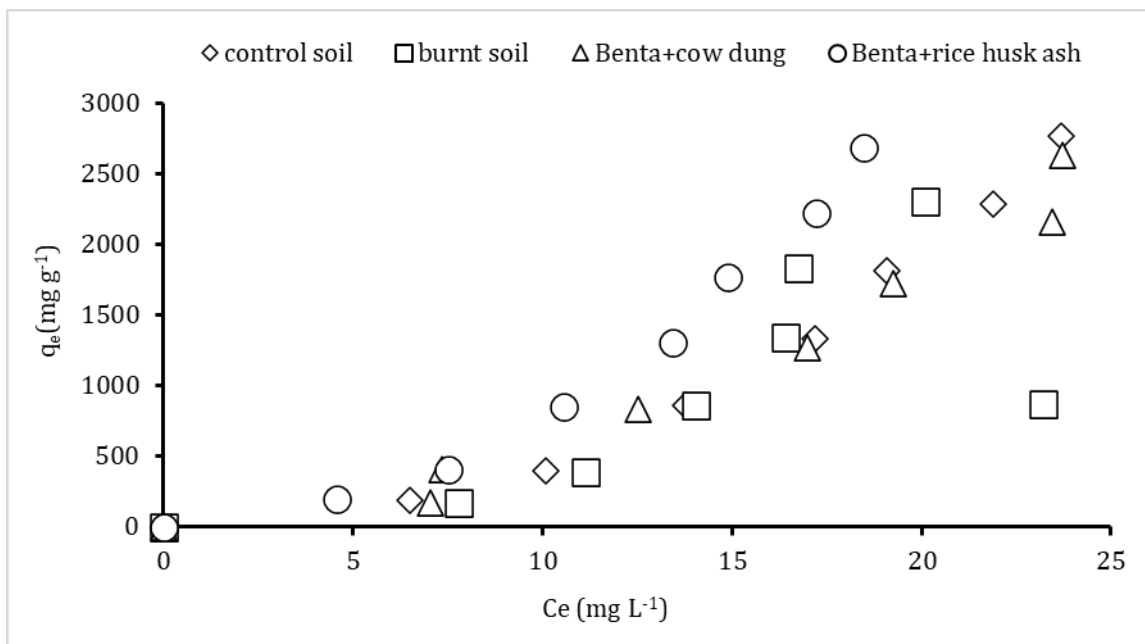

Figure 3. Glyphosate adsorption isotherms for the different adsorbents.

The glyphosate adsorption isotherm data for both adsorbent were fitted to the four different models listed in Table 2 and the results of these model constant were shown in Table 5. Of all the models, control soil best fitted to Freundlich (r^2= 0.997) which followed by linear (r^2= 0.964), Langmuir (r^2= 0.905) and Temkin (r^2= 0.871). The soil applied with rice husk ash also followed a similar trend, however, the soil + cow dung has the trend of linear > Freundlich > Temkin > Langmuir. Meanwhile, the isotherm data for glyphosate adsorption on the burnt soil very poorly fitted to all models except Langmuir (r^2= 0.959). The soil applied with rice husk ash (178.386 mg g^{-1}) and control (151.325 mg g^{-1}) had higher values of K_d constant of the linear model compared to soil + cow dung (127.983 mg g^{-1}) and burnt soil (0.888 mg g^{-1}). The K_F constant of Freundlich isotherm model was higher in the burnt soil (387.238 mg g^{-1}), then soil amended with rice husk ash (9.768 mg g^{-1}), soil amended with cow dung (6.751 mg g^{-1}) and control was the least (3.187 mg g^{-1}). Meanwhile, the values of 1/n constant of the model showed the trend of control > soil + rice husk ash > soil + cow dung > burnt soil. The burnt soil had higher Q_{max} (233.739 mg g^{-1}) of the Langmuir model. This followed by the soil applied with rice husk ash (36.649 mg g^{-1}), then

soil + cow dung (27.937 mg g^{-1}) and control (24.374 mg g^{-1}). The values of b constant have the following trend soil + cow dung < control < soil + rice husk ash < burnt soil. The calculated Langmuir separation factor (R_L) for both adsorbents is < 1 and so, ranged from 0.194 to 0.447. The Temkin isotherm constant A for the adsorbents had the following trend burnt soil > soil + rice husk ash > soil + cow dung > control soil. Similar pattern was observed from the b constant which had ranged of 1.275 to 26.585 j mole^{-1}. The result of the calculated MPSD revealed that, linear model had values range of 0.040 to 8.377, Freundlich; 0341 to 0.430, Langmuir; 0.447 and Temkin; 5.663 to 95.310.

It is obvious, the best fitting relationship that measure the distribution of the adsorbate is describe by the correlation coefficient (r^2). It is also used in the corroboration of the consistency of the isotherm models, hence, describe the association between the experimental isotherm data and linear form of the adsorption isotherm model. The major defect of r^2 is that, it does not take into account the changes in error that occur during transformation of the isotherm models into linearized form. This makes it necessary to use an error function analysis to find out the model with best

description of the experimental isotherm data. The MPSD is one of the error function use to determine the suitability of the isotherm model to describe experimental data [32]. Therefore, any model having less MPSD values fits the experimental isotherm data best. The order of Freundlich > Langmuir > linear > Temkin was emanated from MPSD values of the present study.

Table 5. Models' constant for glyphosate adsorption by the adsorbents, correlation coefficients and error functions.

Models	Parameters				
Linear	K_d (mg g^{-1})	m	r^2		MPSD
Control soil	151.325	1050.986	0.964		6.767
Burnt soil	0.888	1145.960	0.008		0.040
Soil + cow dung	127.783	702.188	0.963		6.000
Soil + rice husk ash	178.386	865.281	0.959		8.377
Freundlich	K_F (mg g^{-1})	1/n	r^2		MPSD
Control soil	3.189	2.132	0.997		0.341
Burnt soil	387.238	0.255	0.092		0.430
Soil + cow dung	6.751	1.864	0.941		0.349
Soil + rice husk ash	9.768	1.905	0.994		0.350
Langmuir	Q_{max} (mg g^{-1})	b	r^2	R_L	MPSD
Control soil	24.374	0.037	0.905	0.219	0.447
Burnt soil	233.739	0.262	0.959	0.044	0.447
Soil + cow dung	27.937	0.033	0.560	0.234	0.447
Soil + rice husk ash	36.649	0.044	0.940	0.194	0.447
Temkin	A (mg g^{-1})	b (j mole^{-1})	r^2		MPSD
Control soil	4.389	1.275	0.871		95.310
Burnt soil	987.950	26.585	0.017		5.663
Soil + cow dung	6.000	1.463	0.909		87.072
Soil + rice husk ash	7.664	1.448	0.856		86.024

Freundlich isotherm model assumes a heterogeneous surface coverage hence stronger binding site are occupied first and binding strength increases with increasing surface coverage until equilibrium is attained [33]. The K_F and 1/n constant of the model denotes adsorption affinity and intensity, respectively. Even though applying cow dung or rice husk ash an increase affinity (K_F) for glyphosate adsorption by this soil but a greater increased was observed from the burnt soil. This can be attributed to the structural changes of minerals smectite, mica and kaolinite which was reported to occur at 500°C [4,17,25], a degree lower than that of the present study (550°C). This change result to dihydroxylation which increase soil acidity due to release of H^+ and Al^{3+} from these minerals, and so, an increase the net positive charges on the soil surface for greater glyphosate adsorption. Soil pH, mineral group and cations considerably affect glyphosate adsorption. Result of the physicochemical analysis (Table 3) revealed the pH of this soil to be of near neutral (6.763) and a significant content of Fe, Mn and Zn. The resultant ash of burning this soil might increase its pH and contents of these cations and many more, hence, forming a strong complex with glyphosate phosphonic and carboxylic moieties. Glyphosate had amphoteric properties, and so, a good chelating agent therefore it can form strong complexes with metal ion, especially at near-neutral pH levels due to deprotonation of its carboxylate and phosphonate moieties [34]. Unlike K_F values, amending this soil resulted into decrease of 1/n values compared to control, thus, indicating an increasing intensity. The 1/n values of burnt soil was 0.255 and was < 1, accordingly, glyphosate adsorption by the burnt soil was favourable. Meanwhile the 1/n values for both control and soil amended with cow dung or rice husk ash were between 1.864 and 2.132 which denotes a cooperative adsorption.

Langmuir isotherm model assumes monolayer coverage of adsorbate occurring at a homogenous site on adsorbent. It further presumes equal adsorption energy, therefore, no transmigration of adsorbate in the adsorbent's surfaces [33]. The Q_{max} which represent a monolayer coverage and b which denote adsorption affinity are the model constant. In addition to these, the model has a dimensionless separation factor (R_L) which describe it favourability. Based on this R_L, the adsorption of glyphosate was more favourable by soil + cow dung > control soil > soil + rice husk ash > burnt soil. The present study revealed that both application of these agricultural waste or burning its natural organic matter led to an increase in glyphosate adsorption by this soil. The resultant increase in monolayer coverage owing to applying cow dung or rice husk ash can be attributed to additional functional group, bases and more surface area. Our previous study [35] showed that these agricultural waste contains phenols, carboxylic, ethers, Fe, Al and high surface area. Therefore, incorporating of them were suggested to increase the surface area and functional group of the soil leading to an increased glyphosate adsorption. The higher increase in Q_{max} (233.739 mg g^{-1}) obtained from burnt soil was not unexpected because the burning was done in a muffle furnace, thus, is an oxygen-limited condition. This can resulted into charring of the soil organic matter, formation of pyrogenic carbon and more accumulation of aromatic compounds [25] hence, an increase in adsorption capacity of the soil. The higher values of Langmuir constant b obtained from the burnt soil (0.262) indicated higher affinity of glyphosate ions for this soil. This possibly could be due to the lime effect of the resultant ash which can increases the concentration of amorphous Fe and Al oxides [36]. The result of the b values also shows that application of rice husk ash increases glyphosate affinity of the study soil

but, soil applied with cow dung showed a decrease in affinity of this compound.

Linear model is the simplest among the adsorption isotherm model, it assumes constant partitioning of adsorbate in the adsorbent inter facial region, thus, differs straight with the equilibrium concentration of the adsorptive. The model constant K_d denotes a partitioning coefficient of the adsorbate while the constant m was added by Maurya and Mittal, [37] to increase degree of freedom of the model hence its fitness in describing the isotherm data. Based on this model the glyphosate adsorption by the studied soil has the trend of soil applied with rice husk ash > control > soil + cow dung > burnt soil. Both cow dung and rice husk ash are porous in nature with surface area of 9.731 m^2 g^{-1} and 21.5000 m^2 g^{-1}, respectively [35]. Their application was therefore suggested to result into proportionate increase in the soil adsorption surfaces and greater entrapment of glyphosate ions.

Temkin isotherm model assumes that heat of adsorption decreases linearly with increasing surface coverage as a result of adsorbate-adsorbents interaction. It also gives account of the variation of binding energy for adsorbate retention by the adsorbents [38]. The model had two constant A and b which are related to binding energy and heat of adsorption, respectively. According to the model constant A, burnt soil had higher binding energy (987.950 mg g^{-1}) for glyphosate adsorption and it followed by soils amended with rice husk ash (7.664 mg g^{-1}) and cow dung (6.000 mg g^{-1}) while control soil had the least (4.389 mg g^{-1}). The values of b constant are all positive which indicated that, glyphosate adsorption reaction by all adsorbents was endothermic and the range of the values obtained (b = 1.275 – 26.585 j mole^{-1}) was an indication of a physical adsorption process [39]. Therefore, based on the present result the mechanisms of glyphosate adsorption by these adsorbents can be suggested to either be an ion entrapment within the inter facial region of the adsorbent, complexation reaction between cations and, phosphonic and carboxylic moieties of glyphosate or through a ligand exchange between these moieties and surface functional groups of the adsorbents.

3.4 Desorption and predicted mobility of glyphosate

Table 6 shows the glyphosate desorption efficiency from the adsorbents. Of the concentration range applied, the percent glyphosate desorption was generally high at low concentration. The desorption decreases with increasing initial concentration except from control and burnt soils where at 300 mg L^{-1} 42.624% and 12.333% of the respective mass was recovered. Amendment with cow dung or rice husk ash was shown to decrease desorption of glyphosate from this soil to the extent that no glyphosate was detected at 300 mg L^{-1} from the soil amended with cow dung. This indicated that incorporation of these agricultural waste can augment the adsorption strength and glyphosate affinity for this soil. The result further revealed that, burning this soil increases it glyphosate desorption efficiency, hence, it possible mobility compared to control and soils amended with cow dung or rice husk ask. The present result concur with the earlier studies which reported glyphosate desorption from sandy and sandy loam soils of Malaysia [40,41].

Table 6. Glyphosate desorption efficiency by the control and amended soils.

Initial concentration (mg l^{-1})	Control soil	Burnt soil	Soil + cow dung	Soil + rice husk ash
0	0	0	0	0
25	13.332	38.289	17.271	10.572
50	14.718	21.402	12.504	12.379
100	9.363	11.734	8.999	8.563
150	6.868	8.737	7.307	7.159
200	5.252	5.214	5.941	6.264
250	4.772	4.329	5.572	6.944
300	42.624	12.333	nd	4.828
Mean	13.847	14.577	9.599	8.101

The Freundlich isotherm model fit well for glyphosate desorption isotherm data (Table 7) from soil added with cow dung (r^2 = 0.996) or rice husk ash (r^2 = 0.951) compared to burnt soil (r^2 = 0.683) and control (r^2 = 0.423). The values of K_F for glyphosate desorption ranged from 244. 682 mg g^{-1} for control soil to as low as 0.022 mg g^{-1} for the burnt soil. Meanwhile the values for 1/n constant for the absorbents were between 0.529 and 4.632. The values of constant K_F and 1/n were greater in glyphosate desorption compared to those for adsorption. Similar trend was reported from the literature [19,36,42,43]. The present study revealed that glyphosate desorption was of two types; reversible and hysteretic. Desorption of glyphosate was strongly hysteretic (HI = 0.248) in control soil but was reversible in the other adsorbents. Thus, glyphosate desorption was highly reversible in the burnt soil (HI = 18.180) then followed by soil added with cow dung (1.037). In contrast, in addition of being reversible technically hysteresis was absent in desorption of glyphosate from the soil added with rice husk ash (HI = 0.732). Mamy and Barriuso [42], reported that no hysteresis can be definite in practice when 0.7 < H < 1.0.

In other to confirm these two types of desorption obtained from the calculated hysteresis index, the glyphosate adsorption and desorption isotherms were compared as shown in Figure 4. Hysteresis tended to be greater in the control soil and this was due to lack of overlap in the adsorption-desorption isotherms. Similarly little hysteretic effect can be seen from glyphosate adsorption-desorption isotherm at high initial concentration in the burnt soil. Meanwhile there was a general overlap, hence, reversible desorption in both burnt soil and soils amended with cow dung or rice husk ash. The greater hysteretic effect observed from the control soil could be due to irreversible binding of

glyphosate ions on the soil native organic matter, mineral content or its Fe and Al oxides. While the little hysteresis shown by glyphosate desorption in the burnt soil at high initial concentration might be attributed to its increased diffusion into the micro pores of this soil [42]. Therefore,

since the native organic matter was removed from this soil via burning, this result in predominance soil and/or mineral surface excess which could be of high energy, hence, an increase in intensity for glyphosate especially at higher concentration.

Table 7. Freundlich model constant, correlation coefficients, and hysteresis index for glyphosate desorption from the adsorbents.

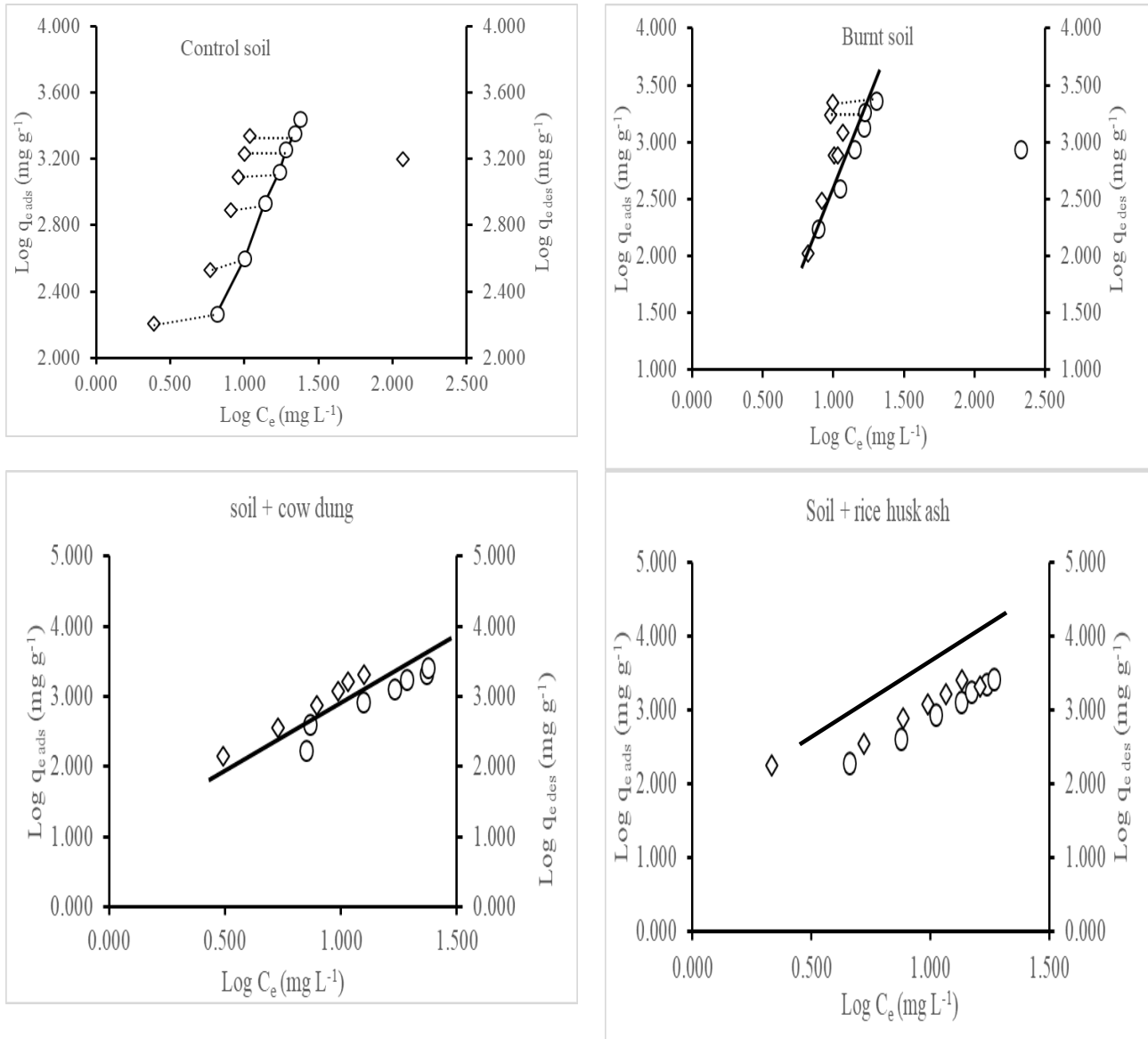| Adsorbents	K_F (mg g^{-1})	1/n	r^2	HI
Control soil	244.68	0.53	0.423	0.25
Burnt soil	0.02	4.63	0.683	18.18
Soil + cow dung	14.98	1.93	0.996	1.04
Soil + rice husk ash	49.59	1.40	0.951	0.73

Figure 4. Relationship between glyphosate Freundlich adsorption-desorption isotherms.

Mamy and Barruiso, [42] further opined that it will sometimes be difficult to draw a conclusion that desorption is controlled by sorption mechanisms only with no additional non-sorptive processes. This is due to reliance of desorption parameters on the initial concentration of adsorptive used for the desorption study. These authors used what they termed as general formalism in defining desorption freely of initial concentration of the adsorptive by bringing into used the Equation 8.

$$K_{Fdes} = K_{Fads} C_{e\,ads}^{nads\,(1-H)} \qquad (8)$$

The Equation 8 was transformed logarithmically into Equation 9.

$$\text{Log}\,(K_{F\,des}) = \text{Log}\,(K_{F\,ads}) + n_{ads}\,(1\text{-}H)\,\text{Log}\,(C_{e\,ads}) \qquad (9)$$

Figure 5 is the result of general formalism in the present study, thus, show the relationship between $K_{F\,des}$ and $C_{e\,ads}$. This relationship from all adsorbents was linear

indicating a control of sorption mechanisms on glyphosate desorption. This result further supports our earlier suggestion that the hysteretic effect observed

from control and burnt soils could be due to glyphosate binding on higher energy sorption sites.
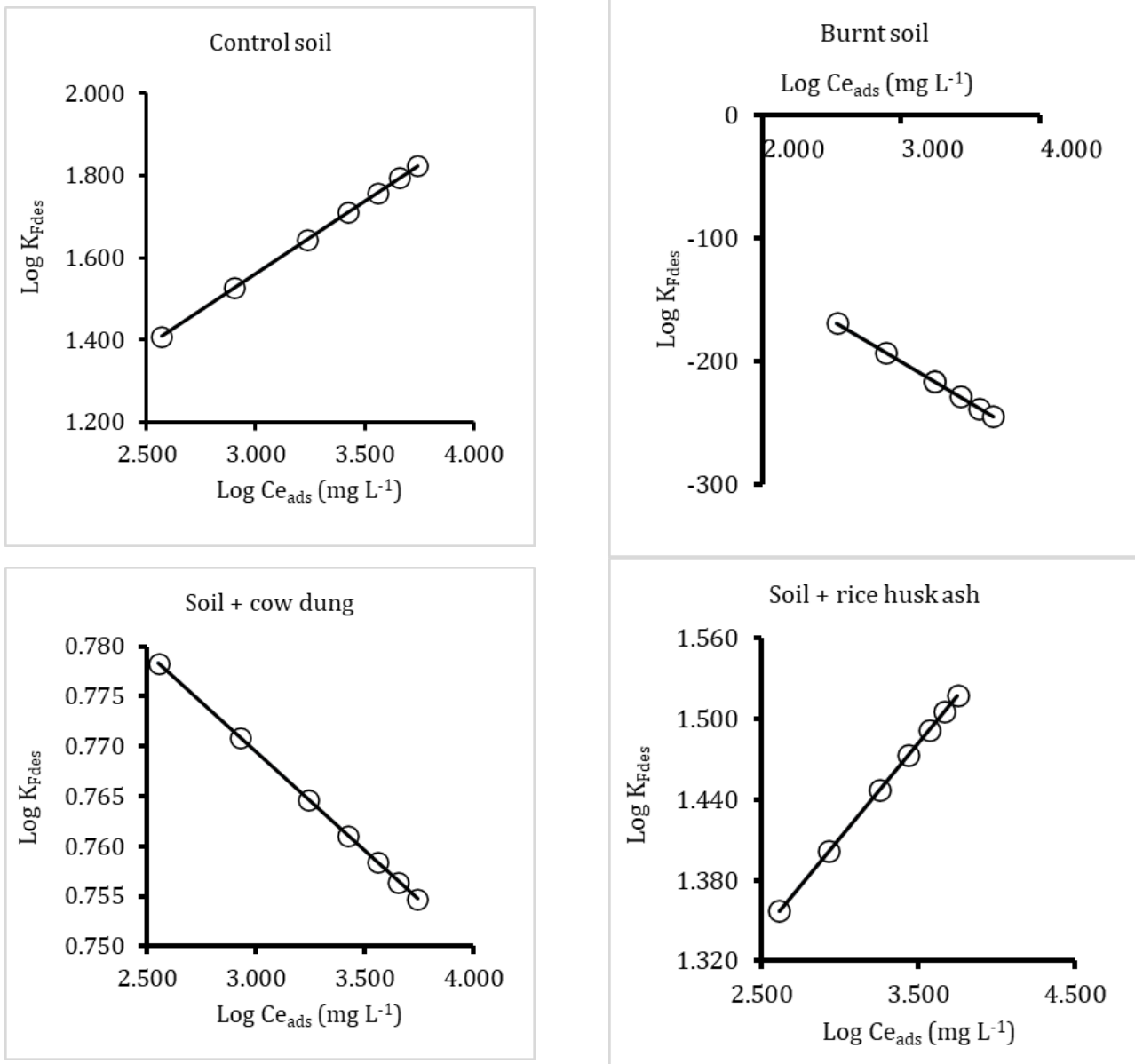

Figure 5. Correlation between the resultant values of K_{Fdes}- Freundlich desorption isotherm constant and Ce_{ads}- concentrations of glyphosate in solution at the commencement of desorption process.

Table 8 depicts the calculated organic carbon normalized adsorption coefficient (K_{oc}) and ground water ubiquity score (GUS) of glyphosate for the adsorbents. Pollutant mobility and persistency are used to assess it leachability in soil and environment [22]. The K_{oc} represent mobility while the persistency is expressed based on the half-life of the pollutant. However, these two indices are both taken into account by GUS to determine the leachability of pollutant in soil and environment. According to this index, Fenoll et al., [44] reports that pollutant with a GUS values of < 1.8 are non-leachers while those with a value range of 1.8 to 2.8 are transitional and those pollutant with values of > 2.8 are potential leachers. Our result showed the calculated GUS for control (2.27) and soil added with cow dung (2.70) or rice husk ash (2.32) to be within the range of 1.8 to 2.8

and thus, glyphosate in these soils was at transitional state. The present result also shows an increase in GUS index owing to addition of cow dung or rice husk ash compared to control. This is suggesting an aging effect on increasing mobility of glyphosate due addition of organic manure. However, due the soil functional biological system these glyphosate ions expected to be released from the adsorption sites will be degraded by microorganisms. The GUS for burnt soil (4.08) was far greater than 2.8 implying the higher possibility of glyphosate mobility and leaching. This is due to killing of soil biota as a result of burning, thus, desorbed glyphosate ions will remain in soil solution which might result in its downward movement and consequent ground water contamination.

Table 8. Organic carbon normalized adsorption coefficient (K_{oc}) and groundwater ubiquity score (GUS) of glyphosate for control and amended soils.

Soil	K_{oc} (µl mg^{-1})	GUS
Control soil	91	2.27
Burnt soil	1	4.08
Soil + cow dung	77	2.70
Soil + rice husk ash	107	2.32

4. Conclusion

Open field burning and manure application are commonly practiced in Malaysia. Benta is one of the Malaysian soil series having sandy texture, high CEC, pH and 2:1 clay mineral, thus, classified as Alfisols according USDA soil taxonomy classification. Burning this soil decreases its uptake of glyphosate but addition of rice husk ash increases its glyphosate removal efficiency. Five different isotherm models were fits into glyphosate batch equilibrium data and based on the MPSD the models were in order of Freundlich > Langmuir > linear > Temkin. Therefore, according to the Freundlich model adsorption of glyphosate was favourable (1/n = 0.255) by burnt soil. Glyphosate desorption was control by adsorption mechanisms and it was inversely proportional (HI = 0.248) to adsorption in control soil, thus, indicating an aging effect of soil organic matter on hysteretic glyphosate desorption. Burning the biota of this soil can be discourage because it increases the mobility (GUS = 4.08) of glyphosate and its potentials in ground water contamination.

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Author contributions

Jamilu Garba: Investigation, methodology, formal analysis, data curation, writing -original draft.
Samsuri Abd Wahid: Conceptualization, supervision, funding acquisition, editing.
Muhammad Saiful Ahmad Hamdani: Supervision, editing, visualization. validation
Tariq Faruq Sadiq: Formal analysis, visualization, data curation

Conflicts of interest

The authors declare no conflicts of interest.

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