Article

Adsorption–Desorption of Aminomethylphosphonic Acid (AMPA) in Sandy Soil Amended with Cow Dung and Rice Husk Ash

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Abstract The present study investigates adsorption–desorption of aminomethylphosphonic acid (AMPA)—a residue of glyphosate herbicide—by sandy soil added with cow dung or rice husk ash. Adsorption study was conducted using different concentrations of AMPA in 0.01 M $CaCl_2$. Desorption study followed immediately by adding 0.01 M $CaCl_2$ solution without any AMPA. The concentration of AMPA in both studies was analysed using high performance liquid chromatography coupled with a fluorescent detector. The result revealed an increase in adsorptive removal of AMPA from the soil due to the addition of cow dung or rice husk. The isotherm data of AMPA adsorption by control and amended soils best fitted the Freundlich model ($r^2 \geq 0.701$). The Freundlich's constant (K_F) for AMPA was highest in the soil + rice husk ash (7.268 mg g^{-1}), followed by cow dung amended soil (5.692 mg g^{-1}) and then control (4.906 mg g^{-1}). The $1/n$ coefficient for AMPA in both soils was >1, indicating cooperative adsorption. However, the results also showed that soil applied with cow dung and rice husk ash had respective increases of 4.22% and 1.784% in AMPA desorption compared to the control. Therefore, the addition of cow dung and rice husk ash can increase AMPA mobility in this soil making it susceptible to degradation or groundwater contamination.

Keywords sorption; AMPA; soil; agricultural waste; Freundlich

Introduction

Soil contamination is an important issue affecting the ecosystem and environment, as it may result in the pollution of soil as well as surface and underground water. Soil contamination by pesticides, organophosphate herbicides in

particular, is of great environmental concern. Surface application, spray drift and root exudation are some of the ways by which these herbicides get into the soil [1]. Glyphosate is a popular organophosphate herbicide generally used for weed control. Meanwhile, microbial degradation of glyphosate in soils resulted in a primary metabolite called Aminomethylphosphonic acid (AMPA) [2]. Therefore, considerable use of glyphosate leads to the incidence of AMPA in the soil and water reservoirs. Glyphosate is widely applied in Malaysia for controlling the *Eleusine indica* weed of rice, weeds in nurseries and young oil palm plantations, as well as removing ground cover vegetation in cocoa and rubber plantations [3]. Similarly, an earlier study reported a significant application of glyphosate for killing the foliage and rhizomes of *Imperata cylindrical* in cultivated and non-cultivated Malaysian soils [4]. Field application of glyphosate at the recommended rate of 1200 g a.i ha^{-1} killed 99% of the weeds in Malaysian oil palm plantation and remained effective for 15 weeks after treatment [5]. Residues of glyphosate and AMPA have been detected in soil [6], surface [7] and underground water [8]. Like its parent compound, AMPA is insoluble in an organic solvent but soluble in water, and it also contains carboxylic, amines and phosphonic moieties (Figure 1). Similarly, recent studies reveal the toxicity of AMPA to humans and animal cells [9]. Therefore, the assessment of sorption, degradation and the mobility of AMPA help in predicting its possibility for soil and water pollution.
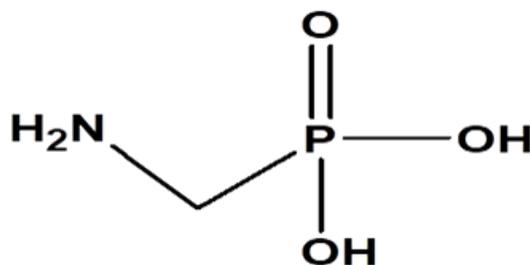

Figure 1. Chemical structure of aminomethylphosphonic acid (AMPA).

Several studies have been reported regarding the sorption processes of glyphosate on different types of an adsorbent such as clay minerals [10,11], humic substances [12,13] and soils [14,15]. However, there is little investigation on AMPA adsorption by soils, and much less the effect on soil organic colloids. The assessment of the sorption processes of AMPA on soil would help in understanding its behaviour and fate in the soil matrix, and evaluating its potential environmental impact. The effect of compost amendment on AMPA degradation in temperate soil was recently reported by Erban et al. [6]. The authors reported an increase in AMPA dissipation due to an increasing dose of compost applied to clay loam soil of Prague–Ruzyne, Czechia. They attributed this to either desorption of the compound from the soil, or an increase in microbial activity. To the best of our knowledge, there was no reported study on the effect of organic matter amendment on the adsorption–desorption of AMPA by tropical sandy soils. The present study is therefore, the first to report the sorption behaviour of AMPA as influenced by the application of agricultural residues in tropical sandy soil. This study is also the first AMPA adsorption characterisation of Malaysian sandy soil. The objective of this research was to investigate the adsorption–desorption of AMPA by sandy soil amended with cow dung or rice husk ash.

Materials and Methods

Sampling, Chemicals and Analysis

The soil used in the present study was sampled from Sementa Hulu (Lat. 3.841663° N, Long. 101.947251° E), located in Raub district, Pahang Malaysia. After identifying the sampling area, the soil was sampled from five different locations at a depth of 0–20 cm and later bulked to one composite sample. The sample of cow dung was obtained from the animal section of the experimental farm, Faculty of Agriculture, Universiti Putra Malaysia.

Meanwhile, rice husk ash was obtained from BERNAS Rice Mill Selangor, Malaysia. (Lat 3°40′32.4″ N Long 100°59′42.5″ E). Prior to analysis and sorption study, all the samples were air dried and sieved (2 mm for soil and 1 mm for cow dung and rice husk ash). The procedure of pipette method as described in Teh and Talib [16] was used to determined particle size distribution of the soil. The suspended clay from the particle size analysis was employed to determine the soil's clay minerals using a Phillips PW 3440/60 X'pert Pro diffractometer (Philips, Almelo, Netherlands). The pH was determined as 1:2 (w/v ratio) soil: 0.01 M $CaCl_2$ solution. Soil organic matter content was determined by a weight difference while a leaching method as described by Van Ranst et al. [17] was employed to determined its cation exchange capacity. Free and amorphous Fe and Al oxides were determined using the dithionite and acid ammonium oxalate method as described by Carter and Gregorich [18]. The pH of cow dung and rice husk ash was measured using a 0.5:100 (w/v) sample and water suspension. The cation exchange capacity (CEC) and extractable bases were measured using the modified method of Song and Guo [19]. Total Al and Fe were determined by the double acid digestion method as described by Tariq et al. [20]. The percentages of oxygen-acidic functional groups in the cow dung and rice husk ash were determined by the Boehm titration method [21]. The surface area of cow dung and rice husk ash was measured with a Quantachrome version 2.01 (Quantachrome AS1Win^{TM}) Autosorb 1 surface area analyser. The samples were degassed at 300 °C then adsorption–desorption with liquid nitrogen was carried out at −195.55 °C, and Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BHJ) techniques were used to determine the surface area.

The soil belongs to the Benta soil series which was classified as Alfisols based on USDA Soil Taxonomy classification [22]. The texture of the soil was sandy with 5.233% organic matter, pH of 6.73 and CEC of 126.670 mmol$_+$ kg^{-1} (Table 1). Kaolinite, mica and smectite were the dominant minerals in the soil, thus, contained <0.5% of free and amorphous oxides of Fe and Al. Both cow dung and rice husk ash were alkaline (pH > 8) with carboxylic, lactones and phenolic functional groups (Table 2). They have high a content of poly valent cations (Al, Fe, Ca, and Mg) and the BET surface area of 9.731 and 21.500 m^2 g^{-1} for cow dung and rice husk ash, respectively.

Aminomethylphosphonic acid (AMPA) of 99% purity was purchased from Sigma Aldrich® (Seelze, Germany). Analytical reagent grade $CaCl_2$ was purchased from Emsure® Germany while $HgCl_2$ was purchased from Sigma Aldrich® (India). Stock solution (100 mg L^{-1}) of AMPA was prepared by dissolving 1 mg of its analytical grade powder into 10 mL solution of 0.01 M $CaCl_2$ containing 200 mg L^{-1} of $HgCl_2$ which acted as bioinhibitor to minimize the risk of AMPA degradation [23]. Working solutions were prepared by diluting appropriate amounts of stock solution.

Table 1. Selected properties of the studied soil.

Parameter	Result
pH	6.73 ± 0.03
Sand (%)	74.17 ± 0.833
Silt (%)	5.833 ± 0.833
Clay (%)	20.000 ± 1.433
Soil type	Sandy soil
Clay minerals	
kaolinite	+++
mica	++
smectite	+
Free FeO (%)	0.473 ± 0.012
Amorphous FeO (%)	0.218 ± 0.017
Free AlO (%)	0.476 ± 0.012
Amorphous AlO (%)	0.262 ± 0.093
SOM (%)	5.233 ± 0.120
CEC (mmol$_+$/kg)	126.670 ± 6.718

+++: major, ++: moderate, +: minor, ±: SE.

Table 2. Selected properties of the cow dung and rice husk ash.

Parameter	Cow Dung	Rice Husk Ash
pH	8.14 ± 0.04	9.95 ± 0.02
Oxygen acidic functional group		
Carboxylic (mmol$_+$/kg)	151.24 ± 16.41	113.41 ± 8.12
Lactone (mmol$_+$/kg)	190.83 ± 5.43	148.42 ± 10.37
Phenolic (mmol$_+$/kg)	194.00 ± 10.40	194.02 ± 9.20
BET surface area (m^2/g)	9.731	21.500
Al (mg/kg)	7952.80 ± 7.82	235.07 ± 6.31
Fe (mg/kg)	6808 ± 5.84	637.47 ± 7.36
Ca (g/kg)	7.94 ± 1.53	1.16 ± 0.27
Mg (g/kg)	3.74 ± 0.55	1.81 ± 0.21
CEC (mmol$_+$/kg)	345.01 ± 29.43	102.03 ± 7.30

Batch Equilibrium Sorption Study

Before the sorption study, triplicate samples of soil (1 g) and 0.1 g of either cow dung or rice husk ash were weighed into a centrifuge tubes and homogenized. The samples were added with water to field capacity and incubated for 1 week. This is to simulate the common practice in the tropics in which manure is applied 1–2 weeks before planting and subsequent herbicide application. Soon after, the mixture was allowed to dry to a constant weight and then used for the sorption study. The sorption study was performed as described by Piccolo et al. [13] with some modifications. In brief, 1 g of the control soil weighed in triplicate into centrifuge tubes and the homogenized mixture of soils and cow dung or rice husk ash were added with 20 mL of 0, 4, 8, 17, 25, 33, 42, or 50 mg L^{-1} AMPA solutions. Later on, the tubes were shaken for 24 h on a rotary shaker at 100 rpm at room temperature. After which the tubes were centrifuged at 10,000 rpm for 10 min, then supernatants were decanted and passed through a 0.45 μm P0377 HmbG syringe filter prior to analysis. Desorption study followed as soon as the supernatants in the adsorption study were decanted. Therefore, a 20 mL solution containing only 0.01M CaCl$_2$ and 200 mg L^{-1} HgCl$_2$ was added into each of the centrifuge tube and shaken for 24 h under the same experimental condition as mentioned above. The samples were treated similar to those of the adsorption study. The analysis of AMPA was accomplished using high performance liquid chromatography coupled with a fluorescent detector (HPLC-FLD) method previously developed [24]. Briefly, the AMPA was derivatized with 9-flourenylmethlylchloroformate chloride (FMOC-Cl) and the AMPA-FMOC derivatives were analysed by HPLC-FLD using a stationary phase of Agilent® Zorbax Eclipse plus C$_{18}$ (4.6 × 150 mm, 5 μm) column. The mobile phase solvent was acetonitrile and 0.05 M KH$_2$PO$_4$ mixture (30:70 v/v) using isocratic mode. The flow rate was 0.7 mL min^{-1} with column temperature of 40 °C and 20 μL injection volume. The excitation and emission wave lengths were set at 270 nm and 315 nm respectively. The lowest limits of detection and quantification for the spiked Benta soil were 0.074 mg kg^{-1} and 0.331 mg kg^{-1}, respectively.

Modelling of Experimental Isotherm Data

The quantity of AMPA sorbed at equilibrium [q_e (mg g^{-1})] was calculated using the equation below:

$$q_e = \frac{(C_i - C_e) \times V}{W} \tag{1}$$

The equation below was used to calculate the adsorptive removal of ions from the adsorbents:

$$Removal\ (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

where C_i and C_e are initial and equilibrium concentration (mg L^{-1}) of ions respectively, V is the volume of the solution (L) and W is the weight of the adsorbent (g) used.

The Freundlich's and Langmuir's adsorption isotherm models were applied to the experimental isotherm data in order described the adsorption behaviour AMPA, and their equations are shown below:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max}b} \tag{4}$$

where q_e and C_e were already defined and K_f and n are the Freundlich constants, related to capacity and intensity of adsorption, respectively. Q_{max} and b are the Langmuir constants which are the maximum adsorption capacity (mg g^{-1}) and a constant related to affinity, respectively. The values of K_f and $1/n$ were determined from the intercept and slope of plotting $\log q_e$ vs. $\log C_e$. Furthermore, Q_{max} and b were determined from the intercept and slope of plotting Ce vs. C_e/q_e.

The separation factor (R) was estimated from the constant of the Langmuir isotherm model, and it shows the favourability of the AMPA adsorption, thus:

$$R = \frac{1}{1 + bCo} \tag{5}$$

Results and Discussion

The percentages of AMPA removal from the aqueous solution by natural and amended soil is shown in Figure 2. The removal efficiency of AMPA was greater in soil amended with cow dung (67.28%), followed by soil + rice husk ash (62.41%), then control soil (62.27%). By comparison, the application of cow dung or rice husk ash to this soil resulted in 5.0% and 0.14% increase, respectively, in AMPA removal from the aqueous solution. Furthermore, soil amended with cow dung had a 4.866% increase in adsorptive removal compared to that with rice husk ash.
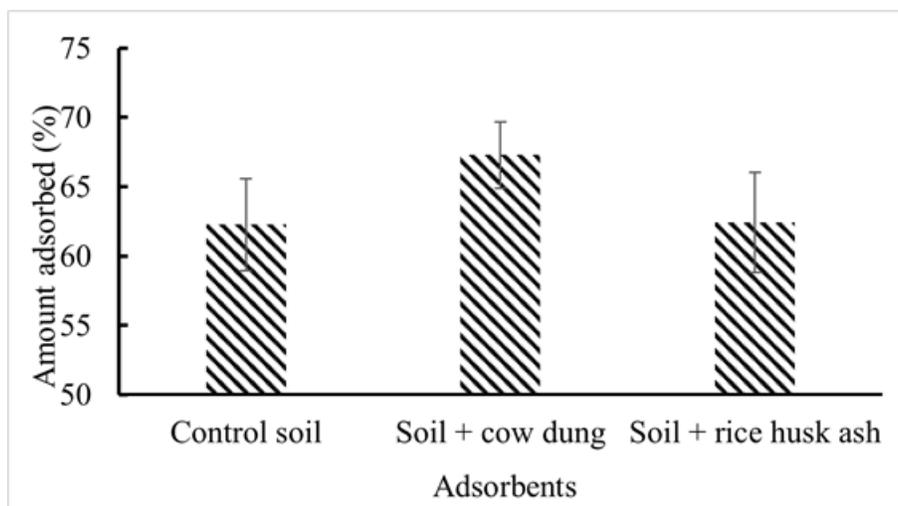

Figure 2. Amount of AMPA adsorbed by the adsorbents.

Cow dung and rice husk ash contains carboxylic, lactones and phenolic functional groups (Table 2). Their application can therefore increase the surface charges of this soil due to the protonation of their functional groups, which can

lead to increased adsorption of AMPA. Song and Guo [19] reported that the application of organic residues in soil resulted in the ionization or protonation of their functional groups, which enhances the adsorption capacity of the soils. Therefore, the resultant increase in AMPA adsorption by soils amended with these residues compared to controls was suggested to be due to selective interaction between the surfaces of cow dung or rice husk ash and AMPA [25]. The application of organic amendment in soil was reported to have increased the surface charges and introduced oxygen-containing functional groups leading to an increase in adsorption of glyphosate by the soil [25].

The isotherm shape for AMPA adsorption onto control and the soils added with cow dung or rice husk ash was S-type (Figure 3). This suggested that at low concentration, the affinity of AMPA for the adsorption surfaces on the soil was also low. However, this affinity increased with concentration [26,27]. The shape of the isotherm also gives an information on adsorption process and the extent of surface coverage by the adsorbate [27], therefore, application of cow dung or rice husk ash did not change the adsorption processes of this soil.
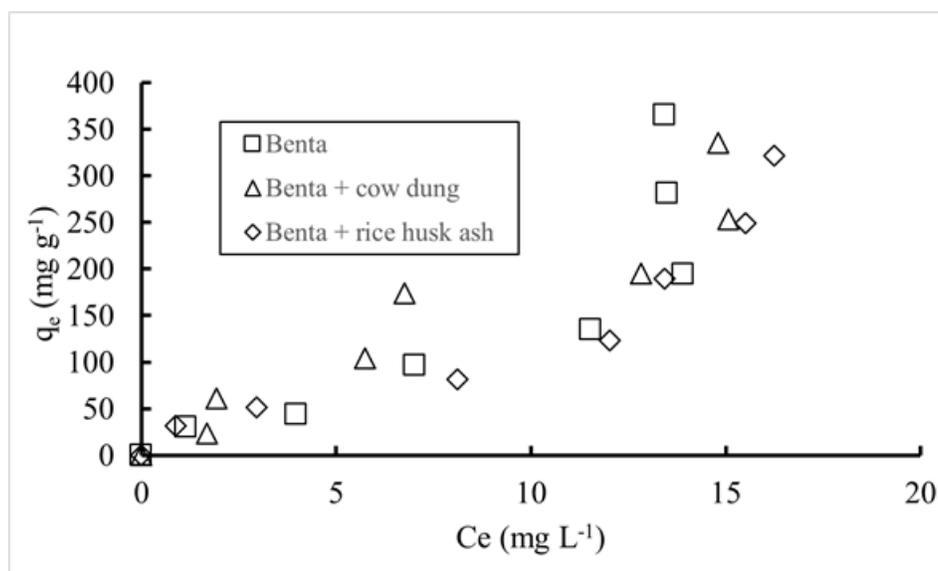

Figure 3. AMPA adsorption isotherm for control and amended soils.

The sorption isotherm data of AMPA for both control and amended soils best fit the Freundlich model ($r^2 \geq 0.701$) compared Langmuir model ($r^2 < 0.500$). This indicates the existence of heterogeneous surface coverage. The Freundlich's constant (K_F) for AMPA was high in the soil amended with rice husk ash (7.268 mg g^{-1}), indicating its high affinity and strong adsorption by this soil added with rice husk ash. This is followed by the cow dung amended soil (5.692 mg/g), then the control soil (4.906 mg g^{-1}). The 1/n value for AMPA in both soils was >1 (Table 3), indicating cooperative adsorption [28]. The cooperative adsorption suggests that sorbate is first adsorbed by high energy sites, then followed by low energy sites [29]. For the Langmuir adsorption model, application of cow dung showed a greater adsorption maximum of AMPA (Q_{max} = 30.488 mg g^{-1}) by this soil, followed by application of rice husk ash (Q_{max} = 30.030 mg g^{-1}), and then control (Q_{max} =25.381 mg g^{-1}). The Langmuir's b constant, which is related to AMPA affinity, was high in the soil added with rice husk ash (0.087), followed by soil with cow dung (0.055), and then control (0.051). The Langmuir separation factor (R) for all the adsorbent was <1, which indicates that adsorption of AMPA was favourable [30], and the most favourable occurred in the soil amended with rice husk ash.

Table 3. Freundlich and Langmuir's models constant for AMPA adsorption by the adsorbents.

Models	Parameters	Control Soil	Benta + Cow Dung	Benta + Rice Husk Ash
Freundlich	K_F **(mg g^{-1})**	4.906	5.692	7.268
	1/n	1.511	1.560	1.265
	r^2	0.778	0.770	0.701
Langmuir	Q_{max} **(mg g^{-1})**	25.381	30.488	30.030
	b	0.051	0.055	0.087
	r^2	0.142	0.224	0.327
	R	0.498	0.481	0.385

The Freundlich and Langmuir adsorption isotherm models are commonly used to describe glyphosate and AMPA adsorption processes. Freundlich is an empirical model which presumes the adsorbent surface heterogeneity and exponential distribution of energy among the surfaces [31], while the Langmuir model deduces uniform energy distribution on the surfaces and no transmigration of the adsorbate in the planer surfaces [32]. The Langmuir model is therefore valid for monolayer sorption on a surface with a finite number of identical sites [33]. The results of the present study, therefore, indicate that adsorption of AMPA by both control and amended soils occurred on heterogeneous adsorption sites. Meanwhile, an increase in values of the constants of Langmuir's model due to the application of cow dung or rice husk ash compared to the control soil (Table 3) suggested a resulting monolayer coverage following the application of these residues. This agrees with Zhelezova et al. [25] who suggested that the application of biochar resulted in specific adsorption site leading to selective interaction with herbicide in soil. On the one hand, both Freundlich and Langmuir models indicated that applying cow dung and rice husk ash increased adsorption capacity of this soil as well its affinity for AMPA. Glyphosate and AMPA exert similar behaviour of adsorption and, therefore, AMPA was reported to be strongly adsorbed by soil containing variable charge surfaces due to oxides of Fe and Al and soil organic matter [14,34–36]. This resulted in less or no adsorption of AMPA on soils containing permanent surface charges [35]. However, an earlier study by Piccolo and Celano [37] reported that glyphosate adsorption by soil organic matter occurred through hydrogen bonding between glyphosate a phosphonic moiety and acidic functional groups of the soil organic matter. This suggests that adsorption of AMPA can occur even in soils with permanent charges provided it had high content of soil organic matter. Durovic et al. [38] reported that sorption interaction of glyphosate involves minerals or organic components of soils or both, but in soil with >5% organic matter the sorption is influenced by organic matter. The soil used in this study had organic matter content of 5.23% (Table 1), therefore, its organic component was suggested to be in the control of AMPA adsorption since this compound exerts the same adsorption behaviour with glyphosate. Borgaard and Gimsing [35] reported that in soil with poorly ordered Al and Fe oxides, a high content of soil organic matter enhances glyphosate adsorption. Table 1 shows a low content of both free and amorphous oxides of Fe and Al in the studied soil. Furthermore, the soil contains mica and smectite which are permanent charge minerals. For these reasons, increasing organic matter content due to addition of cow dung or rice husk ash can increase the adsorption affinity and retention of AMPA by the soils. The reported adsorption mechanisms of glyphosate and AMPA commonly were ion entrapment, surface complexation, H-bonding and ligand exchange [14,39–42]. The present study therefore postulated the adsorption mechanisms of AMPA by this soil to either by AMPA entrapments on the surfaces of cow dung and rice husk ash or H-bonding and ligand exchange between the phosphonic moiety of AMPA and oxygen containing functional groups of the soil organic component.

Few studies previously reported were on AMPA adsorption by natural soils [14,41,43,44] but not on the effects of additional organic matter on AMPA adsorption by these soils. Nonetheless, the present study contradicts the results reported by Gerritsea et al. [43] and Rampazzo et al. [14], who opined that AMPA adsorption by sandy soil decreased with increasing soil organic matter. The probable reason is that the organic matter content used in those studies was <5%, therefore, adsorption of AMPA in their studies was by inorganic soil components. However, in this study, the content of organic matter was >5% and the soil has an evidence of permanent charge surfaces due to its content of smectite and mica. Therefore, its adsorption is solely controlled by soil organic matter [38] and that is why increasing the organic matter by the addition of cow dung or rice husk ash increased AMPA adsorption by this

soil. The Freundlich K_F values obtained in the present study were less than those values reported by Báez et al. [44] and Sidoli et al. [41]. Meanwhile, the reported 1/n values in both of their studies were <1, which attributed to the differences in soil properties and composition. The Alfisol used in Báez et al. [44] contained hematite minerals and high clay particles compared to our soil. For those reasons, the soil used in their study would have a strong affinity for AMPA compared to the one used in the present study. Similarly, Sidoli et al. [41] used a soil of temperate climate with content of oxide minerals ranged between 0.12 and 1.35%. These attributes might be a reason why the soils of their study had a stronger adsorption and higher affinity for AMPA than the soil of the present study.

The results of desorption study revealed an increased in AMPA desorption by 4.22% and 1.78%, respectively, due to addition of cow dung and rice husk ash (Figure 4). This was attributed to an increase in soil pH due to the application of cow dung or rice husk ash which resulted in more AMPA repulsion because of net negative charge surfaces of the molecule and soil [40,41]. The hydrogen bonding occurring between AMPA phosphonic moiety and OH-containing functional groups of soil organic matter was said to be stronger at a low pH [36]. Therefore, any increase in soil pH resulted in the weakening of the hydrogen bonds between AMPA and the sorbate resulting in easier desorption of AMPA previously adsorbed by the adsorption sites. The present result agrees with Erban et al. [6], who reported an increase in AMPA dissipation due to its desorption from the clay loam soil of Prague–Ruzyne, Czechia following the application of compost.
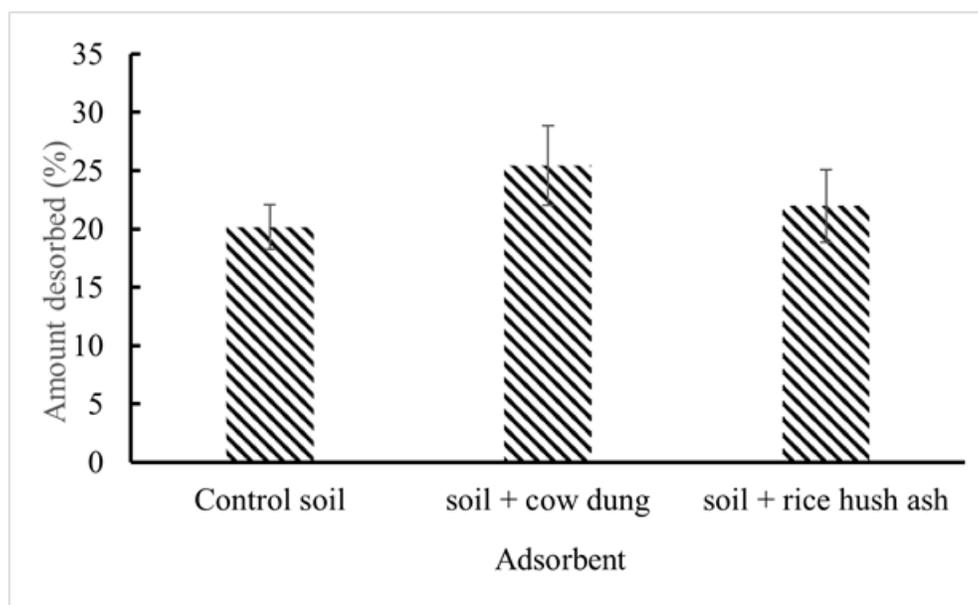

Figure 4. Amount of AMPA desorbed from the adsorbents.

Conclusion

The present study revealed that the application of cow dung and rice husk ash increased AMPA adsorption on this soil. The adsorption isotherm data best fitted to the Freundlich isotherm model ($r^2 \geq 0.701$) and the model constant K_F was high in soil amended with rice husk ash (7.268 mg g^{-1}) indicating its high affinity and strong adsorption for AMPA. This is followed by the cow dung amended soil (5.692 mg/g), and then control soil (4.906 mg g^{-1}). The model constant 1/n for AMPA in both control and amended soils was >1, indicating cooperative adsorption of the compound. However, the desorption study revealed an increase in AMPA desorption by 4.22% and 1.78%, respectively, due to the addition of cow dung and rice husk ash. Therefore, the application of these residues can result in AMPA desorption from this soil, and hence be susceptible to microbial degradation. However, if the soils

have insignificant microbial populations, the application of these materials can result in ground water contamination with AMPA.

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Conflicts of Interest: The authors declared no conflict of interest with the parties or products mentioned in the manuscript.

References

1. Giesy, J.P.; Dobson, S.; Solomon, K.R. Ecotoxicological Risk Assesment for Roundup Herbicide. *Rev. Environ. Contam. Toxicol.* **2000**, *167*, 35–120.

2. Sviridov, A.V.; Shushkova, T.V.; Ermakova, I.T.; Ivanova, E.V.; Epiktetov, D.O.; Leontievsky, A.A. Microbial Degradation of Glyphosate Herbicides (Review). *Appl. Biochem. Microbiol.* **2015**, *51*, 188–195. [CrossRef]

3. Jalaludin, A.; Yu, Q.; Powles, S.B. Multiple resistance across glufosinate, glyphosate, paraquat and ACCase-inhibiting herbicides in an Eleusine indica population. *Weed Res.* **2015**, *55*, 82–89. [CrossRef]

4. Mohamad, R.B.; Awang, Y.; Jusoff, M.S.; Puteh, A. Effect of glufosinate-ammonium, glyphosate and imazapyr herbicides at two spraying volumes on *Imperata cylindrica* (L.) Raeuschel. *J. Food Agric. Environ.* **2011**, *9*, 854–857.

5. Wibawa, W.; Mohamad, R.B.; Omar, D.; Zain, N.M.; Puteh, A.B.; Awang, Y. Comparative impact of a single application of selected broad spectrum herbicides on ecological components of oil palm plantation. *Afr. J. Agric. Res.* **2010**, *5*, 2097–2102.

6. Erban, T.; Stehlik, M.; Sopko, B.; Markovic, M.; Seifrtova, M.; Halesova, T.; Kovaricek, P. The different behaviors of glyphosate and AMPA in compost-amended soil. *Chemosphere* **2018**, *207*, 78–83. [CrossRef]

7. Coupe, R.H.; Kalkhoff, S.J.; Capel, P.D.; Gregoire, C. Fate and transport of glyphosate and aminomethylphosphonic acid in surface waters of agricultural basins. *Pest Manag. Sci.* **2012**, *68*, 16–30. [CrossRef]

8. Van Stempvoort, D.R.; Roy, J.W.; Brown, S.J.; Bickerton, G. Residues of the herbicide glyphosate in riparian groundwater in urban catchments. *Chemosphere* **2014**, *95*, 455–463. [CrossRef]

9. Alexis, G.; Stephanie, P.; Estella, B. AminoMethylPhosphonic acid (AMPA) in natural waters: Its sources, behavior and environmental fate. *Water Res.* **2017**, *117*, 187–197.

10. Glass, R.L. Adsorption of Glyphosate by Soils and Clay Minerals. *J. Agric. Food Chem.* **1987**, *35*, 497–500. [CrossRef]

11. Jonsson, C.M.; Persson, P.; Sjöberg, S.; Loring, J.S. Adsorption of glyphosate on goethite (α-FeOOH): Surface complexation modeling combining spectroscopic and adsorption data. *Environ. Sci. Technol.* **2008**, *42*, 2464–2469. [CrossRef]

12. Piccolo, A.; Celano, G.; Pietramellara, G. Adsorption of the herbicide glyphosate on a metal-humic acid complex. *Sci. Total Environ.* **1992**, *123–124*, 77–82. [CrossRef]

13. Piccolo, A.A.; Celano, G.; Conte, P. Adsorption of Glyphosate by Humic Substances. *J. Agric. Food Chem.* **1996**, *44*, 2442–2446. [CrossRef]

14. Rampazzo, N.; Rampazzo Todorovic, G.; Mentler, A.; Blum, W.E.H. Adsorption of glyphosate and aminomethylphosphonic acid in soils. *Int. Agrophysics* **2013**, *27*, 203–209. [CrossRef]

15. Ismail, B.S.; Kadir, Z.A.; Jusoh, K.; Mat, N. Adsorption-Desorption, Mobility and Degradation of 14 C-Glyphosate in Two Soil Series. *J. Sains Nukl. Malays.* **2002**, *20*, 17–29.

16. Teh, C.B.S.; Talib, J. *Soil Physics Analyses: Volume 1*; Universiti Putra Malaysia Press: Selangor, Malaysia, 2006; ISBN 9833455646.

17. Van Ranst, E.; Verloo, M.; Demeyer, A.; Pauwels, J.M. *Manual for the Soil Chemistry and Fertility Laboratory: Analytical Methods for Soils and Plants Equipment, and Management of Consumables*; University of Ghent: Ghent, Belgium, 1999; ISBN 9076603014.

18. Carter, M.R.; Gregorich, E.G. *Soil Sampling and Methods of Analysis*; CRC Press: Boca Raton, FL, USA, 2006; ISBN 0873718615.

19. Song, W.; Guo, M. Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 138–145. [CrossRef]

20. Tariq, F.S.; Samsuri, A.W.; Karam, D.S.; Aris, A.Z. Phytoremediation of Gold Mine Tailings Amended with Iron-Coated and Uncoated Rice Husk Ash by Vetiver Grass (Vetiveria zizanioides (Linn.) Nash). *Appl. Environ. Soil Sci.* **2016**, *2016*, 4151898. [CrossRef]

21. Boehm, H.P. Surface oxides on carbon and their analysis: A critical assessment. *Carbon* **2002**, *40*, 145–149. [CrossRef]

22. Paramananthan. Malaysian Soil Taxonomy—A Unified Malaysian Soil Classification System. In *Soils of Malaysia*; Param Agriculture Soil Surveys (M) Sdn. Bhd.: Serdang, Selangor, Malaysia, 2000; Volume 1.

23. Akma, N.M.H.; Samsuri, A.W.; Ainie, H.K.; Rosenani, A.B. Sorption-Desorption Study of a Herbicide 2,4-Dichlorophenoxyacetic Acid on Acidic Tropical Soils. *Malays. J. Soil Sci.* **2009**, *13*, 119–131.

24. Garba, J.; Samsuri, A.W.; Othman, R.; Ahmad Hamdani, M.S. Simplified method for derivatization of extractable glyphosate and aminomethylphosphonic acid and their determination by high performance liquid chromatography. *Environ. Res. Technol.* **2018**, *1*, 19–30.

25. Zhelezova, A.; Cederlund, H.; Stenström, J. Effect of Biochar Amendment and Ageing on Adsorption and Degradation of Two Herbicides. *Water Air Soil Pollut.* **2017**, *228*, 216. [CrossRef]

26. Sparks, D.L. *Environmental Soil Chemistry*; Academic Press: Boston, MA, USA, 2003; ISBN 0080494803.

27. Tan, K.H. *Principles of Soil Chemistry*; CRC Press: Boca Raton, FL, USA, 2010; ISBN 1439894604.

28. Wang, H.; Lin, K.; Hou, Z.; Richardson, B.; Gan, J. Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. *J. Soils Sediments* **2010**, *10*, 283–289. [CrossRef]

29. Yu, Y.; Zhou, Q.X. Adsorption characteristics of pesticides methamidophos and glyphosate by two soils. *Chemosphere* **2005**, *58*, 811–816. [CrossRef]

30. Guo, S.; Li, W.; Zhang, L.; Peng, J.; Xia, H.; Zhang, S. Kinetics and equilibrium adsorption study of lead(II) onto the low cost adsorbent-Eupatorium adenophorum spreng. *Process Saf. Environ. Prot.* **2009**, *87*, 343–351. [CrossRef]

31. Maurya, N.S.; Mittal, A.K. Biosorptive Color Removal: Applicability of Equilibrium Isotherm Models. *Pract. Period. Hazard. Toxic Radioact. Waste Manag.* **2010**, *14*, 25–36. [CrossRef]

32. Hamdaoui, O.; Naffrechoux, E. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *J. Hazard. Mater.* **2007**, *147*, 381–394. [CrossRef]

33. Hameed, B.H.; Tan, I.A.W.; Ahmad, A.L. Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon. *Chem. Eng. J.* **2008**, *144*, 235–244. [CrossRef]

34. Piccolo, A.A.; Celano, G.; Arienzo, M.; Mirabella, A. Adsorption and desorption of glyphosate in some European soils. *J. Environ. Sci. Health B* **1994**, *29*, 1105–1115. [CrossRef]

35. Borggaard, O.K.; Gimsing, A.L. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: A review. *Pest Manag. Sci.* **2008**, *64*, 441–456. [CrossRef]

36. Albers, C.N.; Banta, G.T.; Hansen, P.E.; Jacobsen, O.S. The influence of organic matter on sorption and fate of glyphosate in soil—Comparing different soils and humic substances. *Environ. Pollut.* **2009**, *157*, 2865–2870. [CrossRef]

37. Piccolo, A.; Celano, G. Hydrogen-bonding interactions between the herbicide glyphosate and water-soluble humic substances. *Environ. Toxicol. Chem.* **1994**, *13*, 1737–1741. [CrossRef]

38. Durovic, R.; Gajic-Umiljendic, J.; Dordevic, T. Effects of organic matter and clay content in soil on pesticide adsorption processes. *Pesticidi i Fitomedicina* **2009**, *24*, 51–57. [CrossRef]

39. Mazzei, P.; Piccolo, A. Quantitative evaluation of noncovalent interactions between glyphosate and dissolved humic substances by NMR spectroscopy. *Environ. Sci. Technol.* **2012**, *46*, 5939–5946. [CrossRef]

40. De Jonge, H.; De Jonge, L.W. Influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil. *Chemosphere* **1999**, *39*, 753–763. [CrossRef]

41. Sidoli, P.; Baran, N.; Angulo-Jaramillo, R. Glyphosate and AMPA adsorption in soils: Laboratory experiments and pedotransfer rules. *Environ. Sci. Pollut. Res.* **2016**, *23*, 5733–5742. [CrossRef]

42. Gimsing, A.L.; Szilas, C.; Borggaard, O.K. Sorption of glyphosate and phosphate by variable-charge tropical soils from Tanzania. *Geoderma* **2007**, *138*, 127–132. [CrossRef]

43. Gerritsea, R.G.; Beltranb, J.; Hernandeg, F. Adsorption of atrazine, simazine, and glyphosate in soils of the Gnangara Mound, Western Australia. *Aust. J. Soil Res.* **1996**, *34*, 599–607. [CrossRef]

44. Báez, M.E.; Espinoza, J.; Silva, R.; Fuentes, E. Sorption-desorption behavior of pesticides and their degradation products in volcanic and nonvolcanic soils: Interpretation of interactions through two-way principal component analysis. *Environ. Sci. Pollut. Res.* **2015**, *22*, 8576–8585. [CrossRef]