Leaching of Polar Herbicides in the Presence of Designed Carbon Sorbents in Soil

Saba Yavari

Universiti Teknologi Petronas: Universiti Teknologi PETRONAS

Robabeh Asadpour

Universiti Teknologi PETRONAS

Hesam Kamyab (✉ hesam_kamyab@yahoo.com)

Universiti Teknologi Malaysia (UTM) <https://orcid.org/0000-0002-5272-2297>

Sara Yavari

Universiti Teknologi PETRONAS

Shamsul Rahman Mohamed Kutty

Universiti Teknologi PETRONAS

Lavana Baloo

Universiti Teknologi PETRONAS

Teh Sabariah Binti Abd Manan

Universiti Malaysia Terengganu

Shreeshivadasan Chelliapan

Universiti Teknologi Malaysia

Azwadi Bin Che Sidik

Universiti Teknologi Malaysia Malaysia-Japan International Institute of Technology

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Abstract

Imidazolinones are polar herbicides with high leaching potential making them potential threat to environment quality. Biochar, a carbon sorbent, can efficiently stabilize substances and could be used to reduce the pesticides leaching. This work was conducted to study biochar effects on leaching of imazapic, imazapyr, and a mixture of them (Onduty®) for the first time. Leaching columns were used during lab experiments. Soil amendment with biochars produced from oil palm empty fruit bunch and rice husk significantly reduced the herbicides leaching percentages. 16% of imazapic was leached from biochar-free soil. For rice husk and empty fruit bunch biochar-amended soils the amounts were 4.3% and 3.6%, respectively. The highest percentage of imazapyr was leached out from non-amended soil (14.2%) followed by rice husk (4.0%) and empty fruit bunch (2.8%) biochar-amended soils. 15.2% of the applied Onduty® was leached from non-amended soil. Rice husk and empty fruit bunch biochars could reduce the herbicide leaching to 4.2% and 3.0%, respectively. Soil amended with biochars retained the higher percentages of the herbicides in top 7.5 cm depths. Total herbicides amounts adsorbed by biochars were more than 95%. It was concluded that biochar application has the potential to decrease imidazolinones leaching and their environmental pollution.

Introduction

Information about leaching of pesticides applied in crop lands is important to control the chemicals contamination in aquatic ecosystems and potable waters (Briceno, Palma, and Duran 2007). Once applied to agricultural soils, pesticides can be leached down from the plants root zones by water. Leaching is the most problematic process of chemicals movement through which the applied pesticides transfer downward through the soil into the groundwaters by rainfall or irrigation water (Rathore and Nollet 2012). The main factors determining the extent of pesticides leaching are soil and pesticide characteristics, site conditions, pesticide application method and climatic conditions. These factors control pesticides leaching process mostly through their influence on the adsorption capacity of the soil.

There are several techniques that have been used for stabilization of pollutants in the soil environment including electrokinetic (Rezaee, Ghomesheh, and Hosseini 2017), encapsulation (Shen et al. 2019), and application of sorbents such as organophilic clays, ferrous sulfate, and carbon sorbents (Zhang et al. 2010; Shen et al. 2019). Biochar is a carbonaceous sorbent derived from biomass pyrolysis under limited supply of O₂ and at temperatures of less than 700°C (Lehmann and Joseph 2015). Effects of biochar amendment on leaching of pesticides in soils have been investigated frequently (Albarrán et al. 2004; Li et al. 2013; Tatarková, Hiller, and Vaculík 2013). According to Larsbo et al. (2013), application of biochar can have opposing impacts on pesticides leaching depending on soil type and sorption strength of compounds. Effects of biochar application on leaching were shown to be insignificant in loam soil. In clay soil, leaching of moderate mobile pesticides was reduced while that of immobile pesticides enhanced in the presence of biochar. It was concluded that matters originated from the applied biochar facilitated the transfer of the immobile pesticides. Reduction of atrazine leaching in the presence of pine chip biochar was investigated in both lab and field experiments (Delwiche, Lehmann, and Walter 2014).

The results showed that biochar amendment has the potential to decrease leaching of the herbicide in the soil profile. Imidazolinones are the type of polar herbicides that show high mobility and leaching potential. This is due to their high solubility in water and low organic carbon partition coefficients (Moraes et al. 2011; Zanella et al. 2011; Martini et al. 2013). Off-site transport of imidazolinones can cause severe ecological effects because of their high persistent nature and biological activities. Currently, a mixture of two members of this family namely imazapic (5-methyl-2-[4-methyl-5-oxo-4-(propan-2-yl)-4,5-dihydro-1H-imidazol-2-yl] pyridine-3-carboxylic acid) and imazapyr (2-(4-Methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl) pyridine-3-carboxylic acid)) under the trade name of Onduty® is used in Clearfield® production system (CPS) which is applied to herbicide-tolerant crops to control weeds in paddy fields. The physical and chemical characteristics of imazapic and imazapyr herbicides are presented in Table 1.

Table 1
Physical and chemical characteristics of the studies herbicides (Moraes et al. 2011;
Zanella et al. 2011; Martini et al. 2013)

Properties	Imazapic	Imazapyr
Chemical formula	C ₁₄ H ₁₇ N ₃ O ₃	C ₁₃ H ₁₅ N ₃ O ₃
Molar mass (g/mol)	275.303	261.28
Water solubility (mg/L) (25°C, pH = 7)	2,200	11,272
Adsorption-partition coefficient (cm ³ /g)	0.13–4.07	0.07–0.19
Vapor pressure (mPa) (20°C)	< 0.013	< 0.013
Organic carbon-water partition coefficient (L/Kg)	7-267	4-170
Octanol-water partition coefficient	0.393	0.11
Acid dissociation constant	2; 3.9–11.1	1.9; 3.6–11.0
Soil half-life (day)	31–233	30–210

There are several studies which address the intensity of leaching and toxicity of imidazolinones in the environment (Battaglin et al. 2000; Wyk and Reinhard 2001). It was reported that imidazolinone herbicides were one of the most frequently found herbicides groups in Iowa and Illinois states' groundwaters (Battaglin et al. 2000). Presence of imazapyr was reported in groundwater of Sweden after 8 years of its application in agricultural fields (Börjesson, Torstensson, and Stenström 2004). It has been indicated that leaching of imidazolinones is higher in tropical soils in comparison with temperate areas because of intensive leaching due to heavy rainfall (Souza et al. 2000; Oliveira, Koskinen, and Ferreira 2001). Imazethapyr was detected in rivers and groundwaters in southern Brazil where the application was widely used in paddy fields (Battaglin et al. 2000). Leaching potential of imazapyr herbicide in different Brazilian soils was investigated under an artificial irrigation with intensity of 40 mm/hour similar to the rain intensity of the area. Depending on soil texture, up to 34% of the herbicide leached out from the soil (Oliveira, Koskinen, and Ferreira 2001). Type of soil and the rainfall amount influence the rate of leaching

(Wyk and Reinhard 2001). The leaching of imazethapyr can go beyond 30 cm of soil column. Souza et al. (2000) showed that the imazapyr mobility was higher in sandy loam soil than in clay soil. There is no available knowledge on imidazolinones leaching in the presence of biochars in tropical soils. Thus, this study aimed to evaluation the effects of agricultural wastes biochars application in Malaysian paddy field soil on the retention and leaching of imazapic, imazapyr, and Onduty® herbicides.

Materials And Methods

Collection and characterization of soil samples

The soil sample for this experiment was taken from the paddy fields of federal land consolidation and rehabilitation authority (FELCRA) Seberang Perak where is one of the main paddy fields in Malaysia applying CPS. This area is located at 4° 7′ North and 101° 4′ East. The soil sampling was done following a simple random pattern (Huang, Legarsky, and Othman 2007) and from 0 to 15 cm soil depth. Three replicates of samples were evaluated for their properties. The air-dried soil samples were grinded, sieved through a 2 mm mesh, and then characterized.

The measured physical and chemical properties of the soil were included particle size distribution (pipette method), total organic carbon (TOC) (TOC analyzer instrument, SSM-5000A, Shimadzu, Japan), cation exchange capacity (CEC) (ammonium acetate extraction method), and pH (pH meter, HACH, sension 2) (Jones Jr 2001; Minasny et al. 2011; Beretta et al. 2014). The physical and chemical properties of the soil sample are shown in Table 2.

Table 2 Physical and chemical properties of the soil sample taken from FELCRA area paddy fields					
Particle size distribution (%)			TOC (%)	CEC (cmol(+)/kg)	pH
Clay	Silt	Sand	0.99 ± 0.08	12.55 ± 0.6	6.36 ± 0.1
37.99 ± 2.5	21.58 ± 1.1	40.29 ± 2.6			

Preparation and characterization of the designed biochars

Oil palm empty fruit bunch (EFB) and rice husk (RH) were used as low-cost and sustainable pyrolysis feedstock in this study. EFB and RH biomasses were obtained from a plantation of oil palm and a rice mill in Perak state, respectively. EFB biomass was shredded into small pieces (< 3 cm) before conversion process. Each biomass was dried (80°C, 12 hours) and then pyrolyzed in an optimized condition by a N₂-purged tube furnace (OTF-1200X-80, USA). The optimized pyrolysis conditions were peak temperature of 300°C, heating rate of 3°C/min, and reaction residence time of 1 hour (for EFB biochar) and 3 hours (for RH biochar) as were determined through our previous work (Yavari et al. 2017). In these conditions the biochars adsorption capacities were maximized. The characteristics of the designed biochars (see Table 3) and Freundlich sorption coefficients (K_f) of biochar-free and biochar-amended soils (1.0% w/w) were also measured previously (Yavari et al. 2017).

Table 3
Physical and chemical characteristics of the designed EFB
and RH biochars (Yavari et al. 2017)

Characteristics	Designed biochars	
	EFB	RH
Yield (%)	46.25	58.12
Moisture (%)	4.85	3.43
Volatile matter (%)	7.03	6.56
Ash content (%)	22.58	22.24
pH	6.13	6.32
CEC (cmol+)/kg)	83.90	70.73
Carbon (%)	58.60	48.26
Oxygen (%)	31.48	25.08
Hydrogen (%)	3.80	2.30
Nitrogen (%)	1.61	0.11
Sulfur (%)	0.48	0.21
O/C (molar ratio)*	0.40	0.38
H/C (molar ratio)**	0.38	0.28
(O + N)/C (molar ratio)***	0.42	0.39
Total surface area (m ² /g)	1.46	1.99
Total pore volume (mL/g)	0.005	0.006
Pore radius (Å)	104.30	186.89
* Hydrophilicity index, ** Aromaticity index, *** Polarity index		

Chemicals and instruments

Standards of each imazapic and imazapyr herbicide (99.9% purity) and Onduty® herbicide were purchased from Sigma-Aldrich (Seelze, Germany) and baden aniline and soda factory (BASF, Malaysia), respectively. Stock solution (1000 mg/L) of each herbicide was prepared in background electrolyte that was ultra-pure water (Millipore Milli-Q® system) containing 0.01 M calcium chloride (CaCl₂) and 200 mg/L mercury chloride (HgCl₂). All chemicals and solvents were bought from Fisher Chemical (UK). Solid phase extraction (SPE) cartridges and vacuum extraction manifold assembly were purchased from

Agilent Technologies (USA). High-performance liquid chromatography (HPLC) grade solvents were provided by Merk (KGaA, Darmstadt, Germany).

Leaching experiment

Leaching columns accompanied with rainfall simulator were used to perform this experiment. The columns were made from 24 cm lengths of 10 cm inner diameter acrylic glass pipe. The bottom of each column was closed with a perforated plate which allowed the leachate to drain into collecting containers. The bottom of each leaching column was filled with 3 cm thick layer of gravel to avoid losses of soil particles. The columns were then packed with free soil and biochar-amended soils (1.0% w/w) uniformly to a height of 15 cm.

The leaching experiment was carried out at a steady-flow state by applying background solution to the soils surfaces using the rainfall simulator. The solution flow was conducted from a reservoir to the top of each column through tubes by a peristaltic pump and the solution was poured into the soil column through 10 fine holes. Flow rate was adjusted by the pump to 6.8 mL/min that simulates the highest rain intensity recorded in the soil sampling area (Shah et al. 2013). The soil columns were saturated during 2 hours and allowed to drain for 48 hours to obtain uniform moisture content and re-arrangement of the soil particles. After the incubation period, each herbicide (imazapic, imazapyr and Onduty®) was applied separately to a set of media (soil, EFB biochar-amended soil and RH biochar-amended soil). For that, a 2 mL aliquot of 100 mg/L herbicide solution was applied to the surface of soil column giving an initial herbicide concentration of 0.2 µg/g in soil, equivalent to the herbicides field application rates (Azmi et al. 2012). The columns were then subjected to constant down-ward flows of background solution. The leachates were collected in 200 mL fractions. Sample collection was continued until the herbicides concentrations reached the lowest amount. Reaching this point took 10 hours when the volume of eluted leachate was at quantities equivalent to 7 pore volumes of the soil (4000 mL). 24 hours after completion of the leaching process, the soil in each column was divided into 2 equal parts in length (each 7.5 cm) and the amount of remaining herbicide in each section was determined. Each experimental run was performed in triplicate.

Extraction of herbicides from collected leachates and soils

Improved SPE procedures for imidazolinone herbicides extraction were applied to the herbicides from both aqueous and soil samples (Lao and Gan 2006; Ramezani 2008). Extraction of the herbicides from the leachate was performed using Bond Elut-PPL cartridge. During its conditioning step, the cartridge was primed with two rinses of 3 mL dichloromethane (CH₂Cl₂) followed by two rinses of 3 mL methanol (CH₃OH) and then three rinses of 2 mL ultra-pure water (pH = 2). 5 L of each aqueous sample (pH = 2) were loaded into the conditioned cartridge. The herbicide was then eluted by two rinses of 3 mL CH₂Cl₂. The solvent was evaporated to near dryness using the nitrogen gas evaporator. Finally, an aliquot of 4 mL isopropanol (C₃H₈O) was added and evaporated to get the solvent final volume of 1 mL.

In order to extract the studied herbicides from the soils, each soil sample was mixed with 0.5 M sodium hydroxide (NaOH) in a ratio of 1:4 (soil: NaOH) and then was shaken for 1 hour. The shaken suspension was centrifuged (6000 rpm, 10 minutes) and then filtered through glass fiber filter (GF/C, 70 mm, and pore size 1.2 μm). The extract was acidified (pH = 2). Bond Elut- C_{18} and Bond Elut-SCX cartridges were used in series to clean up the soil extract. C_{18} cartridge was primed with 5 mL CH_3OH followed by 5 mL ultra-pure water and SCX cartridge was conditioned with 5 mL hexane (C_6H_{14}), then 5 mL CH_3OH followed by 5 mL ultra-pure water. During sample loading step, the extract of soil was passed through C_{18} cartridge. For elution of the herbicide from C_{18} cartridge, the cartridge was stacked on top of the SCX cartridge and the herbicide was eluted by 20 mL CH_3OH :ultra-pure water (1:1). C_{18} cartridge was removed and SCX cartridge was washed by 5 mL ultra-pure water. 20 mL 0.05 M phosphate buffer (pH = 2) was used to elute the herbicide from SCX cartridge. The herbicide was partitioned by 3 vigorous washes with 15 mL CH_2Cl_2 . The solvent was evaporated to near dryness under a gentle stream of N_2 gas and then the herbicide was re-dissolved in 1 mL $\text{C}_3\text{H}_8\text{O}$.

HPLC analysis

Concentrations of the herbicides in the solutions were measured using HPLC (Agilent 1100 series) equipped with variable wavelength (240 nm) and diode array detectors, a quaternary pump, and a vacuum degasser. The chromatographic column was ZORBAX SB- C_{18} (150 mm $\times$ 4.6 mm, 5 μm particle size). Isocratic mobile phase (acetonitrile ($\text{C}_2\text{H}_3\text{N}$):1.0% acetic acid in ultra-pure water = 35:65) was used in 1 mL/minute flow rate. The volume of injection was 20 μL . In this chromatographic condition, the retention time was 2.9 minutes for imazapic herbicide and 2.3 minutes for imazapyr herbicide.

Statistical analysis

Breakthrough curves related to leaching of each herbicide in the media were obtained using the Excel® spreadsheet program. Correlation coefficient between the media K_f and both total amount of each herbicide leached and total amount of each herbicide remained in the soil was determined with 95% confidence level. Duncan's multiple range tests at probability levels of $\alpha = 0.05$ were applied to examine the significance between the sets of means. The calculations were conducted using statistical analysis system (SAS) (version 9.1 for Windows; SAS Institute, Inc. Cary, NC, USA).

Results And Discussion

Breakthrough curves of imazapic in non-amended and biochars-amended soils are presented in Fig. 1. The patterns of the curves were significantly different. Generally, in the biochar-free soil imazapic was leached out earlier in comparison with the biochars-amended soils. Maximum value of relative concentration (ratio of herbicide amount in leachate to its initial amount applied to the soil, C_t/C_0) of imazapic leached from biochar-free soil was 0.0240 which was obtained after collection of 1800 mL leachate from the column, while the maximum values for EFB and RH biochars-amended soils were 0.0075 and 0.0090, respectively. These amounts were obtained at higher cumulative volumes of

leachates, 3000 mL for EFB biochar- and 2800 mL for RH biochar-amended soils. These results obviously showed that the biochars applications delayed the leaching of imazapic from the soils columns. Data presented in Table 4 show the percentages of total amounts of herbicides leached out from biochar-free and biochar-amended soils. Based on achieved data, 16.1% of applied imazapic was leached from biochar-free soil. Amendment of soil with biochars significantly reduced ($P < 0.05$) the herbicide leaching. The total amount of imazapic leached out from EFB biochar-amended soil was 3.6% and that of RH biochar-amended soil was 4.3%.

Table 4 Freundlich sorption coefficients (K_f), percentages of herbicides leached out from soil columns and herbicides remained in different depth of soils

Media	Herbicide	K_f	Amount of leached herbicides (%)	Amount of remained herbicides (%) in different soil depths (cm)	
				0-7.5	7.5-15
Soil	Imazapic	1.80	16.1 ± 0.2 a*	54.8 ± 2.9 d	28.6 ± 1.3 ab
	Imazapyr	1.91	14.2 ± 0.3 a	58.6 ± 2.4 d	26.7 ± 2.4 bc
	Onduty®	1.87	15.2 ± 0.2 a	56.9 ± 3.1 d	27.5 ± 1.7 bcd
EFB biochar-amended soil	Imazapic	4.497	3.6 ± 0.2 b	65.7 ± 4.7 c	30.3 ± 3.4 a
	Imazapyr	6.382	2.8 ± 0.1 b	72.8 ± 3.5 a	24.3 ± 3.3 d
	Onduty®	5.435	3.0 ± 0.2 b	70.6 ± 2.2 ab	25.9 ± 2.6 cd
RH biochar-amended soil	Imazapic	4.385	4.3 ± 0.3 b	64.6 ± 4.3 c	30.6 ± 2.0 a
	Imazapyr	4.742	4.0 ± 0.1 b	66.7 ± 2.5 bc	28.9 ± 1.6 ab
	Onduty®	4.521	4.2 ± 0.2 b	67.0 ± 1.8 bc	28.3 ± 2.5 ab
*Different letters indicate significant differences ($p < 0.05$)					

Application of the designed biochars to the soil also decreased total amount of leached imazapyr herbicide from soil after 7 soil pore volumes (4000 mL) (Table 4). The highest percentage of imazapyr leached out from non-amended soil (14.2%), followed by RH biochar- (4.0%) and EFB biochar-amended soils (2.8%). Different breakthrough curve patterns were obtained in free and biochars-amended soils (Fig. 2). Leaching of imazapyr in the pure soil occurred earlier and the maximum value of relative concentration (0.02) was obtained after leaching of 2200 mL effluent. The maximum concentrations of imazapyr in leachates of soils amended with EEB biochar (0.0072) and RH biochar (0.0047) were seen at higher cumulative volumes of leachates equal to 3400 mL and 2600 mL, respectively.

Leaching of Onduty® herbicide followed similar pattern to those of imazapic and imazapyr herbicides (Fig. 3). Relative concentration of Onduty® reached to its maximum (0.0218) in leachate of biochar-free soil after collection of 2000 mL effluent. The maximum relative concentrations were 0.0061 for EFB biochar- and 0.0072 for RH biochar-amended soil which were obtained at leachates cumulative volumes

of 3200 mL and 3000 mL, respectively. According to the data presented in Table 4, 15.2% of the applied Onduty® was leached from non-amended soil. Addition of EFB and RH biochars to soil could significantly reduce the herbicide leaching to 3.0% and 4.2%, respectively.

Percentages of the remained herbicides in upper and lower parts of the soils columns are presented in Table 4. In all media, the higher amounts of the herbicides were retained in the top 7.5 cm soil depths. Comparison of the herbicides amounts in each soil depth between the media shows that the soil amended with EFB biochar retained the highest amounts of herbicides followed by RH biochar-amended soil and the lowest amounts were measured in the biochar-free soil. Highest and lowest effects were observed for imazapyr and imazapic herbicide, respectively. Amounts of herbicides retained in the soils were inversely related to the amounts of herbicides leached out from each column. This was possible because of higher capacity of designed EFB biochar in herbicides sorption and also higher affinity of imazapyr herbicide to bind to the media (Table 4). Correlations between media K_f values and both percentages of total amounts of herbicides leached out from columns and amounts of herbicides remained in the soils after leaching process are shown in Table 5. The results indicated that the amounts of herbicides leached out from the soils were negatively correlated with the media sorption capacities. As K_f values increased, the percentages of herbicides leached out from the columns reduced. The correlation between K_f values and the amounts of herbicides remained in the soils was positive, indicating that mobility of herbicides decreased with increasing media sorption capacities.

Herbicide	Amount of leached herbicides (%)	Amount of remained herbicides (%)
Imazapic	-0.98* $p < 0.01$	0.95* $p < 0.04$
Imazapyr	-0.98* $p < 0.01$	0.98* $p < 0.01$
Onduty®	-0.95* $p < 0.04$	0.96* $p < 0.03$

Table 5 Pearson's r and level of significance (p -value) for correlations between the media K_f values and the percentages of leached out and remained herbicides

*Correlation is significant at 0.05 level

According to Table 4, the percentages of total amounts of imazapic, imazapyr and Onduty® adsorbed by the biochar-free soils columns were 83.4%, 85.3% and 84.4%, respectively. 96.0% imazapic sorption was achieved in presence of designed EFB biochar in soil. Removal of 97.1% for imazapyr and 96.5% for Onduty® herbicide were achieved in soil with biochar application. Addition of designed RH biochar to the soil increased imazapic, imazapyr and Onduty® herbicides stabilization to 95.2%, 95.6% and 95.3%,

respectively. Therefore, reductions of the herbicides leaching were promising findings to reduce the environmental threats of the applied herbicides.

Many studies have also reported the enhanced sorption of pesticides in biochar-amended soils that resulted in reduction of their leaching when compared to biochar-free soils. (Albarrán et al. 2004; Tatarková, Hiller, and Vaculík 2013; Delwiche, Lehmann, and Walter 2014). During a study conducted by Li et al. (2013), low-temperature wood biochar was evaluated as a sorbent to decrease the mobility of 2,4-D and acetochlor herbicides using leaching columns. According to their results, the biochar had potential to control leaching of herbicides significantly and could reduce the amounts of leached herbicides by half. In other attempt, Hagner et al. (2013) showed that birch wood-derived biochar can decrease the leaching rate of glyphosate herbicide in soil. So, addition of biochar can be considered as an effective strategy to decrease the impact of pesticides residue on the environment and ecosystem.

Conclusion

Leaching of imidazolinones can be a risk to aquatic environment particularly those with high biological activity and enclosed in nature. This study shows that application of designed EFB and RH biochars has the potential to impact the fate of imazapic, imazapyr and Onduty[®] herbicides in the soil by reducing their leaching. So that the highest percentage of the herbicides was leached out from non-amended soil followed by RH biochar- and EFB biochar-amended soils. Higher amounts of the herbicides were retained in top part (7.5 cm) of the soil columns and the biochar-amended soils retained the highest percentages of the herbicides (> 95%). As a conclusion, the designed EFB and RH biochars have the potentials to be used as eco-friendly and cost-effective bio-sorbent in soil to reduce the leaching of imidazolinone herbicides and protect the environment against their pollution. Short- and long-term experiments in field are recommended to be conducted for better understanding of biochar effects on the binding and leaching reduction of pesticides.

Declarations

Availability of data and materials

Not applicable.

Competing interests

Acknowledgment

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Authors' contribution

Conceptualization: S.Y, R.A, H.K, S.C,A.B.C.S, S.Y, S.R.M.K, L.B and T.S.B.A.M; Methodology: S.Y, R.A, and H.K.; Investigation: S.Y in the field; Formal analysis: S.Y, R.A, and S.C; Writing: S.Y, R.A, H.K, S.C, A.B.C.S, S.Y, S.R.M.K, L.B and T.S.B.A.M; Supervision: S.R.M.K, L.B and T.S.B.A.M.

Code availability

Not applicable.

Conflict of interest

The authors declare that there are no conflicts of interest

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Figures

Figure 1

Breakthrough curves of imazapic herbicide in non-amended and EFB and RH biochars-amended soils

Figure 2

Breakthrough curves of imazapyr herbicide in non-amended and EFB and RH biochars-amended soils

Figure 3

Breakthrough curves of Onduty® herbicide in non-amended and EFB and RH biochars-amended soils