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The fate of imazapyr herbicide in the soil amended with carbon sorbents

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Abstract

Excessive application of agro-chemicals is a major factor in undesired environmental problems. Imidazolinone herbicides having high activity, leaching potential, and persistence are probable risks to ecosystems. Herbicides' stabilization using biochar is an efficient and cheap strategy to protect the environment against their contaminations. The present study aimed to evaluate the effects of biochars produced from oil palm empty fruit bunches (EFB) and rice husk (RH) on imazapyr fate in soil. Initially, the optimized biochars were compared for their sorption-desorption capacities as soil modifiers. The herbicide leaching in the amended soils was investigated by leaching columns. The herbicide photolysis and bio-degradations' rates in the media were also evaluated during 70 days. Results indicated that the soil amendment significantly increased soil sorption capacity (up to 2.34-folds) and reduced the herbicide leaching. The lowest percentage of leached herbicide (2.8%) and the highest percentage of retained herbicide (97.1%) were achieved in EFB biochar-amended soil. The herbicide photo-degradation rate significantly reduced with a half-life of 38.5 days in non-amended soil to 53.3 days in EFB biochar-amended soils. The herbicide bio-degradation, however, increased with the biochars applications. In a conclusion, the optimized biochars have a high potential to protect the environment against herbicides hazards.

Keywords Imidazolinones; · Carbon sorbent; · Leaching; · Photo-degradation; · Bio-degradation

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1 Introduction

In West Africa, Elaeis guineensis (an oil palm species) is widely used. Today, the aforementioned oil palms are grown as the most important economic plantation crop in tropical countries [3]. The majority of edible oils come from oil palm fruits, which can produce up to 38.5 106 t of oils per year in terms of oil palm biomass [18, 19]. The application of pesticides in agricultural areas can pose potential risks to the environment [2]. Imidazolinones, a family of herbicides, have attracted environmental concerns due to their high leaching potential, persistent nature, and high phytotoxicity [27, 30]. Characteristics of imazapyr, a member of this family are shown in Table 1. Imidazolinones can be used in the Clearfield® production system (CPS). Currently, the application of CPS is growing in paddy fields [5]. Therefore, consideration of effective solutions to remove their contaminations is critical.

There are a variety of techniques that have been used for environmental remediation mainly applying the process of degradation (e.g., bio-degradation, photolysis, and

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Table 1 Physico-chemical characteristics of imazapyr herbicide [27, 30]

Characteristic	Value
Molecular formula	$C_{13}H_{15}N_3O_3$
Water solubility at 25 °C, pH=7 (mg/L)	11,272
Adsorption partition coefficient (K_d) (L/kg)	0.07–0.19
Vapor pressure at 20 °C (mPa)	< 0.013
Organic carbon partition coefficient (K_{oc}) (L/Kg)	4–170
Octanol/water partition coefficient (log K_{ow})	0.11
Acid dissociation constant (pK_a)	1.9; 3.6–11.0
Soil half-life (day)	30–210

chemical degradation) [13, 26, 33], extraction (e. g. phytoremediation and electrokinetic) [31, 38], or stabilization [10, 35]. Mitigation of pollutants availability through increasing their sorption is a widely used technique to remediate the polluted media. A wide range of organic compounds including biochar can be used for immobilization of the soil and water contaminants [1, 36]. Biochar is a carbonaceous material produced during the pyrolysis process which is a thermo-chemical decomposition (< 700 °C) of biomass in the limited supply of O_2 [23]. Biochar is produced as a cost-effective and eco-friendly sorbent. The ability of biochar to stabilize organic and mineral compounds is due to its Physico-chemical properties such as porous structure, expanded specific surface area, high organic carbon content, active functional groups, and high cation exchange capacity (CEC) [25]. Many studies have demonstrated immobilization of applied pesticides in agricultural fields amended with biochars which led to control their environmental risks [17, 20].

Based on Larsbo et al. [22], biochar can have opposing impacts on pesticides leaching depending on soil type and sorption strength of the 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 material originating from the applied biochar facilitated the transfer of the immobile pesticides. Reduction of atrazine leaching in the presence of pine chip biochar was reported in both lab and field ([4, 12]).

Amendment of soil with biochar is predicted to decrease pesticides availability and the rate at which they are degraded in the soil [9]. However, some studies showed that pesticides micro-degradation can be stimulated by biochar in soil. Biochar can change the nature and activity of microbial communities and thus the soil microbiological characteristics (37, 28).

According to the available knowledge, hydrolysis is not generally considered an important process in the

disappearance of imidazolinones [15]. It is shown that photolysis and bio-degradations are the main processes for imidazolinone herbicides losses in the environment [8]. Given the persistent nature of these herbicides, it is important to investigate the factors affecting their leaching and degradation in soil. There is no existing information on imidazolinones fate in the presence of biochars in soils. Therefore, the objective of this study was to investigate the effects of designed biochars application on the behaviour and fate of imazapyr in soil. Empty fruit bunch (EFB) of oil palm and rice husk (RH), the locally-available agricultural wastes, were used as sustainable and cheap pyrolysis materials in this study.

2 Materials and methods

2.1 Soil, biochars, and chemicals

Soil sample (0–15 cm depth) was collected from paddy fields located in the federal land consolidation and rehabilitation authority (FELCRA) Seberang Perak area which is the biggest Malaysian paddy estate applying CPS. The sample was taken from the plots with no previous history of imidazolinones application. The air-dried sample was passed through a 2-mm sieve and then characterized using standard methods as were applied in our previous works [39]. The soil texture was clay loam (37.99% clay). Its pH, total organic carbon, and CEC values were 6.36, 0.99%, and 12.55 cmol(+)/kg, respectively.

The collected EFB and RH biomasses were dried and pyrolyzed using a pure nitrogen-purged tube furnace (OTF-1200X-80, USA). The conditions were temperature of 300 °C, a heating rate of 3 °C/min, and reaction retention time of 1 h and 3 h for EFB and RH biochars, respectively. These conditions in which the maximum capacity for stabilization of imazapyr was achieved had been determined through our previous study [39]. The characteristics of the designed biochars are presented in Table 2.

The analytical standard of imazapyr (purity > 99.9%) was purchased from Sigma-Aldrich (Seelze, Germany). The herbicide stock solution (1000 mg/L) was prepared in a background electrolyte of 0.01 M calcium chloride ($CaCl_2$) and 200 mg/L mercury chloride ($HgCl_2$). Chemicals were purchased from Fisher Chemical (UK). Vacuum extraction manifold assembly and solid-phase extraction (SPE) cartridges were bought from Agilent Technologies (USA). Ultra-pure water was provided using a Millipore Milli-Q® system. High-performance liquid chromatography (HPLC) grade solvents were purchased from Merk (KGaA, Darmstadt, Germany).

Table 2 Physico-chemical characteristics of the designed EFB and RH biochars [39]

Characteristic	Biochar	
	EFB	RH
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
O/C (molar ratio) (Hydrophilicity index)	0.40	0.38
H/C (molar ratio) (Aromaticity index)	0.38	0.28
(O+N)/C (molar ratio) (Polarity index)	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

2.2 Sorption-desorption experiment

The designed EFB and RH biochars were separately mixed into the soil (1.0% w/w) in plastic containers. Non-amended soil was also evaluated as control. Each media was wetted with de-ionized water to its field water holding capacity (FC) (21.61%) and then incubated at 25–30°C. The moisture contents were maintained constant during the experiment period. Sorption capacities of the media were measured just after incorporation of the biochars to the soil and at 10-day intervals until the readings reached constant amounts (70 days). Batch equilibrium technique [32] was applied for the sorption experiment during which different concentrations (0, 0.5, 1, 2, 4, 6, 8, and 10 mg/L) of the imazapyr solution (20 mL) were separately added to 10 g of each media in centrifuge tubes. The suspensions were shaken (250 rpm, 24 h, and 25 °C) and centrifuged (7000 rpm, 10 min). The supernatants were filtered by a polyvinylidene difluoride (PVDF) membrane filter (0.45 μm of pore size) and then analysed for the herbicide concentration. The conventional single-step decant-refill technique was applied for the desorption experiment [40]. After the sorption experiment, 10 mL of background solution was added to the remaining slurry of each tube to achieve the initial volumes (20 mL) of the herbicide solution. Then, the suspensions were shaken, centrifuged, filtered, and analyzed.

2.3 Leaching experiment

Leaching columns (24 cm height × 10 cm diameter) accompanied with a rainfall simulator were used to perform this experiment. The columns were filled with gravel (3 cm) then packed with each media uniformly to a height of 15 cm.

The background solution flow (6.8 mL/minute) was conducted from a reservoir to the top of each column through tubes by a peristaltic pump. The soil columns were saturated for 2 h. After an incubation period (48 h), the herbicide was applied to the media in an initial herbicide concentration of 0.2 μg/g in soil [5]. The columns were then subjected to the constant down-ward flows of background solution simulating the highest rain intensity in the area [34]. The leachates were collected in 200 mL fractions. Sample collection was continued until the herbicide concentration reached the lowest amount after 7 soil pore volumes (4000 mL eluted leachate). 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 also determined.

2.4 Photolysis and bio-degradation experiments

Photo-degradation of imazapyr herbicide was evaluated on the surface of the soil in the presence and absence of each EFB and RH biochar (1.0% w/w) for 70 days. 30 g of each biochar-free and biochar-amended soil was placed into glass Petri dishes (2.5 cm height × 14 cm diameter) and spread (2 mm depth). After autoclave-sterilizing, each media was uniformly spiked with the herbicide (0.2 μg/g). The solar irradiation was simulated using a high-pressure mercury vapour fluorescent lamp (400 W/m^2) located at 30 cm above the samples [7]. A series of experimental units were kept in the dark at 25 °C to evaluate the possible impacts of chemical and bio-degradation throughout the experiment.

To conduct the bio-degradation experiment, 10 g dry weight of each media was placed in dark glass containers and moisturized to FC with de-ionized water. There were two sets for each media. One set was sterilized through autoclaving. The other set was non-sterilized and the containers were covered with perforated parafilm sheets. Each media was homogeneously spiked with imazapyr herbicide to give an initial concentration of 0.2 μg/g and then were incubated with constant moisture contents in darkness (25 °C) for 70 days. For each degradation experiment, the sample collection (10 g) and analysis were conducted at the intervals of 0, 7, 14, 28, 42, 56, and 70 days after the herbicide application.

2.5 Herbicide extraction and analysis

To extract the herbicide from leachates, the Bond Elut-PPL cartridge was conditioned with dichloromethane, methanol, and then ultra-pure water (pH = 2) (each 6 mL). Five liters of each aqueous sample (pH = 2) was loaded into the conditioned cartridge. The herbicide was then eluted by 6 mL dichloromethane. The solvent was evaporated to near dryness by the N$_2$ evaporator. Then, an aliquot of 4 mL isopropanol was added and evaporated to get the volume of 1 mL.

To extract the herbicide from the media, each sample was mixed with 0.5 M sodium hydroxide in a ratio of 1:4 (soil: sodium hydroxide) and shaken for 1 h. The suspension was centrifuged (6000 rpm, 10 min) and then filtered through a glass fiber filter (GF/C, pore size 1.2 μm, 70 mm). C_{18} cartridge was primed with 5 mL methanol followed by 5 mL ultra-pure water and SCX cartridge was conditioned with 5 mL hexane, then 5 mL methanol followed by 5 mL ultra-pure water. Then, the soil extract (pH = 2) was passed through C_{18} cartridge. To elute the herbicide from C_{18} cartridge, the cartridge was stacked on top of SCX cartridge and the herbicide was eluted by 20 mL methanol:ultra-pure water (1:1). C_{18} cartridge was discarded and SCX cartridge was washed with 5 mL ultra-pure water. Elution of the herbicide from SCX cartridge was done by 20 mL 0.05 M phosphate buffer (pH = 2). The herbicide was partitioned by three vigorous washes with 15 mL dichloromethane. The solvent was evaporated to near dryness and then the herbicide was re-dissolved in 1 mL isopropanol.

Herbicide concentrations in the solutions were analyzed using HPLC (Agilent 1100 series). ZORBAX SB-C_{18} (150 mm × 4.6 mm, 5 μm particle size) was used as the detection column. Acetonitrile to 1.0 % acetic acid in ultra-pure water (35:65) was used as isocratic mobile phase with a flow rate of 1 mL/minute. The retention time for imazapyr herbicide was 2.3 minute.

2.6 Data analysis

The amount of the herbicide adsorbed on each media after the adsorption process S_{ads} (mg/kg) was calculated by equation 1.

$$S_{ads} = (C_0 - C_{ads}) \times V/M \tag{1}$$

where C_0 (mg/L) and C_{ads} (mg/L) are initial and final concentrations of the herbicide in the solution, respectively. V (mL) is the solution volume and M (g) is the mass of soil.

The amount of herbicide remaining adsorbed on the soil after the desorption process (S_{des} (mg/kg)) was calculated by equation 2.

$$S_{des} = S_{ads} - [(C_{des} - 1/2 \times C_{ads}) \times V/M] \tag{2}$$

where C_{des} is the herbicide concentration in the solution at desorption equilibrium.

To describe the sorption process, linearized form of the Freundlich model was used like the following equation [32]:

$$\log S_{ads} = 1/n \times \log C_{ads} + \log K_f \tag{3}$$

where K_f ((mg/kg)/(mg/L)$^{1/n}$) is the Freundlich sorption coefficient indicating the soil adsorption capacity and n is a measure of the sorption intensity.

The hysteresis index (HI) was calculated according to equation 4 [40].

$$HI = (S_{ads} - S_{des}/S_{ads}) \tag{4}$$

Breakthrough curves related to leaching of the herbicide in the media were obtained using the Excel® spreadsheet program.

A first-order model was used for the determination of the herbicide degradation rate constants (K) (per day) as shown in equation 5.

$$\ln C_t = \ln C_0 - K \times t \tag{5}$$

where C_t is the herbicide concentration at time t, C_0 is its initial concentration, and t is the time.

After the determination of K values, the herbicide half-life was calculated using equation 6.

$$t_{1/2} = \ln 2/K \tag{6}$$

Each experimental run was performed in triplicate. ANOVA was conducted by a statistical analysis system (SAS) (version 9.1 for Windows; SAS Institute, Inc. Cary, NC, USA). Duncan's multiple range tests were applied to examine the significance between the sets of means. Correlation coefficients between the media K_f and each total amount of the herbicide leached, remained, and herbicide half-life was determined with a 95% confidence level.

3 Results and discussion

3.1 Adsorption-desorption of imazapyr herbicide

Imazapyr showed a high affinity to bind to the biochars. Table 3 presents the parameters related to the adsorption of imazapyr on the non-amended and amended soils. Data were fitted well to the Freundlich model with high R^2 values (≥ 0.93). The value of soil K_f was 1.91. The value was increased (2.34-folds) in soil amended with EFB biochar and reached 6.38. The effect of RH biochar was found to be significantly lower ($K_f = 4.74$, 1.48-folds) than EFB biochar. Data obtained from the desorption experiments demonstrated that the sorption process was more reversible in non-amended soil compared to biochars amended soils (Table 3). HI, the value of soil

Table 3 Freundlich parameters for adsorption and desorption of imazapyr on non-amended and EFB and RH biochars-amended soils

Media	Freundlich adsorption parameters			
	K_f	n	R^2	HI
Soil	1.91±0.05	1.1	0.99	0.16±0.01
EFB biochar-amended soil	6.38±0.02	2.8	0.95	0.01±0.02
RH biochar-amended soil	4.74±0.01	2.7	0.93	0.02±0.01

amounted to 0.16. Among the biochars, a higher value was related to RH biochar (0.02) which had a lower affinity for the herbicide rather than EFB biochar (0.01).

Figure 1 presents the changes in K_f and CEC values of non-amended and amended soils during 70 days' incubation experiment. Generally, capacities of the amended soils in sorption of the herbicide showed increasing trends during the first weeks of incubation. After that, the increases were continued insignificantly. The changes were more considerable in EFB biochar-amended soil. The maximum imazapyr removal was achieved after 50 days as the K_f value increased from 6.38 to 8.97 (40% increases). In RH biochar-amended soil, 37% increases in K_f value was observed. Changes in sorption capacity of the free soil were negligible and were less than 10% for the herbicide.

Post-pyrolysis changes in sorption capacities of biochars can be controlled by soil factors, climatic conditions, and herbicidal properties [21]. Knowing about these changes is necessary for understanding the behaviour of biochar as a sorbent in the environment.

The investigation of changes in CEC values (Fig. 1b) revealed enhancement of the exchange capacities in presence of biochars in soils during the incubation period. It was observed that the initial CEC was 19.68 cmol(+)/kg in the soil mixed with EFB biochar and it reached 22.26 cmol(+)/kg at the end
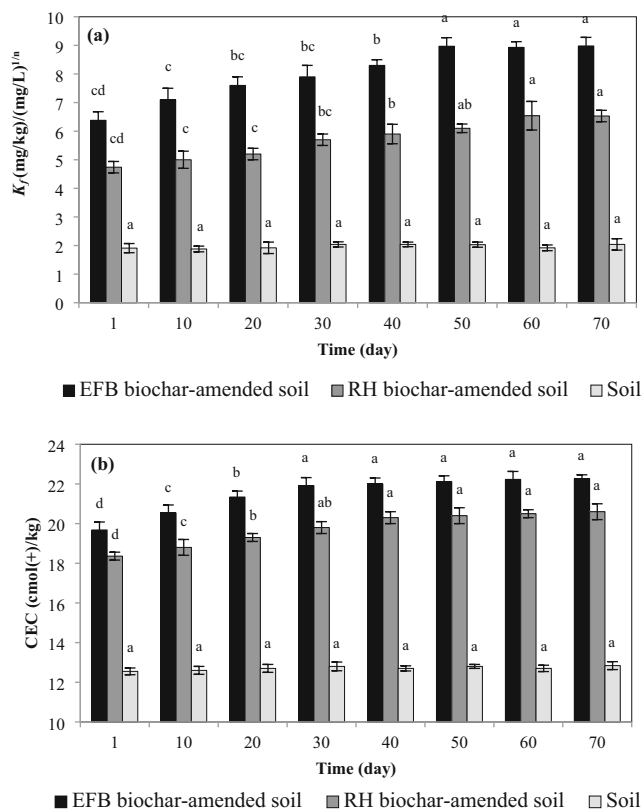
of the incubation period (13%). The increase was from 18.36 to 20.60 cmol(+)/kg in the RH biochar-amended soil (12%). CEC value of the non-amended soil stayed constant at about 12.5 cmol(+)/kg during the incubation time. Similar results were reported by Brodowski et al. [6] who indicated once biochar is applied to the soil, very fast oxidation and hydrolysis reactions happen on its surface during the first several weeks of incubation. However, they can be reduced later by mineral interactions and saturation of biochar active sites in the soils. During oxidation, the oxygen-containing groups like carboxylate and phenolate, increase on the external surface of biochar which can cause specific interaction between biochar and polar organic molecules such as imidazolinone herbicides. The chemisorption of oxygen increases biochar CEC and its surface hydrophilicity which influence biochar sorption behaviour [23].

3.2 Leaching of imazapyr

Breakthrough curves of imazapyr in non-amended and biochars-amended soils are presented in Fig. 2. Generally, in the biochar-free soil, imazapyr was leached out earlier in comparison with the biochars-amended soils. The maximum value of the relative concentration of imazapyr leached from biochar-free soil was 0.02 which was obtained after collection of 2200 mL leachate from the column, while the maximum values for EFB and RH biochars-amended soils were 0.0072 and 0.0047, respectively which were obtained at higher cumulative volumes of leachates, 3400 mL for EFB biochar and 2600 mL for RH biochar-amended soils. These results showed that the biochars applications delayed the leaching of imazapyr from the soils columns.

Based on the data are shown in Table 4, the highest percentage of imazapyr was leached out from non-amended soil (14.2%), followed by RH biochar- (4.0%) and EFB biochar-amended soils (2.8%). In all media, the higher amount of the herbicide was retained in the top 7.5 cm soil depth.
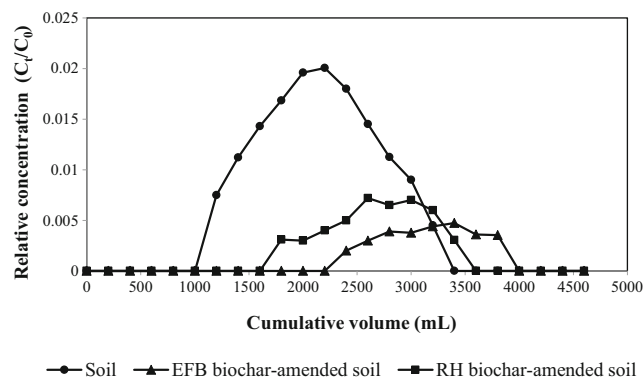

Fig. 1 Changes in K_f (a) and CEC (b) values of non-amended and biochars-amended soils during incubation period

Fig. 2 Breakthrough curves of imazapyr herbicide in non-amended and EFB and RH biochars-amended soils

Table 4 Percentages of herbicide leached out from soil columns and herbicide remained in different depth of soils

Media	Leached herbicide (%)	Remained herbicide (%) in different depths	
		0–7.5 (cm)	7.5–15 (cm)
Soil	14.2±0.3	58.6±2.4	26.7±2.4
RH biochar-amended soil	4.0±0.1	66.7±2.5	28.9± 1.6
EFB biochar-amended soil	2.8±0.1	72.8±3.5	24.3±3.3

Comparison of the amounts of remained herbicide showed that the soil amended with EFB biochar retained the highest amounts of the herbicide (97.1%) followed by RH biochar-amended soil (95.6%) and the lowest amount was measured in the biochar-free soil (85.3%). Amounts of the imazapyr herbicide retained in the soils were inversely related to the amounts of herbicide leached out from each column.

The results shown in Table 5 indicated that the amounts of the herbicide leached out from the soils were negatively correlated with the media sorption capacities. As K_f values increased, the percentages of the herbicide leached out from the columns reduced. The correlation between K_f values and the amounts of the herbicide that remained in the soils was positive, indicating that mobility of herbicide decreased with increasing media sorption capacities.

According to the data reductions of the herbicide leaching in the presence of the biochars was promising a finding to decrease the environmental threats of the applied herbicide. Many studies have also reported the enhanced sorption of pesticides in biochar-amended soils that resulted in a reduction of their leaching when compared to biochar-free soils [1, 39]. During a study conducted by Li et al. [24], 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 the potential to control the leaching of the herbicides significantly and could reduce the amounts of leached herbicides by half. In another attempt, Hagner et al. [16] showed that birch wood-derived biochar can decrease the leaching rate of glyphosate herbicide in soil. So, the addition of biochar can be considered as an effective strategy to decrease the impact of pesticides residue on the ecosystem.

3.3 Photolysis and bio-degradation of imazapyr

Photo-degradation reaction of the herbicide in all media followed the first-order kinetics ($R^2 \geq 96\%$) (Table 6). Figure 3 shows the first-order rate plots of the process. Photolysis of imazapyr was reduced by biochars amendment, with rate constant reducing from 0.018 per day (a half-life of 38.5 days) in non-amended soil to 0.015 per day (a half-life of 46.3 days) in RH biochar-amended soil and 0.013 per day (a half-life of 53.3 days) in EFB biochar-amended soil. During the experiment period, the changes in concentrations of the herbicide in dark-incubated samples, if any, were very minimal and under the detection limits. This result plus the preliminary findings from the hydrolysis experiment indicated that any changes in the herbicide concentrations were only related to photo-degradation reaction and were not caused by bio-degradation or hydrolysis processes.

As a soil amendment, EFB biochar had a greater effect on decreasing the herbicide photo-degradation rate compared to RH biochar applied in the same dosage (1.0% w/w). This can be described by the higher ability of EFB biochar to stabilize the imidazolinone herbicides which is indicated by the greater K_f values of EFB biochar-amended soil for adsorption of the herbicide (Table 3). The higher surface hydrophilic nature, polarity index, and CEC made EFB biochar more efficient in the sorption of the herbicide (Table 2). The half-life of the herbicide was directly correlated to the media sorption capacity (Pearson's $r = 0.9810$, $p < 0.0190$). As the K_f value increased, the half-life of the herbicide in the media enhanced mostly due to the reduction of its availability to the solar radiant.

It has been shown that low sorption of imidazolinone herbicides to soil can enhance photo-degradation processes.

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

Leached herbicide (%)	Remained herbicide (%)
−0.9802[*]	0.9821[*]
$p < 0.0198$	$p < 0.0179$

[*] Correlation is significant at 0.05 level

Table 6 First-order rate constants (K), half-lives ($t_{1/2}$), and correlation coefficients (R^2) of photo-degradation process for imazapyr herbicide

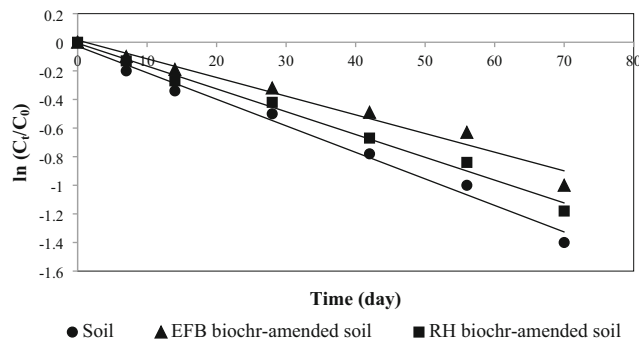| Media	K (per day)	$t_{1/2}$ (day)	R^2
Soil	0.018±0.0007	38.5±1.8	0.98
RH-biochar amended soil	0.015±0.0011	46.3±1.2	0.99
EFB-biochar amended soil	0.013±0.0006	53.3±2.1	0.96

Fig. 3 First-order rate plots of photo-degradation process for imazapyr herbicide

Curran et al. [11] investigated photolytic reactions of several imidazolinone herbicides on different soils and found that photolysis of these herbicides occurred readily in the soil having the lower sorption capacity because of the greater availability of the herbicides' molecules to photochemical reactions. Similar results were obtained by Elazzouzi et al. [14] who indicated that the presence of organic matters in soil could significantly reduce the rate of imazethapyr photo-degradation in the environment.

Acceptable fits to first-order reaction kinetics ($\geq 93\%$) were obtained for bio-degradation of imazapyr herbicide in the media over the incubation time of 70 days (Table 7). First-order rate plots of the process for the herbicide are presented in Fig. 4. Applications of the optimized EFB and RH biochars to the soil reduced bio-degradation of the imazapyr herbicide during the first weeks of the experiment period. After that, the herbicide bio-degradation accelerated significantly ($p < 0.05$) in the presence of the biochars in soil. Rate constants and half-life of the herbicide in the biochar-free and biochar-amended soils are shown in Table 7. The rate constant of bio-degradation in the free soil was 0.015 per day with a half-life of 46.2 days. The addition of EFB biochar in soil increased the rate constant to 0.024 per day with a half-life of 28.8 days. Further increase was obtained in the RH biochar amended-soil with the highest rate constant of 0.026 per day and the shortest half-life of 26.6 days. Concentrations of herbicides incubated in the sterilized condition remained unchanged during the incubation period indicating that the bio-degradation process was the only process responsible for the disappearance of the herbicide in the non-sterilized soils. This result also confirmed the preliminary findings of this study on the resistance of the imidazolinone

herbicides to hydrolysis degradation. The capability of the optimized biochars in adsorbing the herbicide was the main reason for the decrease of their bio-degradation over the first weeks of incubation. Having the higher adsorption capacity, EFB biochar remained more effective than RH biochar in immobilizing the herbicide and thus reducing its bio-availability for soil microbes. Therefore, in comparison with RH biochar, EFB biochar showed smaller influences on the disappearance of the herbicides in the soil during the incubation time.

Many studies have also indicated the enhanced pesticides bio-degradation rate with the presence of biochars in the soil environment. Biochar can stimulate the activity of a variety of important soil microbes by providing them with soluble nutrients, water, and gases. Pores in biochar structure can also be suitable habitat for soil micro-organisms [29, 37]. Based on Zhang et al. [41], the application of biochars produced from maize straw and pig manure at 300 °C enhanced micro-degradation of thiacloprid pesticide due to increasing the abundance of soil microbes.

4 Conclusions

The designed biochars significantly increased soil capacity in sorption of imazapyr (EFB biochar = 2.34 and RH biochar = 1.48-folds) and decreased the herbicides reversibility. Capacities of biochars-amended soils in sorption of the herbicide showed an increasing trend during an incubation period due to enhancement of the biochars CEC values. Leaching of imazapyr can be a risk to the aquatic environment due to high persistence and biological activity. This study showed that application of the biochars can reduce herbicide leaching. So that the lowest percentage of the herbicide was leached out from EFB biochar-amended soil (2.8%). Higher amounts of the herbicides were retained in the top part of the soil columns and the biochars-amended soils retained the higher percentages of the herbicide (> 95%). Degradation experiments demonstrated that the photolysis rate of imazapyr in soil reduced in
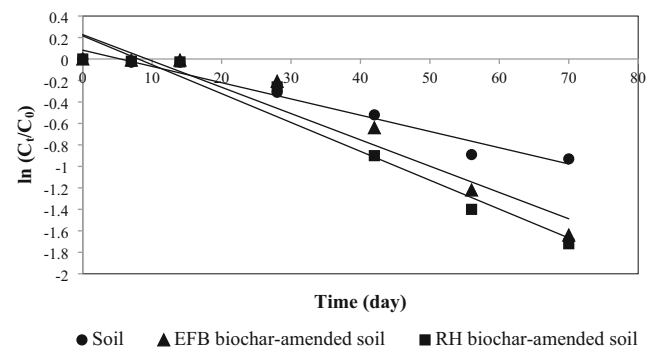
Table 7 First-order rate constants (K), half-lives ($t_{1/2}$), and correlation coefficients (R^2) of bio-degradation process for imazapyr herbicide

Media	K (per day)	$t_{1/2}$ (day)	R^2
Soil	0.015±0.0008	46.2±1.7	0.96
RH-biochar amended soil	0.026±0.0010	26.6±1.8	0.94
EFB-biochar amended soil	0.024±0.0008	28.8±1.3	0.93

Fig. 4 First-order rate plots of bio-degradation process for imazapyr herbicide

the presence of the biochars particularly EFB biochar. The half-life increased from 38.5 days in free soil to 53.3 days in the biochar-amended soil. In contrast, imazapyr biodegradation accelerated significantly with the presence of biochars. RH biochar showed a greater effect. The half-life was 46.2 days in the free soil. The addition of RH biochar decreased it to 26.6 days.

In a conclusion, the designed EFB and RH biochars have the potentials to be used as eco-friendly and cost-effective biosorbent in the soil to reduce the threats of imidazolinone herbicides and protect the environment against their pollution. Further studies are suggested for a better understanding of biochar effects on the fate of pesticides in short- and long-term conditions.

Declarations

Conflict of interest The authors declare no competing interests.

References

1. Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS (2014) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071

2. Aktar W, Sengupta D, Chowdhury A (2009) Impact of pesticides use in agriculture: their benefits and hazards. Interdiscip Toxicol 2(1):1–12. https://doi.org/10.2478/v10102-009-0001-7

3. Asadpour, R., Yavari, S., Kamyab, H., Ashokkumar, V., Chelliapan, S., Yuzir, A. 2021. Study of oil sorption behaviour of esterified oil palm empty fruit bunch (OPEFB) fibre and its kinetics and isotherm studies. Environmental Technology & Innovation, 22, 101397. https://doi.org/10.1016/j.eti.2021.101397

4. Ashokkumar V, Chen WH, Kamyab H, Kumar G, Ala'a H, Ngamcharussrivichai C (2019) Cultivation of microalgae Chlorella sp. in municipal sewage for biofuel production and utilization of biochar derived from residue for the conversion of hematite iron ore (Fe2O3) to iron (Fe)–Integrated algal biorefinery. Energy 189:116128. https://doi.org/10.1016/j.energy.2019.116128

5. Azmi M, Azlan S, Yim KM, George TV, Chew SE (2012) Control of weedy rice in direct-seeded rice using the Clearfield production system in Malaysia. Pak J Weed Sci Res 18:49–53

6. Brodowski S, John B, Flessa H, Amelung W (2006) Aggregate-occluded black carbon in soil. Eur J Soil Sci 57:539–546. https://doi.org/10.1111/j.1365-2389.2006.00807.x

7. Burrows HD, Santaballa JA, Steenken S (2002) Reaction pathways and mechanisms of photodegradation of pesticides. J Photochem Photobiol B Biol 67:71–108. https://doi.org/10.1016/S1011-1344(02)00277-4

8. Carena L, Vione D (2018) Modelling the photochemistry of imazethapyr in rice paddy water. Sci Total Environ 644:1391–1398. https://doi.org/10.1016/j.scitotenv.2018.06.324

9. Cederlund H, Börjesson E, Lundberg D, Stenström J (2016) Adsorption of pesticides with different chemical properties to a wood biochar treated with heat and iron. Water Air Soil Pollut 227:203. https://doi.org/10.1007/s11270-016-2894-z

10. Chianese S, Fenti A, Iovino P, Musmarra D, Salvestrini S (2020) Sorption of organic pollutants by humic acids: A review. Molecules 25:918. https://doi.org/10.3390/molecules25040918

11. Curran WS, Loux MM, Liebl RA, Simmons FW (1992) Photolysis of imidazolinone herbicides in aqueous solution and on soil. Weed Sci 1:143–148. https://www.jstor.org/stable/4045168. Accessed 17 May 2021

12. Delwiche KB, Lehmann J, Walter MT (2014) Atrazine leaching from biochar-amended soils. Chemosphere 95:346–352. https://doi.org/10.1016/j.chemosphere.2013.09.043

13. Dominguez CM, Oturan N, Romero A, Santos A, Oturan MA (2018) Removal of organochlorine pesticides from lindane production wastes by electrochemical oxidation. Environ Sci Pollut Res 25:34985–34994. https://doi.org/10.1007/s11356-018-1425-4

14. Elazzouzi M, Mekkaoui M, Zaza S, El Madani M, Zrineh A, Chovelon JM (2002) Abiotic degradation of imazethapyr in aqueous solution. J Environ Sci Health B 37:445–451. https://doi.org/10.1081/PFC-120014874

15. Espy R, Pelton E, Opseth A, Kasprisin J, Nienow AM (2011) Photodegradation of the herbicide imazethapyr in aqueous solution: effects of wavelength, pH, and natural organic matter (NOM) and analysis of photoproducts. J Agric Food Chem 59:7277–7285. https://doi.org/10.1021/jf200573g

16. Hagner M, Penttinen OP, Tiilikkala K, Setälä H (2013) The effects of biochar, wood vinegar and plants on glyphosate leaching and degradation. Eur J Soil Biol 58:1–7. https://doi.org/10.1016/j.ejsobi.2013.05.002

17. Jones DL, Edwards-Jones G, Murphy DV (2011) Biochar mediated alterations in herbicide breakdown and leaching in soil. Soil Biol Biochem 43:804–813

18. Kamyab H, Chelliapan S, Shahbazian-Yassar R, Din MFM, Khademi T, Kumar A, Rezania S (2017) Evaluation of lipid content in microalgae biomass using palm oil mill effluent (Pome). Jom 69:1361–1367. https://doi.org/10.1007/s11837-017-2428-1

19. Kamyab H, Friedler F, Klemes JJ, Chelliapan S, Rezania S (2018) Bioenergy Production and Nutrients Removal by Green Microalgae with Cultivation from Agro-Wastewater Palm Oil Mill Effluent (POME)-A Review. Chem Eng Trans 70:2197–2202. https://doi.org/10.3303/CET1870367

20. Khorram MS, Zhang Q, Lin D, Zheng Y, Fang H, Yu Y (2016) Biochar: a review of its impact on pesticide behavior in soil environments and its potential applications. J Environ Sci 44:269–279. https://doi.org/10.1016/j.jes.2015.12.027

21. Laird DA, Brown RC, Amonette JE, Lehmann J (2009) Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels Bioprod Biorefin 3:547–562. https://doi.org/10.1002/bbb.169

22. Larsbo M, Löfstrand E, de Veer DV, Ulén B (2013) Pesticide leaching from two Swedish topsoils of contrasting texture amended with biochar. J Contam Hydrol 147:73–81. https://doi.org/10.1016/j.jconhyd.2013.01.003

23. Lehmann J, Joseph S (2015) Biochar for environmental management: science, technology and implementation, 2nd edn. Routledge, London. https://doi.org/10.4324/9780203762264

24. Li J, Li Y, Wu M, Zhang Z, Lü J (2013) Effectiveness of low-temperature biochar in controlling the release and leaching of

herbicides in soil. Plant Soil 370:333–344. https://doi.org/10.1007/s11104-013-1639-7

25. Lian F, Sun B, Song Z, Zhu L, Qi X, Xing B (2014) Physicochemical properties of herb-residue biochar and its sorption to ionizable antibiotic sulfamethoxazole. Chem Eng J 248:128–134. https://doi.org/10.1016/j.cej.2014.03.021

26. Marican A, Durán-Lara EF (2018) A review on pesticide removal through different processes. Environ Sci Pollut Res 25(3):2051–2064. https://doi.org/10.1007/s11356-017-0796-2

27. Martins GL, Friggi CA, Prestes OD, Vicari MC, Friggi DA, Adaime MB, Zanella R (2014) Simultaneous LC–MS/MS determination of imidazolinone herbicides together with other multiclass pesticide residues in soil. CLEAN. 42:1441–1449. https://doi.org/10.1002/clen.201300140

28. Meier S, Curaqueo G, Khan N, Bolan N, Cea M, Eugenia GM, Borie F (2017) Chicken-manure-derived biochar reduced bioavailability of copper in a contaminated soil. Journal of Soils and Sediments 17(3):741–750. https://doi.org/10.1007/s11368-015-1256-6

29. Meier S, Curaqueo G, Khan N, Bolan N, Rilling J, Vidal C, Fernández N, Acuña J, González ME, Cornejo P, Borie F (2017) Effects of biochar on copper immobilization and soil microbial communities in a metal-contaminated soil. J Soils Sediments 17:1237–1250. https://doi.org/10.1007/s11368-015-1224-1

30. Moraes BS, Clasen B, Loro VL, Pretto A, Toni C, de Avila LA, Marchesan E, de Oliveira Machado SL, Zanella R, Reimche GB (2011) Toxicological responses of Cyprinus carpio after exposure to a commercial herbicide containing imazethapyr and imazapic. Ecotoxicol Environ Saf 74(3):328–335. https://doi.org/10.1016/j.ecoenv.2009.05.013

31. Rezaee M, Ghomesheh PK, Hosseini AM (2017) Electrokinetic remediation of zinc and copper contaminated soil: a simulation-based study. Civ Eng J 3:690–700. https://doi.org/10.21859/cej-03096

32. Saha A, Tp AS, Gajbhiye VT, Gupta S, Kumar R (2013) Removal of mixed pesticides from aqueous solutions using organoclays: evaluation of equilibrium and kinetic model. Bull Environ Contam Toxicol 91:111–116. https://doi.org/10.1007/s00128-013-1012-9

33. Sanches S, Penetra A, Rodrigues A, Cardoso VV, Ferreira E, Benoliel MJ, Crespo MB, Crespo JG, Pereira VJ (2013) Removal of pesticides from water combining low pressure UV photolysis with nanofiltration. Sep Purif Technol 115:73–82. https://doi.org/10.1016/j.seppur.2013.04.044

34. Shah SM, Yusof KW, Mustaffa Z, Hashim AM, Ehsan A (2013) Turbidity and suspended solids as affected by the sampling procedure under the same rainfall event in a water channel. GJPAAS 1. Available from http://archives.un-pub.eu/index.php/paas/article/viewArticle/2425

35. ul Haq A, Saeed M, Usman M, Naqvi SA, Bokhari TH, Maqbool T, Ghaus H, Tahir T, Khalid H (2020) Sorption of chlorpyrifos onto zinc oxide nanoparticles impregnated Pea peels (Pisum sativum L): Equilibrium, kinetic and thermodynamic studies. Environ Technol Innov 17:100516. https://doi.org/10.1016/j.eti.2019.100516

36. Vithanage M, Rajapaksha AU, Tang X, Thiele-Bruhn S, Kim KH, Lee SE, Ok YS (2014) Sorption and transport of sulfamethazine in agricultural soils amended with invasive-plant-derived biochar. J Environ Manag 141:95–103. https://doi.org/10.1016/j.jenvman.2014.02.030

37. Warnock DD, Lehmann J, Kuyper TW, Rillig MC (2007) Mycorrhizal responses to biochar in soil–concepts and mechanisms. Plant Soil 300:9–20. https://doi.org/10.1007/s11104-007-9391-5

38. Wei Z, Van Le Q, Peng W, Yang Y, Yang H, Gu H, Lam SS, Sonne C (2020) A review on phytoremediation of contaminants in air, water and soil. J Hazard Mater 403:123658. https://doi.org/10.1016/j.jhazmat.2020.123658

39. Yavari S, Malakahmad A, Sapari NB, Yavari S (2017) Synthesis optimization of oil palm empty fruit bunch and rice husk biochars for removal of imazapic and imazapyr herbicides. J Environ Manag 193:201–210. https://doi.org/10.1016/j.jenvman.2017.02.035

40. Zhang H, Lin K, Wang H, Gan J (2010) Effect of Pinus radiata derived biochars on soil sorption and desorption of phenanthrene. Environ Pollut 58:2821–2825. https://doi.org/10.1016/j.envpol.2010.06.025

41. Zhang P, Sun H, Min L, Ren C (2018) Biochars change the sorption and degradation of thiacloprid in soil: insights into chemical and biological mechanisms. Environ Pollut 236:158–167. https://doi.org/10.1016/j.envpol.2018.01.030