Clean Technologies and Environmental Policy (2022) 24:251–260
https://doi.org/10.1007/s10098-021-02113-z

ORIGINAL PAPER

Efficiency of carbon sorbents in mitigating polar herbicides leaching from tropical soil

Saba Yavari[1] · Robabeh Asadpour[2] · Hesam Kamyab[3] · Sara Yavari[1] · Shamsul Rahman Mohamed Kutty[1] · Lavania Baloo[1] · Teh Sabariah Binti Abd Manan[4] · Shreeshivadasan Chelliapan[5] · Azwadi Bin Che Sidik[3]

Received: 31 January 2021 / Accepted: 10 May 2021 / Published online: 25 May 2021

Abstract

Imidazolinones are a group of herbicides with high potential of leaching and long half-lives that are posing a threat to water resources' quality especially in tropical areas. Biochar, a carbon-rich bio-sorbent, has shown its ability to stabilise organic substances in soils and therefore, potentially is able to reduce their leaching. Biochar is a sustainable and cost-effective material which can be produced from locally available wastes. This work, for the first time, evaluated the biochar's effects on leaching of two polar members of imidazolinones family namely imazapic and imazapyr, and also Onduty® which is a mixture of these two herbicides, in heavy soil of tropical paddy fields. Leaching columns accompanied with artificial irrigation were used during the laboratory experiment. The herbicides were extracted from both collected leachates and soil columns. Soil amendment with designed biochars significantly reduced the herbicides' leaching percentages. Oil palm empty fruit bunch (OPEFB) and rice husk (RH) were used as pyrolysis feedstock. About 16% of the applied imazapic was leached out from biochar-free soil. For RH and OPEFB biochar-amended soils, the amounts were 4.3% and 3.6%, respectively. The highest percentage of imazapyr leached out from non-amended soil was (14.2%) followed by RH (4.0%) and OPEFB (2.8%) in biochar-amended soils. Also, 15.2% of the applied Onduty® was leached from non-amended soil. Adding RH and OPEFB 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. The media sorption capacities were negatively correlated to the amounts of herbicides leached out from soils but positively to the amounts of the herbicides remaining in the soil. Total amount of herbicides adsorbed by biochars-amended soils was more than 95%. Cation/water bridging ion exchange, ligand exchange, electrostatic attraction, and hydrophobic partitioning are the main ways imidazolinones can be adsorbed to soil. It was concluded that biochar application has the potential to reduce polar imidazolinones' leaching and their environmental pollution. The custom-engineered biochars can specifically control the pesticides transfer and then can certainly enhance the biochars' commercial values for their applications in the environment.

✉ Hesam Kamyab
hesam_kamyab@yahoo.com; khesam2@live.utm.my

[1] Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Malaysia

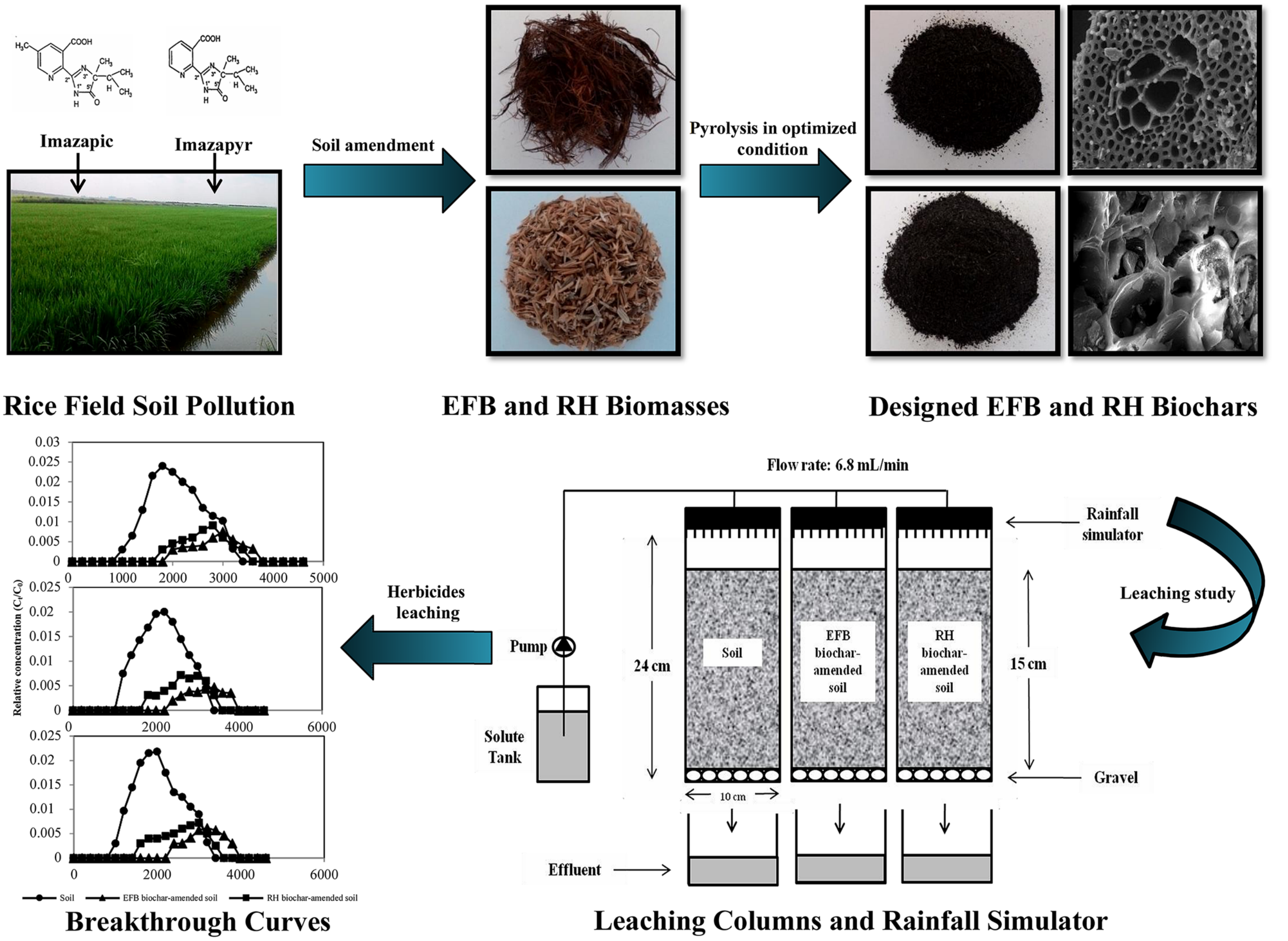
[2] Geosciences and Petroleum Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Malaysia

[3] Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia

[4] Institute of Tropical Biodiversity and Sustainable Development, Universiti Malaysia Terengganu, 21300 Kuala Terengganu, Terengganu, Malaysia

[5] Engineering Department, Razak Faculty of Technology and Informatics, Universiti Teknologi Malaysia, Jln Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia

Graphic abstract



Keywords Imazapic · Imazapyr · Biochar · Pyrolysis · Herbicide leachate

Introduction

Information on pesticides' leaching in crop lands is important in controlling chemicals' contamination in aquatic ecosystems and potable waters (Briceno et al. 2007). Once applied to agricultural soils, pesticides can be stabilised, degraded to metabolic residues through biotic and abiotic factors, and/or transferred. Pesticides leaching from the root zones of plants by water is the most problematic process in chemicals' transfer through which the applied pesticides are carried downwards through the soil into the groundwater 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 can determine the leaching process of pesticides mostly through influencing on soil capacity in adsorption of the chemicals.

There are a variety of techniques used for pollutants' removal from the environment, mainly by applying the degradation process [using silver nanoparticles (Krishnan et al. 2021), TiO_2 nanoparticles (Velu et al. 2021), nanocomposites (Fakhri et al. 2016; Saravanan et al. 2013, 2015), etc.], extraction process [using electrokinetic (Rezaee et al. 2017), electrocoagulation (Ali et al. 2012), encapsulation (Shen et al. 2019), etc.], or stabilisation process [using activated carbon (Gupta et al. 2013) and its nanoparticle-modified forms (Burakov et al. 2018; Nekouei et al. 2015), modified cellulose (Gupta et al. 2016), agro-wastes (Kamyab et al. 2016), biochar (Sharma et al. 2019), etc.].

Biochar is known as a carbonaceous sorbent derived from pyrolysis (a thermochemical process) of biomass under limited supply of O_2 and at temperatures lesser than 700 °C (Lehmann and Joseph 2015). Biochar production has a role in circular economy due to the resource's efficiency, material recycling, and cascade uses (Kua et al. 2020). It can be produced from cheap and locally available waste materials (such as agricultural wastes, sewage sludge, manure, etc.) and unlike activated carbon, it does not require costly activation and regeneration processes (Cederlund et al. 2016). Furthermore, it has energy recovery, resulting in a diverse range of by-products (such as bio-oil and bio-gas) that can be used in a number of applications. As a result, in terms of energy consumption, it can be called self-sufficient (Zielińska and Oleszczuk 2015). Therefore, biochar helps in obtaining balanced and sustainable development in agriculture and environment sectors; a necessity in today's world (Muo and Azeez 2019). Production of biochar at application site, near feedstock sources, and in small-scale, the use of agricultural wastes as pyrolysis feedstock, and incorporation of energy recovery can significantly reduce biochar production cost (Maroušek et al. 2019; Vochozka et al. 2016). Based on Maroušek et al. (2019), the developments have resulted in decreased biochar production costs (10–30 USD per tonne). It was reported that biochar production with almost zero cost was achieved through operating biogas plants which utilised waste heat for producing biochar from fermented residue. This could efficiently eliminate the costs of residues management and low-grade heat (Maroušek 2014; Maroušek et al. 2020b).

Effects of biochar amendment on pesticides' leaching from soils have been frequently investigated (Li et al. 2013; Tatarková et al. 2013). According to Larsbo et al. (2013), application of biochar can have different effects 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 was enhanced in the presence of biochar. It was concluded that materials originating 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 laboratory and field experiments (Delwiche et al. 2014). The results showed that biochar amendment has the potential to decrease herbicides leaching from the soil profile. Imidazolinones are the type of polar herbicides that shows high mobility and leaching potential (Moraes et al. 2011) as they have high water solubility and low organic carbon partition coefficients (Martini et al. 2013; Zanella et al. 2011). Off-site transport of imidazolinones can cause severe ecological effects from their highly persistent nature and biological activities. Currently, Onduty® which is a mixture of two members from this family namely imazapic and imazapyr is applied in Clearfield® production system. In this system, bred rice which is tolerant to imidazolinones are accompanied with Onduty® herbicide to remove weeds in paddy fields. The properties of these herbicides are shown in Table 1.

There are several studies which have addressed the intensity of leaching and toxicity of imidazolinones in the environment (Battaglin et al. 2000; Wyk and Reinhardt 2001). It was reported that imidazolinone herbicides were one of the herbicide groups frequently found in groundwater of Iowa and Illinois states (Battaglin et al. 2000). Presence of imazapyr was reported in Swedish groundwater after 8 years of its application in agricultural fields (Börjesson et al. 2004). It has been indicated that imidazolinones leaching is higher in tropical soils in comparison to temperate areas because of heavy rainfalls (Oliveira et al. 2001; Souza 2000). Imazethapyr was detected in both rivers and groundwater of southern Brazil following its wide application 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 per 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 et al. 2001). Wyk and Reinhardt (2001) reported that depending on soil type and amount of rainfall, imazethapyr can even be leached beyond 30 cm in soil. Souza (2000) showed that the imazapyr mobility was higher in sandy loam soils rather than clay soils. Leaching of imidazolinones in the presence of biochars in heavy tropical soils is hardly understood. The increasing popularity of these herbicides with farmers and their potential threats to the

Table 1 Physical and chemical characteristics of the studies herbicides

Properties	Imazapic	Imazapyr
Chemical formula	$C_{14}H_{17}N_3O_3$	$C_{13}H_{15}N_3O_3$
Molar mass (g mol^{-1})	275.3	261.2
Solubility (mg L^{-1}) (water at 25 °C and pH 7)	2200	11,272
Adsorption/absorption coefficient (cm^3 g^{-1})	0.13–4.07	0.07–0.19
Vapour pressure (mPa) at 20 °C	Max. 0.013	
Organic carbon/water partition coefficient (L kg^{-1})	7–267	4–170
Octanol/water partition coefficient	0.39	0.11
Half-life in soil (day)	31–233	30–210

environment, make it necessary to consider possible solutions to reduce their application. Thus, this study aimed to evaluate the effects of agricultural wastes biochars applied to Malaysian paddy fields' soil on the retention and leaching of imazapic, imazapyr, and Onduty® herbicides.

Materials and methods

Collection and characterisation of soil samples

The soil sample for this experiment was taken from the paddy fields in Seberang Perak which is one of the main fields in Malaysia applying Clearfield® production system. This area is located at 4° 7′ North and 101° 4′ East. The soil sampling was done following a simple random pattern (Huang et al. 2007) and from 0 to 15 cm soil depth. Three replicates of soil sample were evaluated for their properties. The air-dried samples were grinded, sieved through a 2 mm mesh, and then characterised.

The measured physical and chemical properties of the soil included particle size distribution (pipette method) and soil texture (Jones Jr, 2001), total organic carbon percentage (total organic carbon analyser, SSM/5000A, Shimadzu, Japan), pH value (pH meter, HACH, sension 2), and cation exchange capacity (CEC) ($NH_4CH_3CO_2$ extraction method) (Beretta et al. 2014; Minasny et al. 2011) (Table 2).

Table 2 The values of measured properties of the soil sample

Particle size distribution (%)			Soil texture	Total organic carbon (%)	pH	CEC (cmol(+).kg^{-1})
Clay	Silt	Sand	Clay loam	0.99 ± 0.08	6.3 ± 0.1	12.5 ± 0.6
37.9	21.5	40.2				

Preparation and characterisation of the designed biochars

Oil palm empty fruit bunch (OPEFB) and rice husk (RH) were used as pyrolysis feedstock in this study. OPEFB and RH biomasses were obtained from an oil palm plantation and a rice mill in Perak state, respectively. There was no cost for the feedstock provision. OPEFB biomass was shredded into small pieces (< 3 cm) before conversion process. After drying at 80 °C, for 12 h, the biomasses were pyrolyzed in optimised conditions by a tube furnace (OTF-1200X/80, USA). The applied gas was nitrogen. The optimised pyrolysis were done at peak temperature and rate of heating equal to 300 °C and 3 °C per minute, respectively. The reaction residence time was 1 h for OPEFB biochar and 3 h for RH biochar. These optimised conditions were found out during our previous work in which the maximum adsorption capacities of the biochars were achieved (Yavari et al. 2017). The designed biochars' properties (presented in Table 3) and the amount of Freundlich sorption coefficients (K_f) of free soil and biochar-amended soils (1% w/w) were also previously measured (Yavari et al. 2017).

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

Characteristics	Designed biochars	
	OPEFB	RH
Yield	46.2%	58.1%
Moisture	4.8%	3.4%
Volatile matter	7.0%	6.5%
Ash	22.5%	22.2%
pH	6.13	6.32
CEC	83.9 cmol(+) kg^{-1}	70.7 cmol(+) kg^{-1}
Carbon	58.6%	48.2%
Oxygen	31.4%	25.0%
Hydrogen	3.8%	2.3%
Nitrogen	1.6%	0.1%
Sulphur	0.4%	0.2%
O/C molar ratio	0.4	0.3
H/C molar ratio	0.3	0.2
(O + N)/C molar ratio	0.4	0.3
Total surface area	1.4 m^2 g^{-1}	1.9 m^2 g^{-1}
Total pore volume	0.005 mL g^{-1}	0.006 mL g^{-1}
Pore radius	104.3 Å	186.8 Å

Chemicals and instruments

Imazapic and imazapyr herbicides (99.9% purity) were provided by Sigma-Aldrich (Seelze, Germany) and Onduty® herbicide was bought from baden aniline and soda factory, Malaysia. Stock solutions of the herbicides were prepared at concentration of 1000 mg L^{-1} in background solutions containing $CaCl_2$ (0.01 molar) and $HgCl_2$ (200 mg L^{-1}). All chemicals were purchased from Fisher Chemical, UK. Solid phase extraction (SPE) cartridges and vacuum extraction manifold assembly were purchased from Agilent Technologies, USA.

Leaching experiment

Leaching columns accompanied by rainfall simulator were used to perform this experiment. The columns were made from 24 cm long and 10 cm inner diameter acrylic glass pipe. The bottom of each column was closed with a perforated plate allowing the leachate to drain into collecting containers. The bottom of each leaching column was layered with 3 cm thick gravel to avoid soil particles losses. The columns were then uniformly packed with free soil and biochar-amended soils (1% w/w) to a height of 15 cm.

The leaching experiment was carried out in a steady-flow state by applying background solution to the soil's surfaces using the rainfall simulator. The solution's flow was channelled from a reservoir to the top of each column through tubes by a peristaltic pump and the solution then poured into the soil column through 10 fine holes. Flow rate of the pump was adjusted to 6.8 mL min^{-1} that simulates the highest rain intensity recorded in the soil sampling area (Shah et al. 2013). The soil columns were saturated for 2 h and allowed to drain for 48 h to obtain uniform moisture content and re-arrangement of the soil particles. After incubation period, each herbicide (imazapic, imazapyr, and Onduty®) was separately applied to a set of media (soil, OPEFB biochar-amended soil, and RH biochar-amended soil). For that purpose, a 2 mL aliquot of 100 mg L^{-1} herbicide solution was applied to the surface of soil column giving an initial concentration of 0.2 μg g^{-1} in soil which was equivalent to the application rates of herbicides in the field (Azmi et al. 2012). The columns were then subjected to constant downward flows of background solution. The leachates were collected in 200 mL fractions. Sample collection was continued until the herbicide concentrations reached the lowest value. Reaching this point took 10 h when the volume of eluted leachate was at quantities equivalent to 7 pore volumes of the soil (4000 mL). Then, 24 h after completion of the leaching process, the soil in each column was divided into 2 equal parts length wise (each 7.5 cm) and the amount of remaining herbicide in each section was determined. Each experiment 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). Extracting herbicides from the leachate was performed using Bond Elut-PPL cartridge. During conditioning step, the cartridge was primed with two rinses of 3 mL CH_2Cl_2 followed by two rinses of 3 mL CH_3OH and then three rinses of 2 mL ultra-pure water at pH 2. Next, 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 CH_2Cl_2. The solvent was then evaporated to near dryness using the nitrogen gas evaporator. Finally, 4 mL C_3H_8O aliquot was added and evaporated to get 1 mL of solvent's final volume.

To remove the herbicides from the soils, the samples were mixed with 0.5 molar NaOH in a 1:4 ratio (soil: NaOH) and shaken for one hour and then were centrifuged for 10 min at 6000 rpm before being filtered via a glass fibre filter (GF/C, 70 mm, and pore size of 1.2 m). After that, the extract was acidified to pH 2. Bond Elut-SCX cartridge was primed with 5 mL C_6H_{14}, 5 mL CH_3OH, and then by 5 mL ultra-pure water. Bond Elut-C_{18} cartridge was conditioned with 5 mL CH_3OH and then by 5 mL ultra-pure water. The extract of soil was passed through a C_{18} cartridge during the sample loading stage. C_{18} cartridge was stacked on top of the SCX cartridge and then the herbicide was eluted from the cartridge with 20 mL CH_3OH:ultra-pure water (1:1). The SCX cartridge was then washed with 5 mL ultra-pure water after the C_{18} cartridge was removed. The herbicide was then eluted from the SCX cartridge using 20 mL 0.05 M phosphate buffer (pH 2) and partitioned using three vigorous washes with 15 mL CH_2Cl_2. The herbicide was re-dissolved in 1 mL C_3H_8O after the solvent was evaporated to near dryness under a gentle stream of nitrogen steam.

HPLC analysis

An Agilent 1100 high-performance liquid chromatography (HPLC) system with diode array detector, diode array detectors, a quaternary pump, and a vacuum degasser, was used to determine herbicide concentrations in the solutions. The chromatographic column was ZORBAX SB-C_{18} (150 × 4.6 mm; particle size: 5 μm). Mobile phase was isocratic (C_2H_3N:1% acetic acid, 35:65) and was applied in 1 mL per minute flow rate. The volume of injection was 20 μL. In this chromatographic condition, the retention time was 2.9 min for imazapic herbicide and 2.3 min for imazapyr herbicide.

Statistical analysis

Breakthrough curves related to leaching of each herbicide in the media were obtained using Excel® spreadsheet program. Correlation coefficients between the K_f values of the media and both total amount of each herbicide leached and total amount of each herbicide retained in the soil were determined with 95% confidence level. Duncan's multiple range tests at likelihood levels of $\alpha = 0.05$ was applied to test the significance between the means' sets.

Results and discussion

Breakthrough curves of imazapic in non-amended and biochars-amended soils are presented in Fig. 1. The curves' patterns are 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

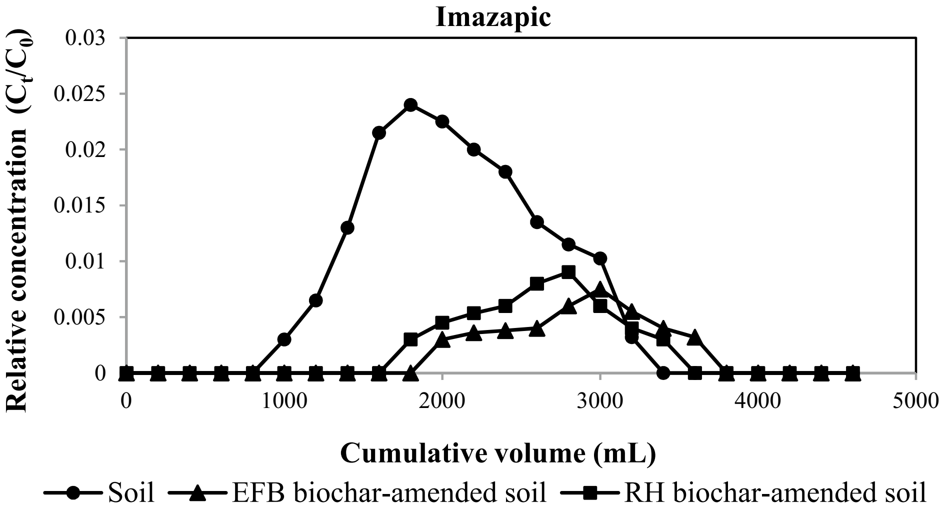


Fig. 1 Breakthrough curves of imazapic herbicide in non-amended and OPEFB and RH biochars-amended soils

to its initial amount applied to the soil, C_t/C_0) of imazapic leached from biochar-free soil was 0.0240 obtained after collecting 1800 mL leachate from the column, while the maximum values for OPEFB 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 OPEFB 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 ($p < 0.05$) reduced the herbicide leaching. The total amount of imazapic leached out from OPEFB biochar-amended soil was 3.6% and that of RH biochar-amended soil was 4.3%.

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 OPEFB biochar-amended soils (2.8%). Different breakthrough curve patterns were obtained in free and biochars-amended soils (Fig. 2). Leaching imazapyr in 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 equalling to 3400 mL and 2600 mL, respectively.

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

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

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
OPEFB 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 ($p < 0.05$).

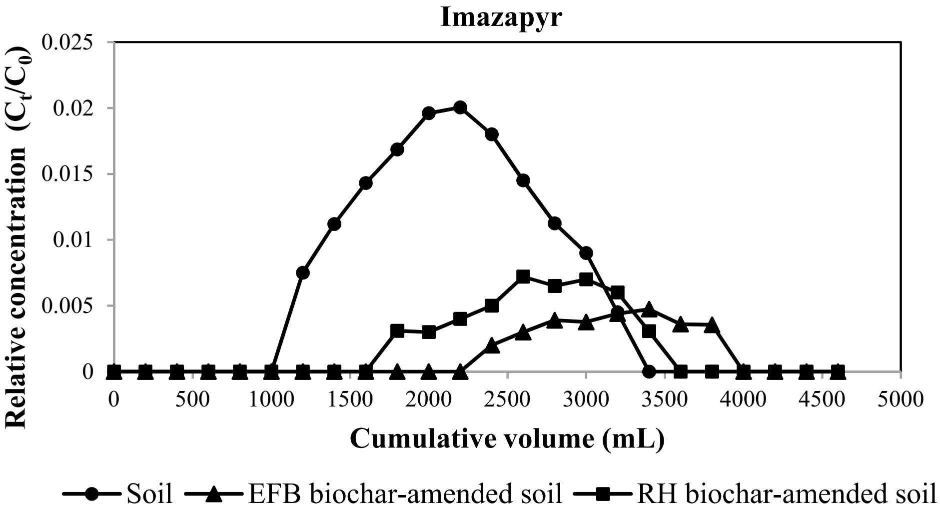


Fig. 2 Breakthrough curves of imazapyr herbicide in non-amended and OPEFB and RH biochars-amended soils

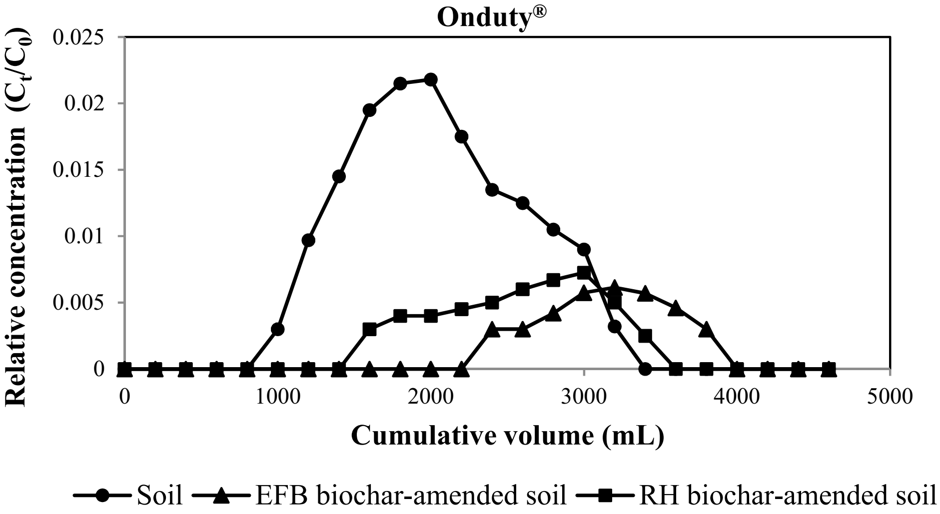


Fig. 3 Breakthrough curves of Onduty® herbicide in non-amended and OPEFB and RH biochars-amended soils

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 OPEFB and RH biochars to soil could significantly reduce the herbicide leaching to 3.0% and 4.2%, respectively.

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

According to Table 4, the percentages of total imazapic, imazapyr, and Onduty® adsorbed by the biochar-free soils columns were 83.4%, 85.3%, and 84.4%, respectively. Also, 96.0% imazapic sorption was achieved in the presence of designed OPEFB biochar in soil. Removal of 97.1% for imazapyr and 96.5% for Onduty® herbicide were achieved in soil with biochar application. Adding designed RH biochar

Table 5 Pearson's r and p values for correlations between the K_f values of media and the percentages of leached out and retained herbicides

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

*Correlation is significant at 0.05 level

to the soil increased imazapic, imazapyr, and Onduty® herbicides stabilisation to 95.2%, 95.6%, and 95.3%, respectively. Therefore, reduction in the herbicides' leaching was promising findings to reduce the environmental threats of the applied herbicides.

Mechanisms proposed for adsorption of imidazolinones to soil constituents include ligand exchange, hydrogen bonding, cation bridging ion exchange, water bridging ion exchange, hydrophobic partitioning interaction, and electrostatic bonding (Regitano et al. 2002). In soils with low pH, these herbicides exist predominantly as uncharged species which interact with the hydrophobic surfaces of soil organic compounds and negatively charged colloids. According to Renner et al. (1988), soil organic materials such as biochar can react with polivalent cations and form chelates or ionic bridges with acidic pesticides which can reduce the impacts of soil pH and increase the chemical stabilisation.

Several studies have also reported enhanced immobilization of pesticides in soils amended with biochar that resulted in reduction of the chemicals' leaching when compared to pure soils (Delwiche et al. 2014; Tatarková et al. 2013) (Table 6). In 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 in a sandy soil in leaching columns. According to their results, biochar had the potential to significantly control the herbicides' leaching and could reduce the amounts of leached herbicides by half. In other attempt, Hagner et al. (2013) showed that birch wood-derived biochar can considerably decrease the leaching rate of glyphosate herbicide in a sandy soil.

Hence, adding biochar can be considered as an effective strategy to reduce the impact of pesticides residues on the environment and ecosystem. This strategy can also be considered as sustainable if it's profitable. Therefore, besides the environmental and humanitarian motives, the profit motive is also needed to be taken into account (Nefzi 2018). Development of new and profitable biochar manufacturing methods can be helpful to produce valuable carbon products as suggested by Maroušek et al. (2020a).

More experiments are needed for better understanding of biochar effects on leaching of pesticides during short- and long-periods. Field trials and in situ studies in different climate and soil conditions must also be conducted to formulate any recommendations for commercial scale agriculture.

Conclusions

This study evaluated the potential of designed OPEFB and RH biochars, as eco-friendly and cost-effective bio-sorbents, in mitigating imazapic, imazapyr, and Onduty® herbicides' risks to aquatic environment through reduction of leaching from soil profile. It is found that the highest percentage of the herbicides was leached out from non-amended soil followed by RH biochar- and OPEFB 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%).

Table 6 Effects of biochars on pesticides' leaching in different soils

Biochar	Pesticides	Soil	Leaching reduction (%)	References
Wheat straw biochar (300 °C)	MCPA	Silt loam	21	Tatarková et al. (2013)
Wood chips (700–750 °C)	Atrazine	Silt loam	55	Delwiche et al. (2014)
Wood chips (350 °C)	2,4-D	Sandy	57	Li et al. (2013)
	Acetochlor		48	
Birch wood (450 °C)	Glyphosate	Sandy	40	Hagner et al. (2013)
OPEFB (300 °C)	Imazapic	Clay loam	12.5	The present study
	Imazapyr		11.5	
	Onduty®		12.2	
RH (300 °C)	Imazapic		11.8	
	Imazapyr		10.2	
	Onduty®		11	

As a conclusion, it was confirmed that the designed biochars derived from oil palm empty fruit bunches and rice husk are efficient to control the leaching of polar imidazolinone herbicides from heavy soils of tropical paddy fields and can protect the environment against their polluting threats. Short- and long-term experiments in field are recommended to be conducted for better understanding of biochar's effects on the binding and leaching of the pesticides.

Acknowledgements This paper is dedicated to the memory of the late Associate Professor Dr. Amirhossein Malakahmad. This study was supported by Malaysian Ministry of Higher Education under fundamental research grant scheme (FRGS, 0153AB-L33), by Universiti Teknologi PETRONAS (UTP) under Yayasan UTP (YUTP, 015LC0-027), and by Universiti Teknologi Malaysia, Post Doctoral Fellow (Teaching & Learning) under MJIIT-UTM-Kl. Technical support and assistance of FELCRA throughout this research work is highly appreciated.

Authors' contribution Conceptualization: SY, RA, HK, SC, ABCS, SY, SRMK, LB and TSBAM; Methodology: SY, RA, and HK; Investigation: SY in the field; Formal analysis: SY, RA, and SC; Writing: SY, RA, HK, SC, ABCS, SY, SRMK, LB and TSBAM; Supervision: SRMK, and LB.

Declaration

Conflict of interest The authors declare that there are no conflict of interest.

References

Ali I, Gupta VK, Khan TA, Asim M (2012) Removal of arsenate from aqueous solution by electro-coagulation method using Al–Fe electrodes. Int J Electrochem Sci 7(2012):1898–1907

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

Battaglin WA, Furlong ET, Burkhardt MR, Peter CJ (2000) Occurrence of sulfonylurea, sulfonamide, imidazolinone, and other herbicides in rivers, reservoirs and ground water in the Midwestern United States, 1998. Sci Total Environ 248(2):123–133. https://doi.org/10.1016/S0048-9697(99)00536-7

Beretta AN, Silbermann AV, Paladino L, Torres D, Bassahun D, Musselli R, García-Lamohte A (2014) Soil texture analyses using a hydrometer: modification of the Bouyoucos method. Cienc Invest Agrar 41(2):263–271. https://doi.org/10.4067/S0718-340.16202014000200013

Börjesson E, Torstensson L, Stenström J (2004) The fate of imazapyr in a Swedish railway embankment. Pest Manag Sci 60(6):544–549. https://doi.org/10.1002/ps.864

Briceno G, Palma G, Duran N (2007) Influence of organic amendment on the biodegradation and movement of pesticides. Crit Rev Environ Sci Technol 37(3):233–271. https://doi.org/10.1080/10643380600987406

Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, Gupta VK (2018) Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. Ecotoxicol Environ Saf 148:702–712. https://doi.org/10.1016/j.ecoenv.2017.11.034

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(6):1–12. https://doi.org/10.1007/s11270-016-2894-z

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

Fakhri A, Rashidi S, Tyagi I, Agarwal S, Gupta VK (2016) Photodegradation of Erythromycin antibiotic by γ-Fe_2O_3/SiO_2 nanocomposite: response surface methodology modeling and optimization. J Mol Liq 214:378–383. https://doi.org/10.1016/j.molliq.2015.11.037

Gupta VK, Ali I, Saleh TA, Siddiqui MN, Agarwal S (2013) Chromium removal from water by activated carbon developed from waste rubber tires. Environ Sci Pollut Res 20(3):1261–1268. https://doi.org/10.1007/s11356-012-0950-9

Gupta VK, Carrott PJM, Singh R, Chaudhary M, Kushwaha S (2016) Cellulose: a review as natural, modified and activated carbon adsorbent. Biores Technol 216:1066–1076. https://doi.org/10.1016/j.biortech.2016.05.106

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

Huang H, Legarsky J, Othman M (2007) Land-cover classification using Radarsat and Landsat imagery for St. Louis, Missouri. Photogramm Eng Remote Sens 73(1):37–43. https://doi.org/10.14358/PERS.73.1.37

Jones JB Jr (2001) Laboratory guide for conducting soil tests and plant analysis. CRC Press, New York

Kamyab H, Din MFM, Hosseini SE, Ghoshal SK, Ashokkumar V, Keyvanfar A, Abd Majid MZ (2016) Optimum lipid production using agro-industrial wastewater treated microalgae as biofuel substrate. Clean Technol Environ Policy 18(8):2513–2523. https://doi.org/10.1007/s10098-016-1212-1

Krishnan S, Zulkapli NS, Kamyab H, Taib SM, Din MFBM, Abd Majid Z, Othman N (2021) Current technologies for recovery of metals from industrial wastes: an overview. Environ Technol Innov. https://doi.org/10.1016/j.eti.2021.101525

Kua HW, Mašek O, Gupta S (2020) Biochar-based circular economy. In: Biochar emerging applications. IOPscience

Lao W, Gan J (2006) High-performance liquid chromatographic separation of imidazolinone herbicide enantiomers and their methyl derivatives on polysaccharide-coated chiral stationary phases. J Chromatogr A 1117(2):184–193. https://doi.org/10.1016/j.chroma.2006.03.094

Larsbo M, Löfstrand E, de Veer DVA, 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

Lehmann J, Joseph S (eds) (2015) Biochar for environmental management: science, technology and implementation. Routledge, London

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(1–2):333–344. https://doi.org/10.1007/s11104-013-1639-7

Maroušek J (2014) Significant breakthrough in biochar cost reduction. Clean Technol Environ Policy 16(8):1821–1825

Maroušek J, Strunecký O, Stehel V (2019) Biochar farming: defining economically perspective applications. Clean Technol Environ Policy 21(7):1389–1395

Maroušek J, Kolář L, Strunecký O, Kopecký M, Bartoš P, Maroušková A et al (2020b) Modified biochars present an economic challenge to phosphate management in wastewater treatment plants. J Clean Prod 272:123015. https://doi.org/10.1016/j.jclepro.2020.123015

Maroušek J, Maroušková A, Kůs T (2020a) Shower cooler reduces pollutants release in production of competitive cement substitute at low cost. Energy Sources Part A Recov Util Environ Effects 1–10

Martini LFD, Mezzomo RF, Avila LAD, Massey JH, Marchesan E, Zanella R, Peixoto SC et al (2013) Imazethapyr and imazapic runoff under continuous and intermittent irrigation of paddy rice. Agric Water Manag 125:26–34. https://doi.org/10.1016/j.agwat.2013.04.005

Minasny B, McBratney AB, Brough DM, Jacquier D (2011) Models relating soil pH measurements in water and calcium chloride that incorporate electrolyte concentration. Eur J Soil Sci 62(5):728–732. https://doi.org/10.1111/j.1365-2389.2011.01386.x

Moraes BS, Clasen B, Loro VL, Pretto A, Toni C, de Avila LA et al (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

Muo I, Azeez AA (2019) Green entrepreneurship: Literature review and agenda for future research. Int J Entrep Knowl 7(2):17–29

Nefzi N (2018) Fear of failure and entrepreneurial risk perception. Int J Entrep Knowl 6(2):45–58

Nekouei F, Nekouei S, Tyagi I, Gupta VK (2015) Kinetic, thermodynamic and isotherm studies for acid blue 129 removal from liquids using copper oxide nanoparticle-modified activated carbon as a novel adsorbent. J Mol Liq 201:124–133. https://doi.org/10.1016/j.molliq.2014.09.027

Oliveira RS, Koskinen WC, Ferreira FA (2001) Sorption and leaching potential of herbicides on Brazilian soils. Weed Res 41(2):97–110. https://doi.org/10.1046/j.1365-3180.2001.00219.x

Ramezani M (2008) Environmental fate of imidazolinone herbicides and their enantiomers in soil and water. Doctoral dissertation

Rathore HS, Nollet LM (eds) (2012) Pesticides: evaluation of environmental pollution. CRC Press, New York

Regitano JB, Prata F, Rocha WSD, Tornisielo VL, Lavorenti A (2002) Imazaquin mobility in tropical soils in relation to soil moisture and rainfall timing. Weed Res 42(4):271–279. https://doi.org/10.1046/j.1365-3180.2002.00284.x

Renner KA, Meggitt WF, Penner D (1988) Effect of soil pH on imazaquin and imazethapyr adsorption to soil and phytotoxicity to corn (*Zea mays*). Weed Sci 36:78–83. https://doi.org/10.1017/S0043174500074488

Rezaee M, Ghomesheh PK, Hosseini AM (2017) Electrokinetic remediation of zinc and copper contaminated soil: a simulation-based study. Civ Eng Jo 3(9):690–700. https://doi.org/10.21859/cej-03096

Saravanan R, Karthikeyan S, Gupta VK, Sekaran G, Narayanan V, Stephen AJMS (2013) Enhanced photocatalytic activity of ZnO/CuO nanocomposite for the degradation of textile dye on visible light illumination. Mater Sci Eng C 33(1):91–98. https://doi.org/10.1016/j.msec.2012.08.011

Saravanan R, Khan MM, Gupta VK, Mosquera E, Gracia F, Narayanan V, Stephen AJRA (2015) ZnO/Ag/Mn_2O_3 nanocomposite for visible light-induced industrial textile effluent degradation, uric acid and ascorbic acid sensing and antimicrobial activity. RSC Adv 5(44):34645–34651. https://doi.org/10.1039/C5RA02557E

Shah SMH, 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. AWER Proc Adv Appl Sci 1:837–842. https://doi.org/10.7763/IJET.2014.V6.747

Sharma G, Bhogal S, Gupta VK, Agarwal S, Kumar A, Pathania D et al (2019) Algal biochar reinforced trimetallic nanocomposite as adsorptional/photocatalyst for remediation of malachite green from aqueous medium. J Mol Liq 275:499–509. https://doi.org/10.1016/j.molliq.2018.11.070

Shen Z, Jin F, O'Connor D, Hou D (2019) Solidification/stabilization for soil remediation: an old technology with new vitality. Environ Sci Technol. https://doi.org/10.1021/acs.est.9b04990

Souza AD (2000) Lixiviação de glyphosate e imazapyr em solos com diferentes texturas e composição química: I-Método do Bioensaio. Planta Daninha. https://doi.org/10.1590/S0100-83582000000100001

Tatarková V, Hiller E, Vaculík M (2013) Impact of wheat straw biochar addition to soil on the sorption, leaching, dissipation of the herbicide (4-chloro-2-methylphenoxy) acetic acid and the growth of sunflower (*Helianthus annuus* L.). Ecotoxicol Environ Saf 92:215–221. https://doi.org/10.1016/j.ecoenv.2013.02.005

Velu M, Balasubramanian B, Velmurugan P, Kamyab H, Ravi AV, Chelliapan S, Palaniyappan J (2021) Fabrication of nanocomposites mediated from aluminium nanoparticles/*Moringa oleifera* gum activated carbon for effective photocatalytic removal of nitrate and phosphate in aqueous solution. J Clean Prod 281:124553. https://doi.org/10.1016/j.jclepro.2020.124553

Vochozka M, Maroušková A, Váchal J, Straková J (2016) Biochar pricing hampers biochar farming. Clean Technol Environ Policy 18(4):1225–1231. https://doi.org/10.1007/s10098-016-1113-3

Wyk LJ, Reinhardt CF (2001) A bioassay technique detects imazethapyr leaching and liming-dependent activity 1. Weed Technol 15(1):1–6. https://doi.org/10.1614/0890-037X(2001)015[0001:ABTDIL]2.0.CO;2

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

Zanella R, Adaime MB, Peixoto SC, Friggi CDA, Prestes OD, Machado SL et al (2011) Herbicides persistence in rice paddy water in Southern Brazil. Herbicides-mechanisms and mode of action. InTech, New York, pp 183–204. https://doi.org/10.5772/32727

Zielińska A, Oleszczuk P (2015) Evaluation of sewage sludge and slow pyrolyzed sewage sludge-derived biochar for adsorption of phenanthrene and pyrene. Biores Technol 192:618–626. https://doi.org/10.1016/j.biortech.2015.06.032