Evaluation of biochar produced from coffee husks as an alternative treatment for wastewater contaminated with agrochemicals in the southwestern region of Antioquia.

Luisa Piña-Borja[1¶*], Carolina Cañaveral-Ángel[1¶], Marisol Restrepo-Franco[1¶], Camila Gómez-Garcés[2&], Santiago Erazo-Cabrera[2&], Lida Arias-Marín[2&]

[1] Research Group BIOmicro, School of Microbiology, University of Antioquia, Andes, Colombia.

[2] Research Group BIOmicro, School of Microbiology, University of Antioquia, Medellín, Colombia

[*]Corresponding author

E-mail: luisa.pina@udea.edu.co (LP)

[¶]Conceptualization, methodology, investigation, data curation, formal analysis, writing - original draft.

[&]Conceptualization, methodology, investigation, writing - review & editing.

Abstract

Excessive use of herbicides, pesticides, and fertilizers has enhanced agricultural productivity but has also generated significant environmental impacts and public health risks. Chlorpyrifos, an organophosphorus insecticide, is highly persistent in the environment due to its affinity for organic matter and its ability to be transported via runoff into water bodies, where conventional wastewater treatments fail to remove it. In response to this challenge, biochar has emerged as a low-cost adsorbent with high potential, owing to its physicochemical properties derived from pyrolysis. In this study, the adsorption capacity of biochar derived from coffee husks—an abundant agricultural residue in Southwestern Antioquia—was evaluated for chlorpyrifos removal in water samples. The highest biochar yield (20%) was obtained by oven-drying the husks for three hours, producing a material with 9.50% moisture, 48.41% volatile matter, 15.85% ash, 26.24% fixed carbon, pH 10, and an electrical conductivity of 5.38 mS cm^{-1}. Scanning electron microscopy revealed a porous structure with diameters ranging from 3.31 to 42.60 µm. The biochar achieved removal efficiencies of up to 96.28%, exceeding 80% in six of the nine treatments evaluated. These findings demonstrate the strong potential of coffee husk-derived biochar as a sustainable and cost-effective adsorbent for agrochemical removal. Notably, treatments combining higher biochar doses with longer contact times achieved the best performance, underscoring the material's applicability in real-world wastewater treatment systems.

Keywords: Biochar, coffee husks, chlorpyrifos, removal, water treatment.

Introduction

Agrochemicals are synthetic compounds encompassing a broad range of products, including pesticides, herbicides, and fertilizers, each with specific functions directed toward pest and disease control, as well as improving crop quality and yield (1). However, due to the health and environmental risks associated with their uncontrolled use, the application of these compounds requires strict regulation and responsible management, particularly in countries with a strong reliance on agricultural activity (2).

In Colombia, this issue is particularly relevant since, according to the most recent agricultural census conducted by the National Administrative Department of Statistics (DANE), 40.6% of the national territory is dedicated to agricultural activities, and 70.20% of agricultural production units reported the use of synthetic chemical compounds for insect and microorganism control, many of which exhibit high toxicity (3).

One of the most widely used compounds is chlorpyrifos, a broad-spectrum organophosphate insecticide commonly applied in crops in the department of Antioquia (4). Its mode of action is based on the inhibition of the acetylcholinesterase enzyme, leading to neurotoxic effects in humans and non-target species, even at concentrations as low as 0.1 $\mu g\ L^{-1}$ (5). Moreover, its affinity for soil organic matter promotes persistence and facilitates transport into water bodies through runoff and leaching, thereby increasing its potential for bioaccumulation (5).

Despite the high toxicity and persistence of chlorpyrifos and other agrochemicals in aquatic systems, most wastewater treatment plants (WWTPs) in Colombia show limited performance, primarily due to economic and technological constraints. The most widely used treatments in the country—stabilization ponds, wetlands, and activated sludge systems—achieve average removal efficiencies of around 60% for conventional pollutants such as Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD), but are considerably less effective in eliminating emerging contaminants like agrochemicals (6)(7).

Consequently, advanced treatments such as chlorination, which relies on chlorine disinfection; ozonation, based on the oxidation of compounds using ozone; and chemical post-precipitation, which removes impurities through the formation of secondary precipitates, have been implemented (8). Nevertheless, these tertiary treatments involve high investment, operation, and maintenance costs, which restrict their application in resource-limited contexts (9).

For this reason, biochar has been increasingly promoted as an alternative material. Biochar is a carbonaceous solid obtained through the pyrolysis of biomass, whose physicochemical properties—including high porosity, large surface area, and the presence of functional groups—make it an efficient adsorbent (10). Several studies have reported removal efficiencies above 80% for pollutants such as heavy metals, nutrients, and agrochemicals (11)(12)(13). In addition, biochar stands out as a cost-effective, environmentally sustainable, and easily implementable alternative, particularly when produced from locally available agricultural or agro-industrial residues (14).

In this context, the production of biochar from agro-industrial residues represents a dual-benefit strategy, simultaneously addressing water contamination while promoting the valorization of organic byproducts such as coffee husks (15). Coffee husks are particularly abundant in coffee-growing regions such as southwestern Antioquia, where approximately 40 kg of residues—mainly husks and mucilage—are generated for every 100 kg of processed fruit, resulting in tons of waste at a commercial scale (16).

When inadequately disposed of, coffee husks can become an environmental contaminant due to their high caffeine (0.68–2.20%) and polyphenol content (4.00-4.60 mg of gallic acid g^{-1}), compounds capable of acidifying nearby water bodies (16). Nonetheless, their high lignin, cellulose, hemicellulose, protein, and micronutrient content makes them a suitable feedstock for biochar production (17). Accordingly, the objective of this study was to evaluate the efficiency of biochar produced from coffee husks as an alternative treatment for wastewater contaminated with agrochemicals in southwestern Antioquia.

Materials and Methods

Biochar production

Coffee husks used as raw material were collected from the farm La Santiaga, located in the village of Serranías, Jardín (Antioquia, Colombia). The husks were obtained after the coffee pulping process, and 500 g of material were stored in a resealable plastic bag with an airtight closure and kept at 4 °C to prevent fermentation.

To evaluate the drying treatments that would maximize biochar yield, four experimental conditions were tested, as presented in Table 1. For each condition, 10 g of sample were subjected to slow pyrolysis in a muffle furnace (JP Inglobal, Ref. JPMN9, 2022). The furnace was preheated to 105 °C, followed by heating to 400 °C at a rate of 8 °C min^{-1} and held at this temperature for 1 h. To displace oxygen, 3.30 g of a commercial effervescent compound (Alka-Seltzer®) was added per 20 g of sample, generating CO_2 according to the method proposed by Gómez et al. (18).

Table 1. Husk drying treatments

Treatment	Experimental conditions
1	Coffee husk without drying treatment
2	Drying in oven at 80°C for 1 hour
3	Oven-dried at 80°C for 3 hours
4	Drying in oven at 80°C for 3 hours and maceration in mortar.

After pyrolysis, all samples were placed in a desiccator with silica gel for 10 minutes under identical conditions to standardize residual moisture removal. The resulting biochar was weighed on an analytical balance (Precisa XB 220 A), and the recovery percentage (%R) was calculated using Equation (1).

$$\%R = \left(\frac{B}{C_0}\right) \times 100 \qquad (1)$$

Where:

- B: Biochar obtained (g)
- C_0: Initial husk (10 g)

Biochar characterization

Characterization included moisture content, volatile matter, ash content, fixed carbon, pH, and electrical conductivity. Moisture content (%H) was determined by drying 5 g of sample at 105 °C to constant weight, following Equation (2).

$$\%M = \left(\frac{P_i - P_s}{P_i}\right) \times 100 \qquad (2)$$

Where:

- P_i: initial weight (g)
- P_S: dry weight (g)

Subsequently, 1 g of the dried sample was heated at 750 °C for 7 minutes in a muffle furnace to calculate volatile matter (%V) according to Equation (3).

$$\%V = \left(\frac{P_s - P_v}{P_s}\right) \times 100 \quad (3)$$

Where:

- P_v: post-treatment weight (g)

The same sample was then heated again at 750 °C for 90 minutes to quantify ash content (%A) using Equation (4).

$$\%A = (P_v - P_E) \times 100 \quad (4)$$

Where:

- P_E: ash weight (g)

Fixed carbon content (%Cf) was determined by difference, following Equation (5):

$$\%C_f = 100\% - \%M - \%V - \%A \quad (5)$$

For pH and electrical conductivity, 500 mg of biochar were mixed with 10 mL of Type I water, centrifuged (1 h, 3500 rpm), allowed to settle, and analyzed using a multiparameter device (Multi 3510 IDS WTW).

Surface morphology was analyzed using scanning electron microscopy (SEM) at the Advanced Microscopy Center (CAM, SIU) with a JEOL JMS 6490 LV microscope. Samples were mounted on graphite tape, coated with ~12.5 nm of gold (Denton Vacuum Desk IV), and observed under high vacuum using a secondary electron detector. Additionally, an elemental analysis (CHONS) was carried out at an external specialized laboratory to determine the chemical composition of the biochar. The methodology was based on UNE-EN-15407 and ASTM-D5622-95 standards, as well as Application Note 42151 from Thermo Scientific. The analysis was performed using a FLASH2000 Elemental Analyzer (Thermo Scientific), which allowed for precise quantification of carbon, hydrogen, oxygen, nitrogen, and sulfur contents in the sample.

Clorpirifos removal from contaminated water using biochar

To evaluate biochar efficiency in removing chlorpyrifos, an aqueous solution with a final concentration of 200 µg L^{-1} was prepared from the commercial insecticide Lorsban® 4 EC (SODIAK S.A.). Treatments were carried out in 250 mL Erlenmeyer flasks containing 100 mL of contaminated water, to which biochar was added in the amounts specified in Table 2. The flasks were homogenized in an orbital shaker incubator (JPSHID40, 2022) at 100 rpm for the hydraulic retention times (HRTs) defined in Table 2.

Table 2. Removal test treatments.

Treatment	Amount of biochar (g)	HRT (min)
1	0.50	30
2	0.50	60
3	0.50	90
4	1.00	30

5	1.00	60
6	1.00	90
7	2.00	30
8	2.00	60
9	2.00	90

After treatment, samples were filtered through sterile gauze to separate the biochar from the aqueous phase. The filtrates were stored in screw-cap vials and refrigerated at 4 °C for subsequent analysis. All treatments were performed in triplicate, and a control without biochar—consisting of 100 mL of pesticide solution agitated at 100 rpm for 90 minutes—was included. Chlorpyrifos concentrations in the filtrates were then quantified using Gas Chromatography coupled with Mass Spectrometry (GC–MS).

Statistical analysis of chlorpyrifos removal efficiencies was performed using Rstudio (version 4.3.1, open-source license). Assumptions of normality, homoscedasticity, and independence were first verified. Once validated, an analysis of variance (ANOVA) was applied to compare removal efficiencies among treatments. Post-hoc multiple comparison tests (Tukey's HSD) were subsequently conducted to identify statistically significant differences between treatments. A significance threshold of $p < 0.05$ was used.

Results and discussion

Biochar production

Coffee husks demonstrated potential for biochar production, achieving up to 20% recovery of dry biochar per unit of raw material, as shown in Table 3.

Table 3. Percentage of biochar recovery per treatment

Treatment	Biochar obtained (g)	% Recovery
1	0.60	6
2	1.20	12
3	2.00	20
4	0.20	2

Treatments 1 and 4 yielded the lowest recovery percentages (6% and 2%, respectively), which can be attributed to the physical characteristics of the husks (19)(20). In Treatment 1, the presence of residual moisture increased the apparent particle size, thereby hindering efficient heat and mass transfer during pyrolysis (21). In contrast, maceration in Treatment 4 promoted greater disintegration of the material, which limited the decomposition process, the release of volatile compounds, and the effective formation of the solid product due to the accelerated heating rate (22).

Conversely, Treatment 3 achieved the highest recovery (20%), a value close to the expected yield for coffee husk biochar production, which typically ranges from 25% to 30% according to Van Limbergen et al. (23). In their study, a specialized pyrolysis reactor with a continuous nitrogen supply was used to maintain an anoxic atmosphere. Despite employing a simpler methodology in the present work—namely, a conventional muffle furnace combined with effervescent tablets to displace oxygen—a comparable yield was obtained, this finding highlights that pyrolysis can be effective even under basic operational conditions (23).

Such operational simplicity positions pyrolysis as a technically and economically viable alternative compared to other biochar production methods. For instance, gasification requires stringent operational parameters and primarily produces syngas (24), while hydrothermal carbonization involves the use of aggressive chemical agents (e.g., H_3PO_4, $FeCl_3$, $FeSO_3$, or KOH) and generates additional waste streams (25).

Biochar characterization

Physicochemical parameters evaluated during biochar characterization (Table 4) are critical for understanding its structure and adsorption capacity. A low moisture content indicates greater pore availability, whereas high values may block active sites (26). The volatile matter content reflects the presence of residual organic compounds and the efficiency of the pyrolysis process (27). Similarly, the ash content represents the inorganic fraction of biochar; excessive levels may obstruct porosity and reduce the effective surface area. In contrast, a high fixed carbon content is associated with a stable porous structure with a larger specific surface area, which promotes hydrophobic interactions with contaminants (28).

Table 4. Comparison of physicochemical characterization of coffee husk biochar

Proximal analysis	CHB	CHB (29)	CHB (30)
% M	9.50	2.40	5.20
% A	15.85	28.23	16.50
% V	48.41	35.61	22.70
% C_f	26.24	33.76	55.60

CHB: Coffee Husk Biochar

Biochar obtained in this study exhibited a higher moisture content (9.50%) compared with values reported by Seatiawan et al. (29) (2.40%) and Suraj et al. (30) (5.20%). This difference may be associated with the drying time of the coffee husks before analysis, suggesting the need to optimize this step to improve process efficiency.

Regarding ash content (15.85%), the results were similar to those obtained by Suraj et al. (30) (16.50%) and notably lower than those reported by Seatiawan et al. (29) (28.23%). This represents an advantage, since lower ash content indicates a higher proportion of usable carbon and a reduced presence of non-combustible mineral residues, thereby improving biochar applicability in adsorption processes (31).

Volatile matter content (48.41%) was higher than that of fixed carbon (26.24%), which is consistent with the inverse relationship between these two fractions, since a high proportion of volatile compounds suggests that thermoconversion did not completely transform organic matter into solid carbon (32). Nevertheless, fixed carbon content was comparable to that reported by Seatiawan et al. (29) (33.76%), indicating that the method applied in this study can yield biochar with properties similar to those produced using specialized pyrolysis technologies.

Additionally, pH and electrical conductivity of biochar provide valuable insights into its surface chemistry and reactivity. An alkaline pH indicates the predominance of negatively charged functional groups, which can enhance the retention of neutral or slightly polar compounds through hydrophobic and π–π interactions (33). Electrical conductivity, in turn, is related to the presence of mobile ionic species and conductive carbonaceous materials, which may facilitate ion-exchange processes and redox reactions in aqueous systems (34).

Alkaline pH observed (pH 10.00) is mainly attributed to the accumulation of basic inorganic compounds such as carbonates, oxides, and hydroxides of alkali and alkaline earth metals during thermal decomposition of the feedstock (35). This alkaline character is usually accompanied by soluble salts that also influence electrical conductivity. For coffee husk biochars, values typically range between 2.16–9.66 mS cm^{-1} (35)(36). In this study, electrical conductivity was 5.38 mS cm^{-1}, a moderate value within the reported range. Such conductivity is appropriate for adsorption purposes, as it avoids excessive concentrations of soluble ions that could compete with contaminants for active surface sites (37).

Scanning electron microscopy (SEM) analysis (Fig. 1) revealed a well-defined surface structure with a network of open pores of varying sizes, ranging from 3.31 μm to 42.60 μm. This wide pore size distribution indicates good preservation of the original plant matrix and suggests a high effective surface area, favorable for adsorption processes (38) (39) (40) (41). The estimated average pore size was approximately 22.85 μm, indicating the predominance of macropores; such features facilitate the transport of water and contaminants into more reactive internal zones of the material, thereby enhancing adsorption efficiency in water treatment applications (42).

Fig 1. Scanning electron microscopy of biochar produced from coffee husk. Image "a" has a magnification of 450X, where the general porous structure of the material is shown, image b, with a magnification of 650X, allows observing in greater detail the pores and the internal surface. Obtained from the Center for Advanced Microscopy

Additionally, small irregular fragments adhered to the inner pore surfaces were observed (marked with red circles in image b, corresponding to higher magnification). These could correspond to inorganic salt residues, as a similar behavior was reported by Chico-Proaño et al. (43) in biochar derived from coffee husks, where high concentrations of potassium oxide (62.17%) and calcium oxide (19.45%) were identified. According to the authors, such accumulations contribute to improving the thermal conductivity of biochar and may positively influence contaminant removal by acting as hybrid ion-exchange sites, thereby facilitating the retention of charged species (43).

Elemental analysis results (Table 5) were consistent with values reported in the literature for coffee husk biochars (33) (44) (45), indicating that the applied process was effective for biochar production. Based on the proportions of hydrogen, oxygen, and carbon, H/C and O/C ratios of 0.06 and 0.69, respectively, were obtained; these elemental ratios serve as indicators of the carbonization degree (46). The low H/C ratio indicates extensive hydrogen removal, which reflects the formation of aromatic carbon structures; this level of carbonization is sufficiently advanced to promote dehydration and demethylation reactions, thereby improving both chemical resistance and thermal stability (46).

Table 5. Elemental characterization of coffee husk biochar

Elementals	Percentage ($\%_{DB}$)	Uncertainty (±)
C	45.48	4.55
H	2.97	0.30
O	31.23	3.12
N	2.76	0.28
S	<0.10	0.01

(DB): Dry Basis

Conversely, the relatively high O/C ratio suggests a surface still rich in oxygen-containing functional groups, likely resulting from surface oxidation due to pyrolysis conditions that were not completely anoxic, which explains the coexistence of stable aromatic structures with an oxygen-enriched surface (47). Such oxygenated groups may enhance interactions with weakly polar contaminants such as chlorpyrifos by enabling hydrogen bonding and other dipolar interactions with electronegative atoms present in its structure, including oxygen and nitrogen from the phosphorothioate group and the pyridinyl ring (39)(47).

Clorpirifos removal from contaminated water using biochar

Chlorpyrifos removal experiments revealed significant differences in treatment efficiency. Figure 2 provides a graphical representation of the removal percentages based on combinations of biochar dosage and hydraulic retention time (HRT). Among all treatments, Treatment 9 (2.00 g of biochar – 90 min HRT) achieved the highest removal efficiency at 96.28%, followed closely by Treatment 6 (1.00 g – 90 min) at 96.11%, and Treatment 8 (2.00 g – 60 min) at 95.08%. In contrast, Treatment 1 (0.50 g – 30 min) exhibited the lowest removal efficiency (38.12%), followed by Treatments 2 (0.50 g – 60 min) and 3 (0.50 g – 90 min), with removal percentages of 50.24% and 53.83%, respectively. Overall, Treatments 4 to 9 exceeded 80% removal, indicating favorable adsorption under specific operational conditions.

Fig 2. Effect of biochar amount and contact time on percent chlorpyrifos removal. Bars represent mean removal efficiencies, with colors indicating different HRT levels (30, 60, and 90 min).

These findings demonstrate that hydraulic retention time (HRT) directly influences chlorpyrifos adsorption efficiency. A short HRT, such as 30 minutes, may be insufficient to reach adsorption equilibrium, limiting the time available for chlorpyrifos molecules to diffuse into the biochar pore network and bind to active macropore sites (48) (49). By contrast, longer contact times, such as 90 minutes, promote more extensive contaminant diffusion and enable stronger interactions—including hydrogen bonding and hydrophobic interactions—with oxygenated functional groups (-OH, -COOH, -C=O), which were inferred to be abundant in the biochar from elemental characterization (50) (51).

HRT is also closely related to the amount of adsorbent used. When a lower mass of biochar is applied, longer contact times are needed to compensate for the limited availability of active sites. Conversely, higher biochar dosages provide a larger active surface area, enabling high removal efficiencies even at shorter contact times (52). This relationship is consistent with the findings of Kalsoom et al. (53), who reported that pesticide adsorption increases proportionally with biochar dosage due to greater surface availability and higher contaminant retention capacity. Increasing the adsorbent dose expands the surface area and reduces competition between water molecules and chlorpyrifos for adsorption sites (53)(54). This competition is particularly evident at low dosages, such as 0.50 g, where the limited number of functional groups reduces removal efficiency.

To quantitatively support these observations, statistical analysis of the data was performed. Model assumptions were verified, confirming normality, homogeneity of variance, and independence of residuals. This allowed the application of an analysis of variance (ANOVA), whose results (Fig 3) showed, based on p-values, that both biochar dosage and contact time, as well as their interaction, had statistically significant effects on chlorpyrifos removal.

Fig 3. ANOVA table and significant effects. ANOVA table obtained from the analysis of variance for the factors biochar dosage (Biochar), contact time (TRH), and their interaction (Biochar:TRH) on chlorpyrifos removal.

P-values below the significance threshold ($\alpha = 0.05$) for all three factors confirm that the differences observed across treatments were not attributable to random variation. Furthermore, comparison of sums of squares indicated that biochar dosage contributed the most to removal variability (Sum Sq = 12,627.3), followed by contact time (435.1) and, to a lesser extent, the interaction between both factors (124.2). The mean residual square (1.0) suggested that unexplained variability was minimal, indicating a good model fit and reinforcing the validity of the observed effects.

Subsequent multiple comparison analysis using Tukey's test (Fig 4) confirmed significant differences between treatments, consistent with the ANOVA results, and highlighted the strong influence of biochar dosage on chlorpyrifos removal. Treatments with 0.50 g of biochar showed significantly lower removal efficiencies (Figure 4, groups g, f, and e), particularly with a 30 min HRT, although performance improved with extended contact time (90 min). This finding confirms that at low dosages, prolonged contact time enhances adsorption efficiency. In contrast, at dosages of 1.00 g and 2.00 g, removal efficiencies above 90% were achieved with HRTs of 60 and 90 min. These treatments shared groups a, b, and c in Tukey's test (Figure 4), indicating statistically similar effects. Moreover, even at a 30 min HRT, removal efficiencies exceeded 80%, suggesting that higher dosages can offset shorter contact times while maintaining high removal performance.

Fig 4. Boxplot of the combined effects of the factors and Tukey's test. Boxplot showing the combined effects of biochar dosage and contact time (HRT) on chlorpyrifos removal (%). Different letters above the boxes indicate statistically significant differences among treatments according to Tukey's test ($\alpha = 0.05$).

Notably, treatments 6 (1.0 g x 90 min), 8 (2.0 g x 60 min), and 9 (2.0 g x 90 min) achieved the highest removal efficiencies without significant differences among them, as reflected by shared groupings in Tukey’s test (a and ab). This indicates that despite variations in dosage and contact time, their effects on chlorpyrifos removal were statistically comparable. Thus, treatment 6 may be considered optimal when aiming for more efficient biochar use, as it achieved high removal with only 1.00 g. On the other hand, treatment 8 could be preferable in contexts where shorter treatment times are prioritized, while maintaining comparable effectiveness. The choice between these treatments ultimately depends on operational priorities, whether minimizing material consumption or treatment duration.

The interaction plot (Fig 5) illustrates a marked increase in average removal when biochar dosage increased from 0.50 g to 1.00 g. Beyond this point, the curves stabilized between 1.00 g and 2.00 g, suggesting diminishing returns in removal efficiency with higher dosages under the tested conditions. Differences among HRT levels were more pronounced at lower biochar dosages, but became less significant as dosage increased, indicating that contact time is more critical when adsorption capacity is limited, whereas higher dosages reduce time dependency for achieving high efficiencies.

Fig 5. Interaction plot. Interaction plot showing the combined effect of biochar dosage and contact time (HRT) on chlorpyrifos removal (%). Lines represent the mean removal efficiencies for each HRT level (30, 60, and 90 min).

The results of this study are consistent with other reports in the literature. For instance, Melo et al. (55) achieved removal efficiencies of 75–84% using biochar filters derived from plant biomass. Similarly, Li et al. (56) and Pandey et al. (57) reported up to 98% removal of chemical oxygen demand (COD) and approximately 80% removal of nutrients in constructed wetland systems, demonstrating the potential of biochar as a water treatment technology.

Beyond its effectiveness, biochar is also economically viable. Its cost can be up to five times lower than that of activated carbon, ranging from 350–1200 USD per ton compared with 1100–1700 USD per ton for activated carbon (34) (58). This makes biochar a sustainable and cost-effective alternative for large-scale wastewater treatment applications. In particular, biochar derived from coffee husks has demonstrated high efficiency in removing various contaminants under conditions resembling real effluents. For example, Vu & Do (59), reported an ammonium-nitrogen adsorption equilibrium of 2.80 mg N g^{-1}, while Chung et al. (60) achieved efficient removal of 5.00 mg L^{-1} of Pb^{2+} and Cu^{2+} (levels typically found in industrial wastewater) with 2.00 g of biochar, obtaining maximum adsorption capacities of up to 10.00 mg g^{-1} for Pb and 13.10 mg g^{-1} for Cu. Similarly, in the case of an iron oxide–modified coffee husk biochar (CHB-Fe_3O_4), glyphosate removal reached 99.64%, with an adsorption capacity of 22.40 mg g^{-1}, under conditions simulating real contaminated waters (61).

Results demonstrate that coffee husk–derived biochar, at the practical concentrations applied in this study, is capable of removing contaminants that pose critical risks to human health and the environment, supporting its applicability in real wastewater treatment scenarios.

Conclusion

This study demonstrated that biochar produced from coffee husks can be successfully obtained through a slow pyrolysis process and has significant potential as an alternative treatment for wastewater contaminated with agrochemicals in the Southwestern region of Antioquia. Using a practical oxygen-displacement strategy with effervescent tablets, the process achieved a 20% recovery yield relative to the initial biomass, highlighting both the viability of the production method and the applicability of the resulting biochar for chlorpyrifos removal, particularly in resource-limited settings.

Characterization of the obtained biochar revealed similarities with other biochars reported in the literature in terms of elemental composition, proximate analysis, and surface morphology.

The predominance of carbon and the presence of a well-defined porous structure, confirmed by scanning electron microscopy, indicated that even under pyrolysis conditions that were not fully anoxic, the material retained physicochemical properties suitable for application as an adsorbent. However, the relatively high volatile matter and oxygen contents suggest that further optimization of the pyrolysis atmosphere could improve the stability of the final product in future studies.

Application of the biochar to chlorpyrifos removal in contaminated water samples yielded promising results, with efficiencies exceeding 80% in six of the nine treatments evaluated. Notably, treatments 6 (1.0 g biochar x 90 minutes HRT), 8 (2.0 g x 60 minutes HRT), and 9 (2.0 g x 90 minutes HRT) achieved removal efficiencies greater than 95%. These findings demonstrate that 1.0 g biochar x 90 minutes is an efficient alternative of rational adsorbent use, which may be particularly advantageous in batch systems or in processes where material consumption needs to be optimized.

Meanwhile, 2.0 g of biochar x 60 minutes of THR emerges as a strategic option for operational implementations such as biofilters or continuous-flow systems, where reducing retention time may facilitate operation, even if it requires greater biochar consumption. The selection of the optimal treatment will therefore depend on the objectives and constraints of the treatment system being applied.

Looking forward, future works should explore pretreatment strategies for drying coffee husks, as lower initial moisture content could improve pyrolysis yield. Additionally, further optimization of the oxygen-displacement strategy using effervescent tablets—considering variables such as dosage relative to furnace volume or geometry—could significantly enhance biochar recovery and increase its adsorption efficiency.

Acknowledgments

The authors thank the laboratory of the Southwestern Branch of the University of Antioquia and its coordinators for their support during this research. They are also grateful to the Research Group on Environmental Management and Modeling (GAIA) and, in particular, to Professor Carlos Ramos for his assistance with the analysis of the removal experiment samples using GC–MS. Finally, the authors acknowledge Professor Yamilet Arcos, Coordinator of Regional Programs at the School of Microbiology, for her constant support and encouragement.

References

1. Owemigisha E, Rwot AO, Sempebwa D, Birungi CM, Tamale A, Drileyo G, et al. Exploring knowledge, attitudes and practices of farmers at the edge of Budongo forest on agrochemicals usage. Sustain Environ [Internet]. 2024;10(1):1–11. Available from: https://doi.org/10.1080/27658511.2023.2299537

2. Gnanaprakasam PD, Vanisree AJ. Recurring detrimental impact of agrochemicals on the ecosystem, and a glimpse of organic farming as a possible rescue. Environ Sci Pollut Res [Internet]. 2022;29(50):75103–12. Available from: https://doi.org/10.1007/s11356-022-22750-1

3. DANE. Censo Nacional Agropecuario - Presentación de resultados [Internet]. 2015. Available from: https://www.dane.gov.co/files/CensoAgropecuario/avanceCNA/CNA_agosto_2015_new_present.pdf

4. Hernandez-Angel ML, Lopez EP, Jaramillo Granda MC, Posada Usuga AP. Identificación

de microorganismos biorremediadores de suelos agrícolas del norte de Antioquia para degradación del clorpirifos. Rev Politécnica. 2020;16(32):96–110.

5. Pena-Gómez PR, Fernández-San Juan R, Somoza A, Vazquez P, Cortelezzi A. Cuenca del Arroyo Chapaleofú: agriculturización y efecto del insecticida clorpirifos sobre una especie no blanco. Ecosistemas y Recur Agropecu. 2022;9(2):1–11.

6. Vargas AKN, Calderón J, Velásquez D, Castro M, Núñez DA. Biological system analysis for domestic wastewater treatment in Colombia. Ingeniare. 2020;28(2):315–22.

7. Pérez Mesa A, Saldarriaga Molina JC, Ríos LA, Ocampo Echeverri E, Ocampo Echeverri D. Diagnosis of Nutrient Discharges and Management Alternatives in Developing Countries and the Use of Microalgae as a Potential Solution: A Case Study from Different Provinces in Antioquia, Colombia. Water. 2024;16:2215.

8. Kato S, Kansha Y. Comprehensive review of industrial wastewater treatment techniques [Internet]. Vol. 31, Environmental Science and Pollution Research. Springer Berlin Heidelberg; 2024. 51064–51097 p. Available from: https://doi.org/10.1007/s11356-024-34584-0

9. Michel A, Armbruster D, Benz-Birck A, Deppermann N, Doetzer R, Flörs M, et al. Proposal for a tiered approach to evaluate the risk of transformation products formed from pesticide residues during drinking water treatment. Environ Sci Eur [Internet]. 2022;34(1):1–22. Available from: https://doi.org/10.1186/s12302-022-00688-y

10. Issaka E, Fapohunda FO, Amu-Darko JNO, Yeboah L, Yakubu S, Varjani S, et al. Biochar-based composites for remediation of polluted wastewater and soil environments: Challenges and prospects. Chemosphere [Internet]. 2022 Jun 1 [cited 2023 Aug 28];297:134163.

Available from: https://doi.org/10.1016/j.chemosphere.2022.134163

11. Chen Z, Jing Y, Wang Y, Meng X, Zhang C, Chen Z, et al. Enhanced removal of aqueous Cd(II) by a biochar derived from salt-sealing pyrolysis coupled with NaOH treatment. Appl Surf Sci [Internet]. 2020;511(1):145619. Available from: https://doi.org/10.1016/j.apsusc.2020.145619

12. Muoghalu C, Cirrus H, Semiyaga S, Manga M. Adsorptive removal of organics and nutrients from septic tank effluent using oak wood chip biochar : Kinetic analysis and numerical modeling. Clean Water [Internet]. 2025;3(1):100073. Available from: https://doi.org/10.1016/j.clwat.2025.100073

13. Jacob MM, Ponnuchamy M, Kapoor A, Sivaraman P. Bagasse based biochar for the adsorptive removal of chlorpyrifos from contaminated water. J Environ Chem Eng [Internet]. 2020;8(4):103904. Available from: https://doi.org/10.1016/j.jece.2020.103904

14. Veiga PA da S, Schultz J, Matos TT da S, Fornari MR, Costa TG, Meurer L, et al. Production of high-performance biochar using a simple and low-cost method: Optimization of pyrolysis parameters and evaluation for water treatment. J Anal Appl Pyrolysis [Internet]. 2020;148(April):104823. Available from: https://doi.org/10.1016/j.jaap.2020.104823

15. Samuel Olugbenga O, Goodness Adeleye P, Blessing Oladipupo S, Timothy Adeleye A, Igenepo John K. Biomass-derived biochar in wastewater treatment- a circular economy approach. Waste Manag Bull [Internet]. 2024;1(4):1–14. Available from: https://doi.org/10.1016/j.wmb.2023.07.007

16. Triviño Pineda JS, Contreras García J, Amorocho Cruz CM, Sánchez Ramírez JE. Obtención de bioproductos a partir de residuos del beneficio húmedo del café (pulpa). Rev

Colomb Biotecnol. 2022;23(2):6–14.

17. Nguyen D Van, Duong CTT, Vu CNM, Nguyen HM, Pham TT, Tran-Thuy TM, et al. Data on chemical composition of coffee husks and lignin microparticles as their extracted product. Data Br [Internet]. 2023;51(1):109781. Available from: https://doi.org/10.1016/j.dib.2023.109781

18. Gómez KY, Quevedo NR, Molina LDC. Use of the Biochar Obtained by Slow Pyrolysis from Ulex Europaeus in the Removal of Total Chromium from the Bogotá-Colombia River Water. Chem Eng Trans. 2021;86(1):289–94.

19. Zhang L, Yao Z, Zhao L, Yu F, Li Z, Yi W, et al. Effects of various pyrolysis temperatures on the physicochemical characteristics of crop straw-derived biochars and their application in tar reforming. Catal Today [Internet]. 2024;433:114663. Available from: https://doi.org/10.1016/j.cattod.2024.114663

20. Gao N, Wang F, Quan C, Santamaria L, Lopez G, Williams PT. Tire pyrolysis char: Processes, properties, upgrading and applications. Prog Energy Combust Sci [Internet]. 2022;93:101022. Available from: https://doi.org/10.1016/j.pecs.2022.101022

21. Aboelela D, Saleh H, Attia AM, Elhenawy Y, Majozi T, Bassyouni M. Recent Advances in Biomass Pyrolysis Processes for Bioenergy Production: Optimization of Operating Conditions. Sustainability. 2023;15(14):11238.

22. Bianasari AA, Khaled MS, Hoang TD, Reza MS, Bakar MSA, Azad AK. Influence of combined catalysts on the catalytic pyrolysis process of biomass: A systematic literature review. Energy Convers Manag [Internet]. 2024;309:118437. Available from: https://doi.org/10.1016/j.enconman.2024.118437

23. Van Limbergen T, Roegiers IH, Bonné R, Mare F, Haeldermans T, Joos B, et al. Characterisation of Two Wood-Waste and Coffee Bean Husk Biochars for the Removal of Micropollutants from Water. Front Environ Sci. 2022;10:1–18.

24. Gabhane JW, Bhange VP, Patil PD, Bankar ST, Kumar S. Recent trends in biochar production methods and its application as a soil health conditioner : a review. SN Appl Sci [Internet]. 2020;2(7):1–21. Available from: https://doi.org/10.1007/s42452-020-3121-5

25. Krishna Murthy TP, Gowrishankar BS, Krishna RH, Chandraprabha MN, Mathew BB. Magnetic modification of coffee husk hydrochar for adsorptive removal of methylene blue: Isotherms, kinetics and thermodynamic studies. Environ Chem Ecotoxicol [Internet]. 2020;2:205–12. Available from: https://doi.org/10.1016/j.enceco.2020.10.002

26. Hu J, Shen Y, Zhu N. Optimizing adsorption performance of sludge-derived biochar via inherent moisture-regulated physicochemical properties. Waste Manag [Internet]. 2023;169:70–81. Available from: https://doi.org/10.1016/j.wasman.2023.06.033

27. Qiu B, Tao X, Wang H, Li W, Ding X, Chu H. Biochar as a low-cost adsorbent for aqueous heavy metal removal: A review. J Anal Appl Pyrolysis [Internet]. 2021;155:105081. Available from: https://doi.org/10.1016/j.jaap.2021.105081

28. Jagadeesh N, Sundaram B. Adsorption of Pollutants from Wastewater by Biochar: A Review. J Hazard Mater Adv. 2023;9:100226.

29. Setiawan A, Nurjannah S, Riskina S, Fona Z, Muhammad, Drewery M, et al. Understanding the Thermal and Physical Properties of Biochar Derived from Pre-washed Arabica Coffee Agroindustry Residues. Bioenergy Res [Internet]. 2025;18(1):1–13. Available from: https://doi.org/10.1007/s12155-025-10818-y

30. Suraj P, Sreekumar S, Arun P, Muraleedharan C. Feasibility study of coffee husk char-derived carbon dots to enhance solar photovoltaic-thermal applications. J Anal Appl Pyrolysis [Internet]. 2024;179(1):106509. Available from: https://doi.org/10.1016/j.jaap.2024.106509

31. Setter C, Silva FTM, Assis MR, Ataíde CH, Trugilho PF, Oliveira TJP. Slow pyrolysis of coffee husk briquettes: Characterization of the solid and liquid fractions. Fuel. 2020;261:116420.

32. Shah HH, Amin M, Pepe F, Mancusi E, Fareed AG. Overview of environmental and economic viability of activated carbons derived from waste biomass for adsorptive water treatment applications. Environ Sci Pollut Res [Internet]. 2023; Available from: https://doi.org/10.1007/s11356-023-30540-6

33. Manikandan SK, Pallavi P, Shetty K, Bhattacharjee D, Giannakoudakis DA, Katsoyiannis IA, et al. Effective Usage of Biochar and Microorganisms for the Removal of Heavy Metal Ions and Pesticides. Molecules. 2023;28(2):719.

34. Kolganova A, Lal R, Firkins J. Biochar's Electrochemical Properties Impact on Methanogenesis: Ruminal vs. Soil Processes. J Agric Chem Environ. 2023;12(1):28–43.

35. Pouangam Ngalani G, Dzemze Kagho F, Peguy NNC, Prudent P, Ondo JA, Ngameni E. Effects of coffee husk and cocoa pods biochar on the chemical properties of an acid soil from West Cameroon. Arch Agron Soil Sci [Internet]. 2023;69(5):744–58. Available from: https://doi.org/10.1080/03650340.2022.2033733

36. Thuong Huyen D, Uyen Thanh D, Xuan Tien D, Nam Phat L, Thanh Phong L, Rockne K. Biochars from various agro-wastes in Vietnam: Insight into the influence of pyrolysis

temperatures on characteristics for potential of waste management. J Ind Eng Chem [Internet]. 2024;146(1):748–56. Available from: https://doi.org/10.1016/j.jiec.2024.12.001

37. Ottani F, Morselli N, De Luca A, Puglia M, Pedrazzi S, Allesina G. The conductivity dilemma: How biochar grain's chemical composition and morphology hinder the direct measurement of its electrical conductivity. Meas J Int Meas Confed. 2023;222(1):113662.

38. Jiao R, Zha Z, Qi F, Liu X, Diao R, Yan D, et al. Optimized preparation of biochar from large-particle biomass: analysis of process characteristics and structural evolution. J Energy Inst [Internet]. 2025;120:102128. Available from: https://doi.org/10.1016/j.joei.2025.102128

39. Barquilha CER, Braga MCB. Adsorption of organic and inorganic pollutants onto biochars: Challenges, operating conditions, and mechanisms. Bioresour Technol Reports [Internet]. 2021;15:100728. Available from: https://doi.org/10.1016/j.biteb.2021.100728

40. Qiu M, Liu L, Ling Q, Cai Y, Yu S, Wang S, et al. Biochar for the removal of contaminants from soil and water: a review. Biochar [Internet]. 2022;4(1):1–25. Available from: https://doi.org/10.1007/s42773-022-00146-1

41. Zhao L, Sun ZF, Pan XW, Tan JY, Yang SS, Wu JT, et al. Sewage sludge derived biochar for environmental improvement: Advances, challenges, and solutions. Water Res X [Internet]. 2023;18:100167. Available from: https://doi.org/10.1016/j.wroa.2023.100167

42. Raj L, Sur D, Rekha MM, Kundlas M, Krithiga T, Panigrahi R, et al. Biochar derived from pistachio shells: A novel adsorbent for efficient lead sequestration in water treatment. J Mol Struct [Internet]. 2025;1344(June):142930. Available from: https://doi.org/10.1016/j.molstruc.2025.142930

43. Chico-Proano A, Nicolalde JF, Boada M, Bonilla O, Riofrio C, Cueva JA, et al. Biochar from waste coffee husk as a thermal conductivity enhancer in palm stearin BPCMs. Carbon Trends. 2025;19:100501.

44. Konneh M, Wandera SM, Murunga SI, Raude JM. Adsorption and desorption of nutrients from abattoir wastewater: modelling and comparison of rice, coconut and coffee husk biochar. Heliyon [Internet]. 2021;7(11):e08458. Available from: http://dx.doi.org/10.1016/j.heliyon.2021.e08458

45. Islam MA, Parvin MI, Dada TK, Kumar R, Antunes E. Silver adsorption on biochar produced from spent coffee grounds: validation by kinetic and isothermal modelling. Biomass Convers Biorefinery [Internet]. 2022;14(22):28007–21. Available from: https://doi.org/10.1007/s13399-022-03491-0

46. Chungcharoen T, Limmun W, Srisang S, Phetpan K, Ruttanadech N, Youryon P, et al. Enhanced biodiesel purification using coffee husk bioadsorbents: The role of pyrolysis temperature, KOH activation, and adsorption efficiency. Renew Energy [Internet]. 2025;244(December 2024):122700. Available from: https://doi.org/10.1016/j.renene.2025.122700

47. Afessa MM, Olu FE, Geleta WS, Legese SS, Ramayya AV. Unlocking the potential of biochar derived from coffee husk and khat stem for catalytic tar cracking during biomass pyrolysis: characterization and evaluation. Biomass Convers Biorefinery [Internet]. 2024;15:11011–26. Available from: https://doi.org/10.1007/s13399-024-05957-9

48. Ambaye TG, Vaccari M, van Hullebusch ED, Amrane A, Rtimi S. Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from

industrial wastewater. Int J Environ Sci Technol [Internet]. 2021;18(10):3273–94. Available from: https://doi.org/10.1007/s13762-020-03060-w

49. Milanković V, Tasić T, Brković S, Potkonjak N, Unterweger C, Pašti I, et al. The adsorption of chlorpyrifos and malathion under environmentally relevant conditions using biowaste carbon materials. J Hazard Mater. 2024;480:135940.

50. Li A, Ye C, Jiang Y, Deng H. Enhanced removal performance of magnesium-modified biochar for cadmium in wastewaters: Role of active functional groups, processes, and mechanisms. Bioresour Technol [Internet]. 2023;386(June):129515. Available from: https://doi.org/10.1016/j.biortech.2023.129515

51. Saadi AS, Bousba S, Riah A, Belghit M, Belkhalfa B, Barour H. Efficient synthesis of magnetic activated carbon from oak pericarp for enhanced dye adsorption: A one-step approach. Desalin Water Treat [Internet]. 2024;319:100420. Available from: https://doi.org/10.1016/j.dwt.2024.100420

52. Bazarin G, Módenes AN, Espinoza-Quiñones FR, Borba CE, Trigueros DEG, Dall'Oglio IC. High removal performance of reactive blue 5G dye from industrial dyeing wastewater using biochar in a fixed-bed adsorption system: Approaches and insights based on modeling, isotherms, and thermodynamics study. J Environ Chem Eng. 2024;12(1):111761.

53. Kalsoom K, Khan ZA, Khan S, Muhammad N, Jabeen F, Ziad M, et al. Comparative adsorption of selected pesticides from aqueous solutions by activated carbon and biochar. Aqua Water Infrastructure, Ecosyst Soc. 2024;73(10):1994–2012.

54. Okoya AA, Adegbaju OS, Akinola OE, Akinyele AB, Amuda OS. Comparative Assessment of the Efficiency of Rice Husk Biochar and Conventional Water Treatment Method to

Remove Chlorpyrifos from Pesticide Polluted Water. Curr J Appl Sci Technol. 2020;39(2):1–11.

55. Melo N, Menezes O, Paraiso M, Florêncio L, Kato MT, Gavazza S. Selecting the best electron donor and operational temperature for the rapid biotransformation of the insensitive munitions compound 2,4-dinitroanisole (DNAN) by anaerobic sludge. Water Sci Technol. 2021;83(11):2691–9.

56. Li X, Tang M, Yao S, Ma S, Yang Y. Enhanced winter performance of constructed wetlands via biochar-immobilized Psychrotrophic bacteria. J Water Process Eng [Internet]. 2025;76:108184. Available from: https://doi.org/10.1016/j.jwpe.2025.108184

57. Pandey D, Singh SV, Savio N, Bhutto JK, Srivastava RK, Yadav KK, et al. Biochar application in constructed wetlands for wastewater treatment: A critical review. J Water Process Eng [Internet]. 2025;69:106713. Available from: https://doi.org/10.1016/j.jwpe.2024.106713

58. Patel MR, Panwar NL. Evaluating the agronomic and economic viability of biochar in sustainable crop production. Biomass and Bioenergy [Internet]. 2024;188:107328. Available from: https://doi.org/10.1016/j.biombioe.2024.107328

59. Vu NT, Do KU. Insights into adsorption of ammonium by biochar derived from low temperature pyrolysis of coffee husk. Biomass Convers Biorefinery. 2023;13(3):2193–205.

60. Chung NT, Thuy DT, Trang LH, Vu NT. Evaluating coffee husk biochar as a sustainable and novel adsorbent for lead and copper in wastewater. Biomass Convers Biorefinery [Internet]. 2025;15(12):18437–53. Available from: https://doi.org/10.1007/s13399-025-06674-7

61. Lita AL, Hidayat E, Mohamad Sarbani NM, Harada H, Yonemura S, Mitoma Y, et al. Glyphosate Removal from Water Using Biochar Based Coffee Husk Loaded Fe3O4. Water. 2023;15(16):2945.

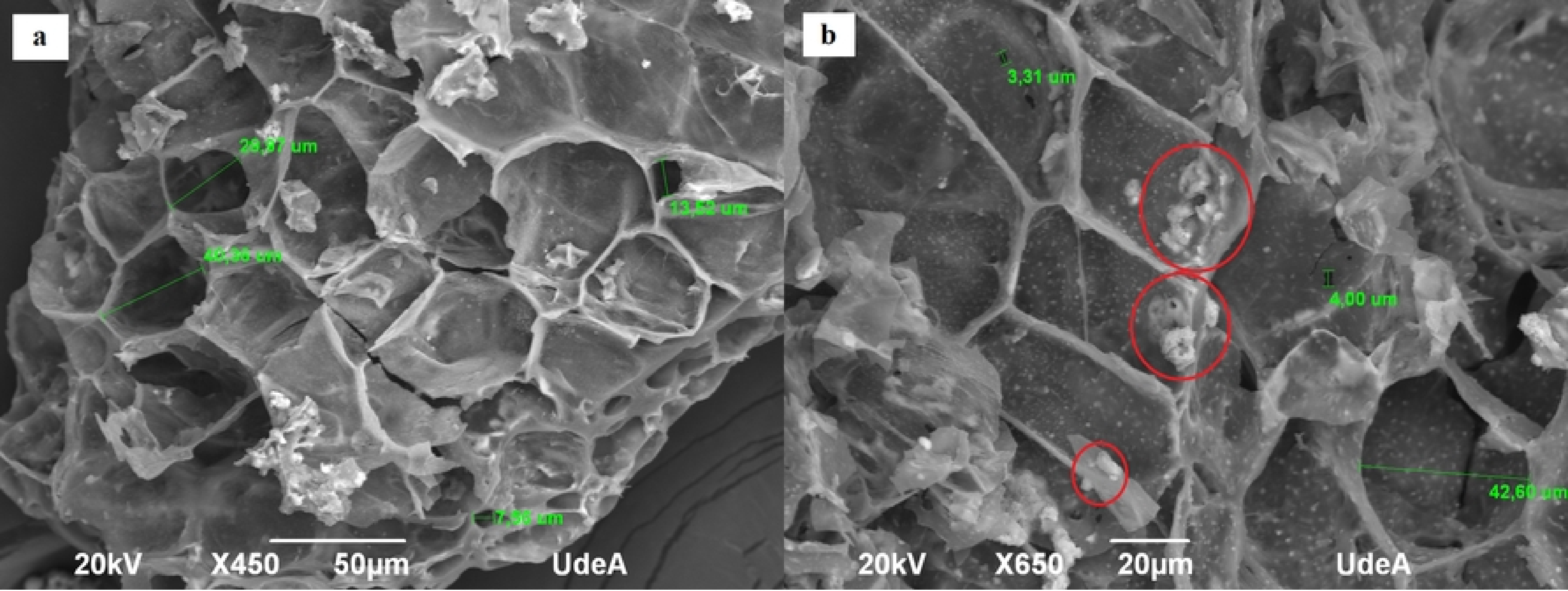
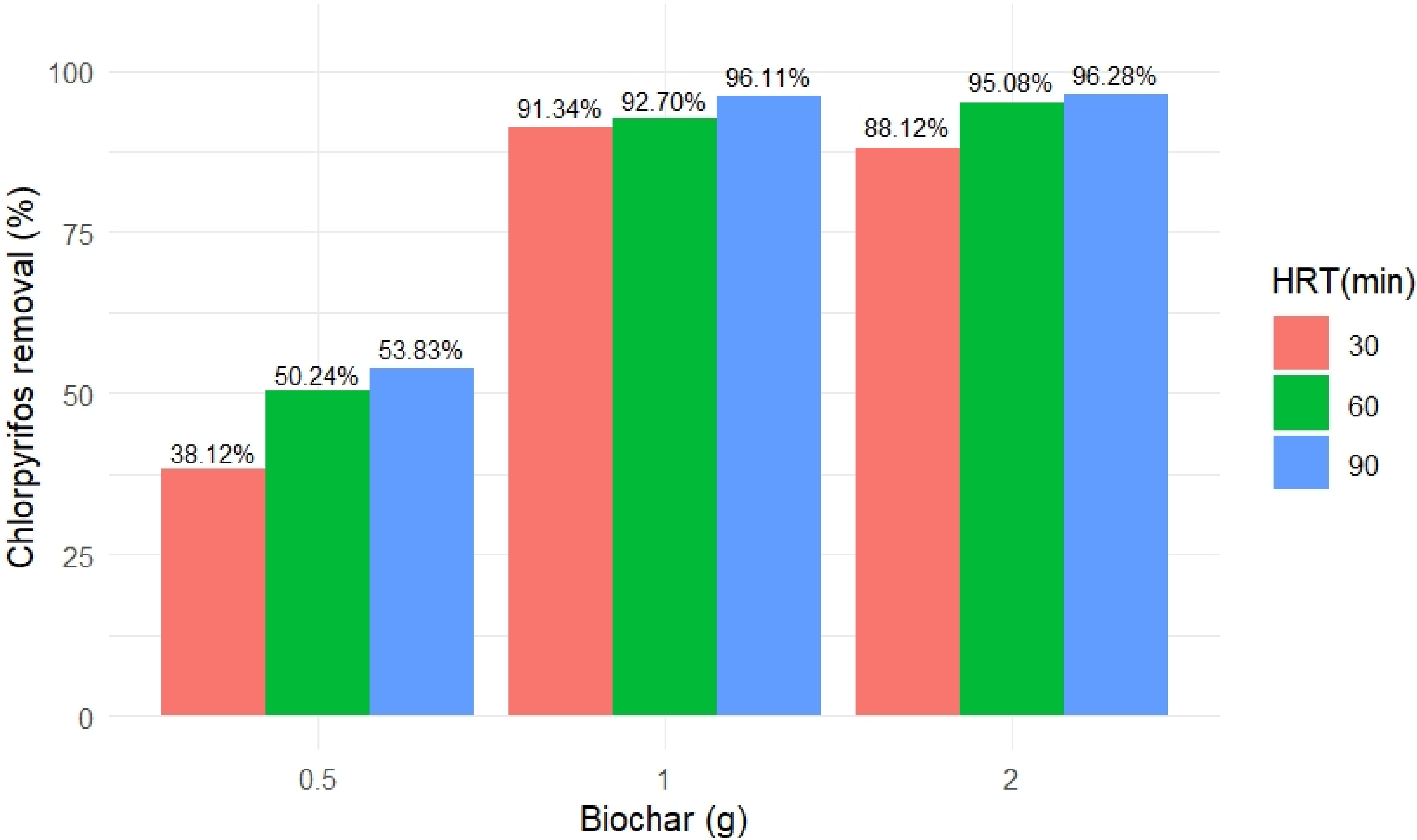

a
28,37 um
13,62 um
46,36 um
7,58 um
20kV
X450
50µm
UdeA
b
3,31 um
4,00 um
42,60 um
20kV
X650
20µm
UdeA

Fig 1.



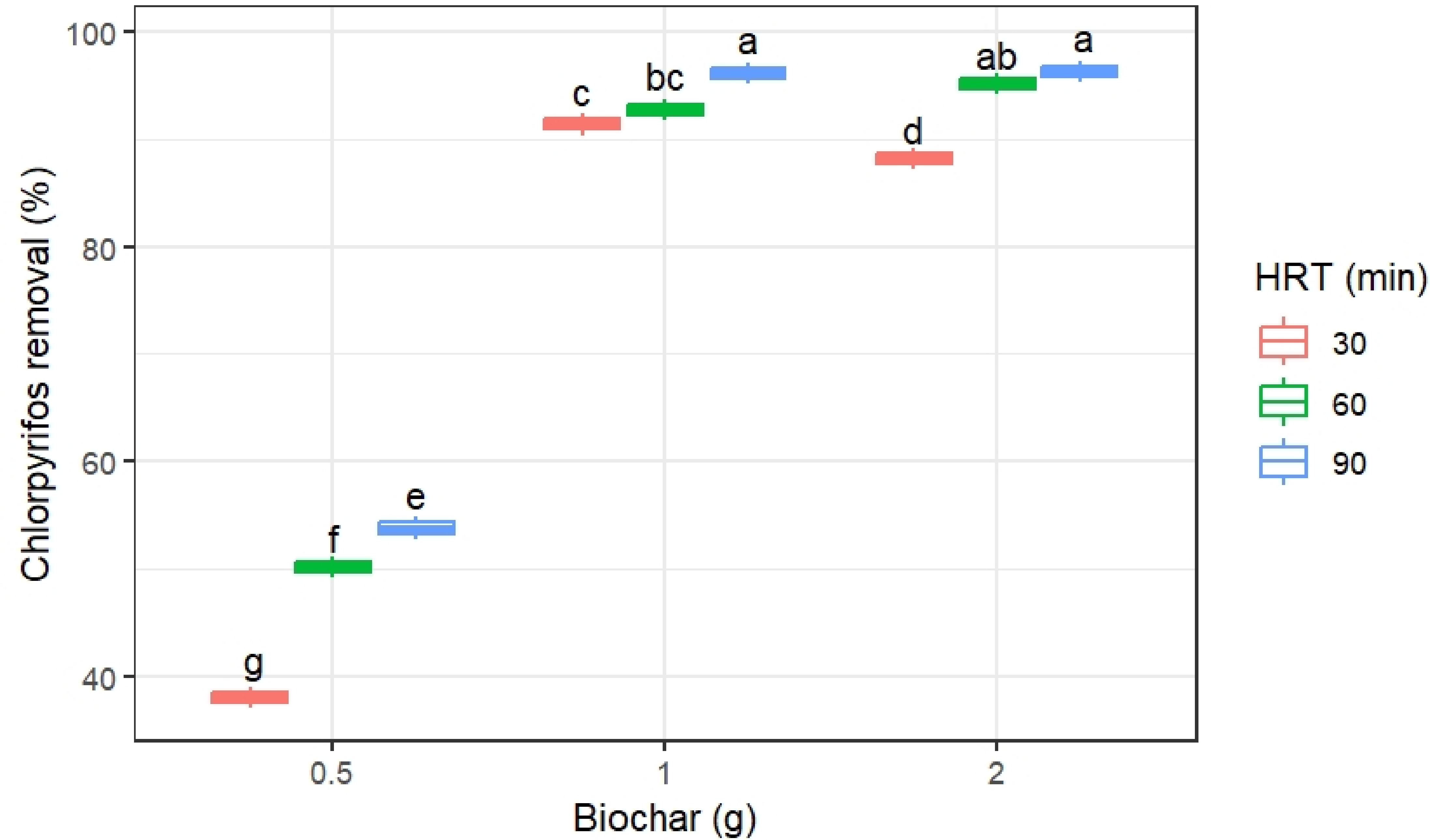
Chlorpyrifos removal (%)
100
75
50
25
0
38.12%
50.24%
53.83%
91.34%
92.70%
96.11%
88.12%
95.08%
96.28%
0.5
1
2
Biochar (g)
HRT(min)
30
60
90

Fig 2.

```
Analysis of Variance Table

Response: Rem
             Df  Sum Sq Mean Sq  F value    Pr(>F)    
Biochar       2 12627.3  6313.7 6313.659 < 2.2e-16 ***
TRH           2   435.1   217.5  217.547 2.465e-13 ***
Biochar:TRH   4   124.2    31.0   31.047 7.398e-08 ***
Residuals    18    18.0     1.0                       
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Fig 3.



Chlorpyrifos removal (%)
100
80
60
40
0.5
1
2
Biochar (g)
g
f
e
c
bc
a
d
ab
a
HRT (min)
30
60
90

Fig 4.

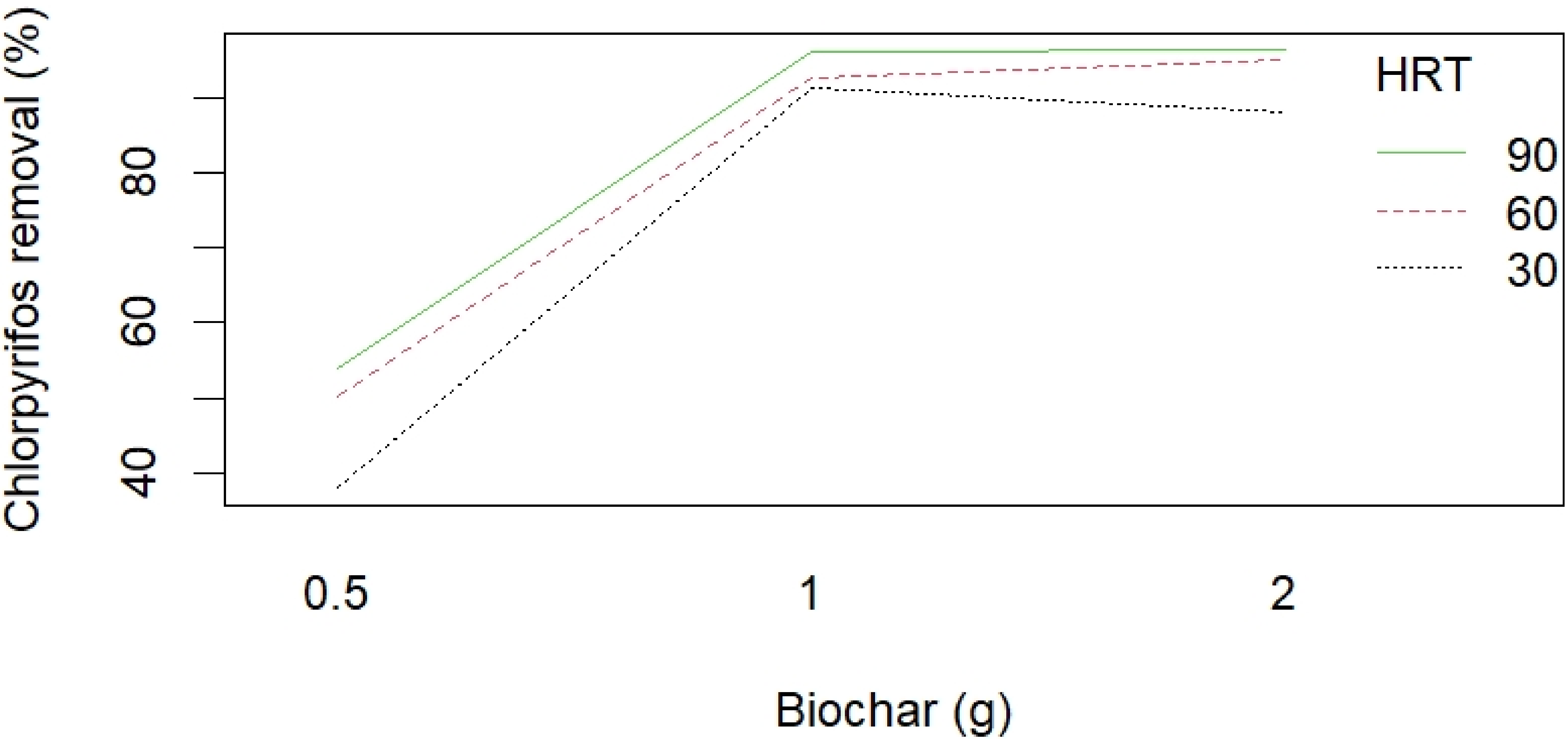


Fig 5.