



Efficient removal of Lambda-cyhalothrin from simulated water using Co-composted-biochar: A modern day substituent of conventional bioadsorbent[☆]

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ABSTRACT

Lambda-cyhalothrin, a type II pyrethroid, is widely employed as an outdoor and indoor insect repellent due to its target specificity and moderate toxicity. However, its extensive use elevated its residual concentration to significant detectable levels in waterbodies, making it an immediate problem. Furthermore, as a lipophile, its accumulation in multicellular organisms has resulted in irreversible acute and chronic effects on numerous physiochemical and biological activities. Thus, to address its removal as a pollutant from waterbodies, bio-adsorbents are considered a cost-effective and environmentally sound cleanup method. Modern day bio-adsorbents like co-composted-biochar, because of their potential adsorption capability rather than the conventional ones, may become a commonly used remediation tool. Therefore, this study aims at producing co-composted-biochar (COMBI) by combining kitchen-derived putrescible waste and biochar to effectively remove Lambda-cyhalothrin (LC) from spiked up water. It has been further analysed for its physico-chemical characteristics using instrumentation such as BET, SEM-EDS and FTIR. The results showed that biochar and COMBI had a much greater surface area ($2.174 \text{ m}^2/\text{g}$ – $1.718 \text{ m}^2/\text{g}$) and pore diameters (3.648 nm – 3.628 nm) than the compost sample. Simultaneously, the response surface methodology (RSM) was employed to optimise the removal efficiency of COMBI against LC. A Box-Behnken Design (BBD) was developed with an experimental layout to perform tests for determining the effects of four basic parameters i.e. pH, contact time (minute), adsorbate concentration (g/l) and adsorbent dose (g) on (%) removal of LC. It was noted that variation among removal efficiencies for the experimental runs ranges between 94.8% and 99.9%, within the majority attaining an efficiency of greater than 95%. During the experiments, the ideal conditions were found to be as pH 2 in a contact time of 140 min and a dose of adsorbent 0.01 g. Thus, COMBI could be a promising and potential candidate for the elimination of LC.

1. Introduction

A general survey conducted by Grainnews (2022) anticipated that the consumption of type II pyrethroids in the global insecticide shares a major portion of 19%, with a market size of USD 14.9 billion. Among this worldwide consumption, India individually consumes 622.08 metric tonnes, of which indigenously produced pyrethroid consumption

varies from 1 million tons M.T. to 674.6 M.T. between 2017 and 2022 (FAOSTAT, 2023; Ahamad & Kumar 2023). Furthermore, being a replacement for high-class inert organophosphate and organochlorine pesticides since the 1980s, pyrethroids usage has increased because of their comparatively gentle nature towards non-target insect pests (Tang et al., 2018). Their basic structure is chemically analogous to that of pyrethrins, originally extracted from *Chrysanthemum cinerariaefolium*.

Abbreviations: B, Biochar; BBD, Box-behnken design; BET, Brunauer-Emmett-Teller; C, Compost; CEC, Cation exchange capacity; CM, Compost Material; COMBI, Co-composted-biochar; EC, Electrical conductivity; FTIR, Fourier transform infrared spectroscopy; LC, Lambda-cyhalothrin; RSM, Response surface methodology; SEM-EDS, Scanning Electron microscopy-energy dispersive spectroscopy; XRD, X-ray diffraction.

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Pyrethroids are broadly classified into type I and type II categories depending on the presence or absence of an alpha-cyano moiety at the alpha position in their chemical composition (Ahmad & Kumar, 2023). Type I pyrethroids comprise Allethrin, Bifenthrin, Tefluthrin, Tetramethrin, and Permethrin, while type II pyrethroids list Cyhalothrin, Cypermethrin, Fenvalerate, Deltamethrin, Flumethrin, etc. Their mass application in the agricultural sector as a replacement for high-class recalcitrant conventional pesticides lays out an effective control over insect pests resulting in satisfactory protection for crop plants (Chen et al., 2021). However, their concentration after such an application for a longer time inevitably leads to their detection among food crops that might accumulate in the fat cells of an organism after ingestion (Feng & Jin, 2007; Ananda Gowda & Somashekhar, 2012; El-saeid & Khan, 2015). Despite possessing a lower half-life and higher biodegradability, pyrethroids, after getting biomagnified or bioconcentrated, are difficult to remove (Tang et al., 2018). Their residues in environmental media are not of great concern, but once they enter inside organism body through food chains, they can cause long-term adverse impacts on land animals as well as on aquatic organisms (Mahboob et al., 2015; Corcellas et al., 2015; Zhao, 2014; Gao et al., 2012; Tang et al., 2018). According to Werner & Moran (2008); Wolansky & Tornero-Velez (2013), pyrethroids enter aquatic bodies via agricultural runoff, creating acute poisoning in fish, lobsters, crabs, etc. A delay in the synthesis of vitellogenin and chorionic, i.e., egg proteins, can be seen in juvenile fish in the presence of bifenthrin and permethrin (Brander et al., 2012). Additionally, pyrethroids like Lambda-cyhalothrin (LC), cypermethrin, and deltamethrin have been found to create histopathological abnormalities in fish tissues by Yang et al. (2020). Further corroborated by the work of Bradberry et al. (2005); Yang et al. (2020), which according to their result concluded that pyrethroids are 2250 and 1000 times more noxious to insects and fish than higher organisms, including mammals and birds. Unlike small vertebrates and invertebrates of aquatic and terrestrial systems, pyrethroids possess less acute harmful effects on human beings, which include dizziness, convulsions, headaches, muscle twitching, and an itching and tingling sensation in the affected area during dermal exposure. A study reported that humans who strictly adhere to a vegan-based diet possess a high level of pyrethroid metabolites in their urine (Prado Lu & Leilanie, 2015).

One of the substantial and actively used insecticides that has been applied indoors and outdoors to prevent insect pests and to control various disease-causing vectors is Lambda-cyhalothrin (LC) (Amweg et al., 2005; Alrawe and Alzubaidy, 2022). Its ingestion via contaminated vegan diets and animal products is solely responsible for its acute toxicity in humans. Because of its lipophilic nature, LC is rapidly absorbed and solubilized among the membranes of the gastrointestinal tract and respiratory system of the human body, which ultimately leads to its accumulation in various organs, i.e., the kidneys, liver, CNS, etc., creating a condition of oxidative stress and cellular damage (Sankar et al., 2012). Additionally, a higher background concentration of LC in aquatic and terrestrial components of the environment induces reproductive toxicity and histopathological changes in small mammals and fishes (Al-Sarar et al., 2014). Several studies conducted by Gong (2013); Zhao (2014); Mahboob et al. (2015); Andrade et al. (2010); Corcellas et al., 2012; Bedi et al. (2015); Tang et al. (2018) highlights the residual concentration of LC in various environmental media in a concentration ranging between not detectable to up to 573 ng g⁻¹.

Seeing these influential deleterious impacts of LC, it is critical to remove it from diverse environmental matrixes. There are several methods which have been employed over time for efficient removal of such pesticides include biological treatment using bioreactors (Navaratna et al., 2016), chemical treatment via oxidation (Zhuan and Wang, 2020), precipitation, ion-exchange and physical treatment with the help of membrane technologies (Asad et al., 2020), filtration and distillation (Saleh et al., 2020). Most of the above mentioned treatment methods possess a major drawback in terms of their high working capital and maintenance cost, also in several cases produce toxic secondary

compounds as by product of their treatment process (Baharum et al., 2020; De Gisi et al., 2016). Therefore, physical adsorption employing bio-based adsorbents is referred as highly desirable treatment method because of being an environment friendly, low operational and maintenance cost with almost negligible production of toxic compounds as by-product (Ma et al., 2019; Tulun et al., 2021; Mojiri et al., 2020). Literature based on adsorption studies utilizing bio-adsorbents determined that biochar derived from bamboo, sewage sludge, wood derivatives, agricultural waste and manures has been proven to be an excellent pocket friendly and eco-friendly sustainable alternative in remediation practices against pyrethroids removal (Chen et al., 2019; Rehman et al., 2024; Abdelhameed et al., 2020; Cederlund et al., 2016; Liu et al., 2015; Taha et al., 2014; Baharum et al., 2020). However, a little information is available about the removal of LC using biochar, making it an area of growing interest. Moreover, using a different bio adsorbent, such as co-composted-biochar (COMBI), instead of standard biochar for LC removal could be a new method, particularly in the realm of pyrethroid remediation.

Although it has been proven that COMBI is an efficient version of biochar (B) and compost material (CM) in terms of retention capacity, surface area, pore volume and hydrophilicity (Hagemann et al., 2017; Prost et al., 2013; Brtnicky et al., 2019; Azeem et al., 2016; Ye et al., 2019). There is essentially not much information available on pesticide removal using COMBI as a substitute of conventional bio adsorbent such as biochar. This study focusses on developing a low-cost, efficient form of pristine biochar that may be utilized to effectively remove emerging contaminants from water and soil matrices without causing harm to the environment.

The experimental study discussed in this research paper demonstrates how a composite bio-based adsorbent, COMBI, is a promising and efficient LC removal tool from wastewater spiked up with the concentration of this particular pesticide. The findings were useful in determining the potential of co-composted biochar as a low-cost, sustainable bio-based adsorbent that may also be used to remove other contaminants. To proceed with this experimental work, the aims were to: Production of co-composted-biochar (COMBI), Its detailed characterization and comparison with parent materials to get an in-depth idea about the modifications that occur in the structure and various physio-chemical parameters during co-composting. Optimization of co-composted-biochar's (COMBI) removal efficiency against an enriched isomeric form of LC from the water sample using a Box-Behnken design (BBD) with response surface methodology (RSM).

2. Materials and methods

2.1. Chemicals and reagents

The samples of technical grade LC (C₂₅H₁₉ClF₃NO₃) with a molecular mass of 449.9 g/mol, were collected from a nearby pesticide production unit. It was beige-colored solid type II non-systemic broad-spectrum pyrethroid that is widely used for crop protection against insect pests. The chemical properties of LC represents a relative density of 1.288 g/cm³, a melting point ranging from 47.5 to 48.5 °C, and a volatility of 2 × 10⁻² Pa m³/mol. Chemicals and solutions other than LC that were used during the experiment include acetone (CH₃COCH₃), 0.1 N HCL, 0.1 N NaOH, and deionized (DI) spectroscopy water of laboratory grade were also purchased.

2.2. Production of Co-composted-biochar

For the making of COMBI, a heap was prepared in a cemented pit having dimension of (90 cm × 90 cm × 75 cm) as a composting unit, which was constructed in a garden area close to the laboratory. The raw materials used for compost material (CM) include kitchen putrescible waste, fruit peels, sugarcane residue, and some plant litter were collected from the local area, whereas the biochar derived from agro-

waste was commercially purchased. The breakdown of organic raw materials and their blending with biochar's nanoparticles was done using the aerobic method of composting (Hagemann et al., 2018; Pandit et al., 2020). The biochar (B) and compost material (CM) were blended initially in different proportions of 60 (CM) and 40 (B), for co-composting. In which, the CM along with biochar was placed in layers, alternatively with cow dung manure as bedding. Spraying water and churning of pit material were done weekly until the maturation of COMBI, to maintain humidity and avoid anaerobic conditions during its production process.

2.3. Preparation of standards and determination of removal efficiency

A stock solution was prepared of 1000 ppm using 1g of LC, solubilized in a volume of acetone which is appropriate for dissolving it completely, which was then made up to 1000 mL with the help of deionized (DI) water. From this stock solution, working standards with a concentration range of 20–80 g/l were prepared. Working standard solutions were analysed as per standard protocol and a linear curve was drawn with the help of UV/visible spectrophotometer at a wavelength of 580 nm (Zahoor et al.,). The Equation used to calculate the removal efficiency of LC is stated below:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_i}{C_i} \times 100 \quad (1)$$

Here, C_o and C_i are the final and initial concentrations in g l^{-1} .

2.4. Optimization design and analysis

The parameter optimization for efficient removal of LC using COMBI was done with the help of box bhenken design, having three levels of each parameter in the design expert version 13.0.5.0. The four independent variables taken into account in the process of optimization include pH, adsorbent dose, adsorbate concentration, and contact time. Whereas, the dependent variable is represented by the evaluated response in terms of removal efficiency (%) that was obtained as a result of 24 experimental runs, in which 3 additional runs were performed as replicates of the center point. The BBD codes, together with the minimum and maximum selected values for each parameter, were listed in Table 1.

2.5. Surface and spectral analysis

Specific surface area (SSA) of samples was analysed using the Autosorb iQ Station 1 surface area analyzer, and Quantachrome instruments. The surface area was obtained using the multi-point BET method with the measurement of gaseous N_2 adsorption at a temperature of 77.35 K, which corresponds to liquid nitrogen. The samples, under continuous N_2 flow, were degassed and analysed approximately for 3 h under a relative pressure range of 0.05–0.30. Fourier Transform infrared spectroscopy of organic material samples was conducted using a "Spectrum Two" PerkinElmer FT-IR spectrometer within the mid-infrared region with a scan range of 4000–400 cm^{-1} . The samples were prepared using the KBr pellets/disks technique, wherein 1–2% of

the samples were mixed and pulverized with KBr to attain maximum homogeneity. The ground powder, with the help of a pellet-forming die, was finally converted into a homogenous and transparent film, which was inserted into the IR sample holder to attain the sample spectrum. SEM micrographs and elemental analysis of all the samples were attained by subjecting samples to a high-resolution 7610F Plus JEOL Field Emission Scanning Electron Microscope (SEM) attached to an energy-dispersive X-ray spectrometer. The samples were first sputter coated with 2–3 nm thick gold and then analysed through SEM-EDS under high vacuum conditions. To identify the crystalline stability of the prepared samples, X-ray diffraction patterns were recorded using the "Smart Lab 3 kW" Rigaku Multipurpose Versatile X-Ray Diffraction System. The operating level of the diffractometer was at 40 kV and 40 mA and the data collected was in the range of 10 to 80° (2 θ) with a scan rate of 0.020° with the help of $\text{Cu K}\alpha$ radiation.

For statistical analysis, a detailed evaluation of observed results of physiochemical parameters were performed, which were then presented as mean $\pm$ Standard deviation of triplicates. The detailed procedure used for the analysis of physiochemical parameters has been provided in the supporting information as text material S1. The Pearson correlation analysis for parametric values was computed and represented with a statistical significance level of $p < 0.05$ to measure the strength of the linear relationship between the physiochemical parameters of biochar (B), compost (C), and co-composted-biochar (COMBI).

3. Results & discussion

3.1. Physical and chemical characteristics

The calculated values of various physio-chemical parameters of B, C, and their blend after co-composting are illustrated in Table 2. Accordingly, samples of B and COMBI showed a neutral pH value of 7.8 and 7.9 respectively, while an alkaline pH value of 9 was observed the C sample. A similar trend was reported for EC values, where the compost observed a higher value of 3.42 ms/cm compared to B and COMBI. On the contrary, a significantly higher CEC value of 12.5 meq/100 g was seen in COMBI, while a lower CEC value of 2.5 meq/100 g was associated with B.

Likewise, moisture and total ash content were higher for the compost sample following a decreasing order of C (5.3%) > COMBI (33.5) > B (5.3) in moisture content and C (53.3%) > COMBI (34.1) > B (24.8%) in ash content. In addition to these proximate analytical characteristics, B

Table 2
Calculated values of physio-chemical parameters of B, C, and COMBI.

Parameters	Units	B	C	COMBI
pH		7.8 $\pm$ 0.02	9 $\pm$ 0.094	7.9 $\pm$ 0.06
EC	ms/cm	0.36 $\pm$ 0.04	3.42 $\pm$ 0.41	0.82 $\pm$ 0.02
CEC	meq/100gm	2.5 $\pm$ 0.40	10.4 $\pm$ 0.36	12.5 $\pm$ 0.12
CaCO_3 equivalence	gm/kg	2.5 $\pm$ 5.03	1.5 $\pm$ 6.02	1.2 $\pm$ 3
Moisture	%	5.3 $\pm$ 0.01	40.3 $\pm$ 0.51	33.5 $\pm$ 0.24
Total Ash	%	24.8 $\pm$ 0.17	53.3 $\pm$ 0.03	34.1 $\pm$ 0.08
Total Carbon	%	43.2 $\pm$ 0.03	25.7 $\pm$ 0.02	37.3 $\pm$ 0.02
Inorganic Carbon	%	16.8 $\pm$ 0.29	15.9 $\pm$ 0.32	17.3 $\pm$ 0.3
Total Nitrogen	%	0.24 $\pm$ 0.01	1.28 $\pm$ 0.03	0.43
Ca	%	79.4 $\pm$ 0.01	104 $\pm$ 0.03	112 $\pm$ 0.01
K	%	0.23	0.64 $\pm$ 0.01	0.24 $\pm$ 0.02
P	mg/kg	1.08 $\pm$ 0.02	3.35 $\pm$ 0.03	2.56 $\pm$ 0.02

Table 1

Selected predictor variables with their codes and values ranging from minimum to maximum.

Code	Factor name	Units	Minimum value	Maximum value	Reference
A	pH		2	12	Zahoor et al.
B	Adsorbent dose	Gram	0.01	3	
C	Adsorbate concentration	Gram/liter	20	80	
D	Contact time	Minute	40	240	

had a significantly greater total organic carbon content (43.2%) than C (25.7%) and their blend COMBI (37.3%). However, only a slight variation was seen in the inorganic carbon content values of B (16.8%), C (15.9%) and COMBI (17.3%). The total nitrogen content of samples varied from 0.24% to 1.28%. The highest 1.28% was exhibited by the C sample, followed by COMBI (0.43%), and B (0.24%). Available nutrients, especially Ca, K, and P listed in Table 2, were more common in COMBI and C samples. In comparison, B was found to contain a lesser amount of Ca (79.4%), K (0.23%), and P (1.08 mg/kg). Similar trend in findings were reported by the previous study conducted for the production of compost, and co-compost biochar by Sánchez-Monedero et al. (2019).

The variation in physiochemical properties of B, C, and COMBI could be attributed to their different raw materials and process parameters used in production (Yang et al., 2019). Plant-based biochars produced under an intermediate temperature range of 400–600 °C were observed to have a neutral pH, low ash content, high aromaticity, and low volatile matter content (Singh et al., 2010). However, the aromaticity of wood-based biochars is an outcome of their higher degree of volatilization, which results in a reduction of acidic functional groups and moisture content. Likewise, B, the alkaline pH value, high moisture content, high ash%, and nitrogen% of the C sample were also dependent on the type of feedstock material and the composting parameters. Vaz-Moreira et al. (2008), in his study, reported various physiochemical parameters of domestic waste, i.e., kitchen-derived vegetable and fruit peel, that were associated with values of 36.2% for moisture content, 38% for organic matter, 0.5 dSm⁻¹ for EC, and a slightly acidic value of 6.8 for pH. In contrast to these reported parameters, the C sample derived from the same kitchen-derived vegetable and fruit peels in this work possessed an alkaline 9 pH value, which might be related to the alkaline functional groups of humic and fulvic compounds that act as a perfect indicator of compost maturity (Sánchez-Monedero et al., 2019). These functional groups were also responsible for the higher EC value of the C sample while the lower EC value of B represents a lower concentration of surface acidic or basic functional groups due to its intense aromatic structure. Furthermore, the CEC value of organic samples, i.e., B, C, and COMBI, was shown concerning the concentration of extractable minerals (Ca, K, and P). A sample with a high concentration of extractable minerals possessed a high CEC value, while a sample with a lower concentration expressed a low CEC value (Merlin et al., 2014). COMBI, while being a composite of B and C material, was detected with an intermediate value of assessed physiochemical parameters that lie between the values of B and C samples. A high carbon content in the COMBI sample indicated the presence of labile carbon, which is an upgraded property of CM as a result of the interaction between biochar's nanoparticles and compost humic substances.

3.2. Characterization analysis

3.2.1. BET

The micro-mesoporosity of B, C and COMBI samples was identified by their obtained N₂ adsorption-desorption isotherms (See in Fig. S2 of Supporting Information) that exhibit characteristics similar to type IV and V physico-sorption isotherms recommended by IUPAC (Kajama et al., 2015). The evaluated values of MBET surface area, t-plot micropore surface area (MSA), and BJH-derived pore parameters are listed in Supporting Information as Table S2. According to the results of the BET analysis, B among all organic samples exhibited a larger MBET surface area (2.174 m²/g), t-plot MSA (1.203 m²/g), and pore diameter (3.648 nm). The prime reason attributed to the larger surface area and pore diameter can be explained by the extreme degree of aromaticity in the B samples, which would probably be associated with a lesser ash content and ultimately increase the microporosity and macroporosity in the biochar structure (Schimmelpfennig and Glaser, 2012; Hung et al., 2017). In consistent with the BET findings of B sample, some comparable results were also observed by Cruz et al. (2020); Ozcimen &

Ersoy-Mericboyu (2010); Mukome et al. (2013); Som et al. (2012) for their BET analysis of biochars derived from raw materials including agrowaste (4.6 m²/g), chestnut shell (0.6717 m²/g), softwood + algal digestate (2 m²/g and 2.8 m²/g) and palm fronds (4 m²/g). Likewise biochar, the COMBI possessed a higher MBET surface area, MSA, and pore diameter in comparison with C samples. In contrast with them, the C sample was observed with a minimum value of MBET surface area (1.056 m²/g) and pore diameter (1.802 nm) while showing an absence of t-plot MSA which is analogous with the surface area of kitchen waste derived organic manure (1.776 m²/g and 0.8267 m²/g) examined by Kaur et al. (2018) in her study. Furthermore, these analysed results of C surface area and pore parameters are strongly corroborated by the obtained sem micrographs of the compost sample, the aggregated smooth, textured structure with minimal porosity was the perfect reflection of humic material abundance in the C sample, which might increase its surface activity while making the micropores accessible to clogging. Clogged external micropores could be an explanation for minimal microporosity, which therefore resulted in an undetectable value of t-plot MSA in the C sample. In the meantime, pore volume, contrary to other surface and pore parameters, adheres to an opposite trend in which a higher pore volume of 0.012 cc/g was reported in COMBI samples, followed by the B sample with 0.009 cc/g and C sample with 0.007 cc/g, which were similar to the results reported by Hagemann et al. (2017).

3.2.2. SEM- EDS

Surface alterations in pure B and C samples with their corresponding blend were depicted by the SEM image for their homogeneity and porous availability. SEM structural images of B, C, and COMBI with different magnifications are represented in Fig. 1. Biochar, being a charred material, was examined at different magnifications and revealed its macroporous structure, comprised of various small and large vascular channels. The honeycomb-shaped macropores (>50 µm) that appeared on the biochar's external surface indicated its production under high-temperature conditions and the predominant existence of lignin as a significant component in its feedstock material (Hung et al., 2017). The C sample, in contrast with B, showed its morphology in the form of an irregular aggregated fluff with numerous micropores covering its entire external surface. The microporosity of the C sample is an outcome of the cellulose-rich feedstock material used in its production, i.e., kitchen-derived fruit and vegetable peels. Likewise, for B and C, the SEM images of COMBI revealed their morphology as a composite of biochar's vascular structure and compost's aggregated fluff in association with a large number of external macro and micropores. However, the macropores in the COMBI sample seemed to be less pronounced than the macropores of pure B. The macropore dissimilarity may be due to the formation of humic material coating over the biochar surface that ultimately blocks some of the external macropores, making them a hotspot for a variety of surface activities (Hagemann et al., 2017). The elemental composition and stability of the samples were delineated according to the obtained EDS plots. Plotting revealed that the samples of B and COMBI had a high carbon concentration, whereas the C sample had a lower concentration which is possibly due to the presence of labile carbon. Contrary to this, the compost sample showed a high concentration of Si, O, N, Ca, Mg, P, K, and Fe. Whereas the B sample showed the lowest concentration of nutrients among all. The highest silicon peak in the C sample was due to the fruit and vegetable waste used as their dominant raw materials during composting. In addition to this, the merged peak of nitrogen and oxygen in the EDS plot of C and COMBI indicated their presence in bounded form as nitrate.

3.2.3. FTIR

FTIR spectroscopy was used to investigate the chemical alteration and functionality shifting in B, C, and COMBI sample. Their spectrum comprises major and minor peaks possessing variability in terms of absorbance or transmittance of IR radiation by their specific functional

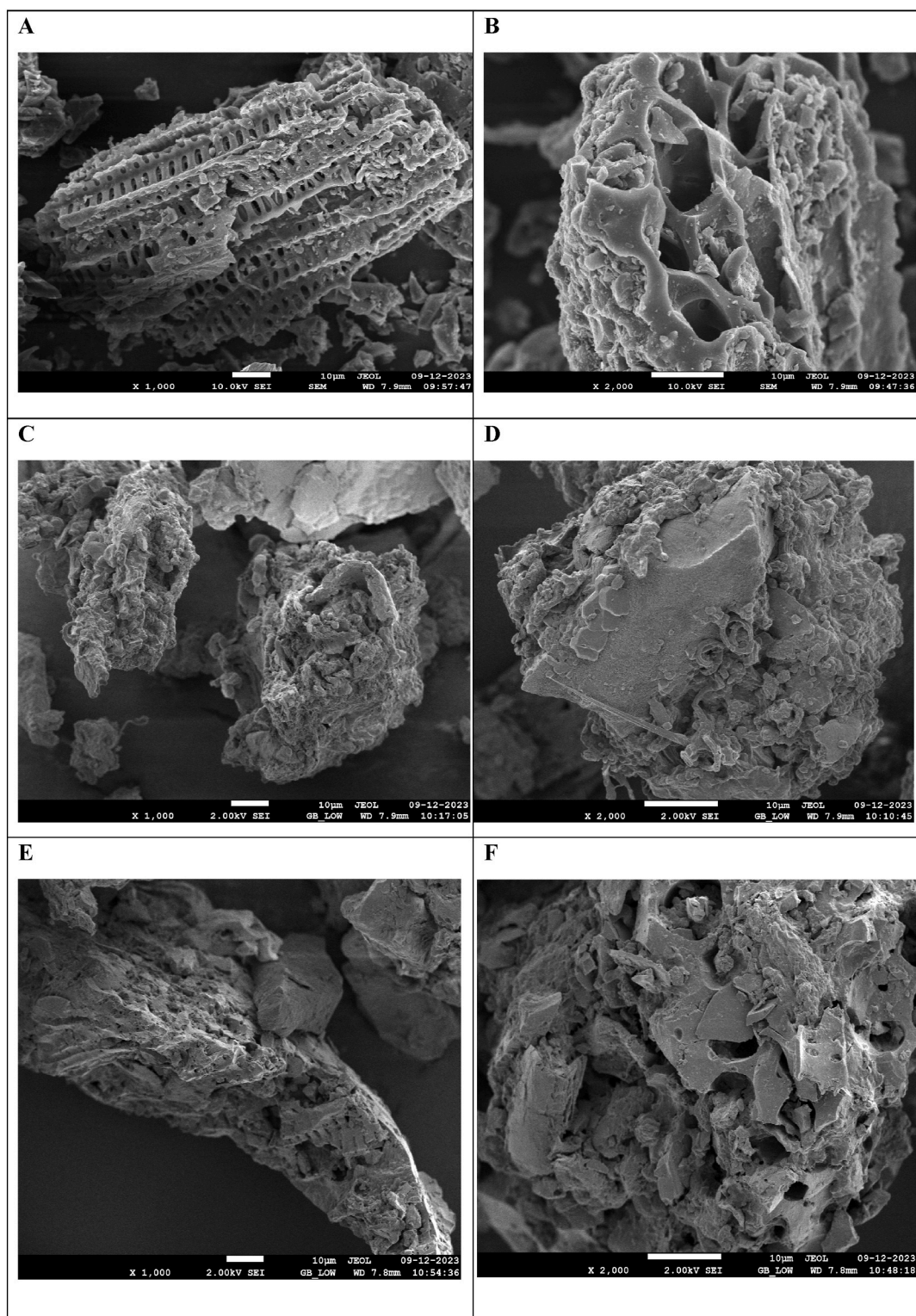


Fig. 1. SEM images of C, B, and COMBI (60:40) at different magnifications; Images A and B represent Biochar at $\times 1000$ magnification and $\times 2000$ magnification; C and D represent Compost at $\times 1000$ and $\times 2000$; E and F represent COMBI 60:40 at $\times 1000$ and $\times 2000$.

group, as presented in Fig. 2 (a). As can be seen from FTIR findings, all organic samples are comprised of similar aromatic and aliphatic functional groups, showing resemblance in their composition while having minimal variations when compared with each other. Samples of B, C, and COMBI possessed some major absorbance peaks in the range of $4000\text{--}400\text{ cm}^{-1}$, revealing the dominant constituents of their structure in the form of water, alcohols, phenols, ketones, quinines,

hemicelluloses, cellulose, and aliphatic compounds. However, their absorbance varied in terms of peak intensity. A high-intensity peak in the range of $1700\text{--}1500\text{ cm}^{-1}$ assigned to ketones, quinine, and aromatic C=O and C=C bonds of humic and fulvic substances was spotted in C samples, followed by COMBI, while a less intense peak associated with C=O of lignin compounds was observed in B samples (Rijo et al., 2024). Organic samples, despite being similar in chemical composition,

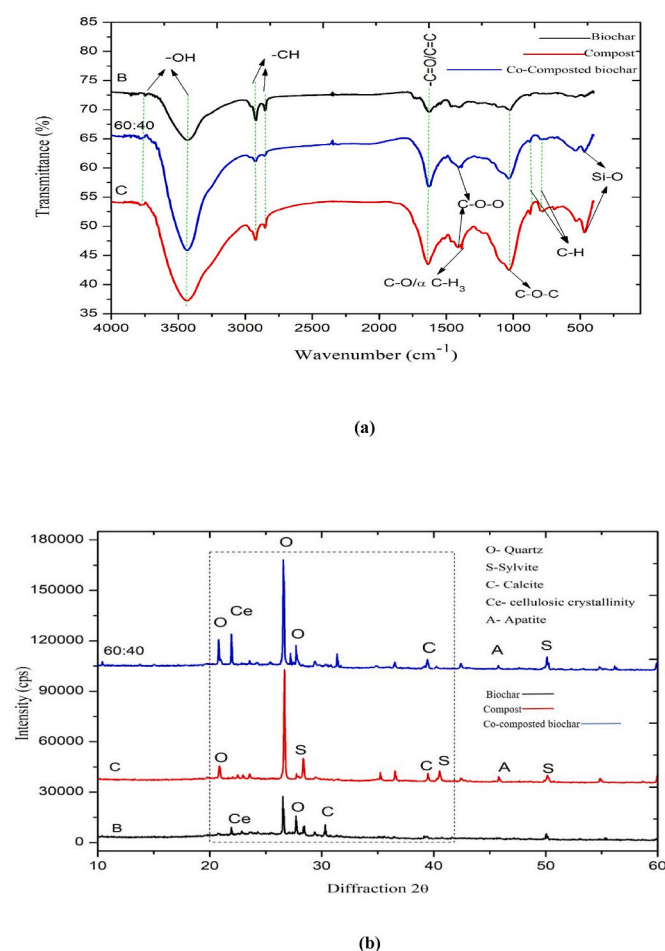


Fig. 2. (a) FTIR and (b) XRD spectrum of B, C and COMBI.

exhibited a noticeable difference around the transmittance range of 1500–400 cm⁻¹. The transmittance spectra of C and COMBI, when compared with the B spectrum, were detected, with some extra peaks at 1384 cm⁻¹ and 1032 cm⁻¹ attributed to C-O bond stretching of polysaccharides and C-O-O-/C-O-C stretching of carboxylates. Likewise, comparisons between C and COMBI revealed a minor difference in their structure, which was spotted in the wavelength range of 885–752 cm⁻¹. The absorption peak observed at 778 cm⁻¹ belongs to C-H out-of-plane vibration in COMBI, which corresponds to their condensed aromatic structure (Keiluweit et al., 2010). In addition to this, an absorption peak at 468 and 469 cm⁻¹ belonging to Si-O bond vibration was also observed. In C and COMBI samples, revealing the existence of quartz as a constituent in their chemical structure. However, the peak intensity of Si-O bond vibration varied between C and COMBI samples, following a decreasing order that commenced with a deep peak in the C sample and ended with a bump-like structure observed in the B sample.

3.2.4. XRD

Fig. 2 (b) shows the XRD spectra of B, C, and COMBI with a variable ratio of biochar and organic feedstock material. These spectra were used to analyze the composition and inorganic crystalline stability of B, C, and their blend as a result of their peak intensity and location. These peaks, based on their sharpness and precise location, confirmed the presence of quartz (SiO₂), sylvite (KCl), calcite (CaCO₃), and the crystallographic planes of various components of B, C, and COMBI. The amorphous nature with high crystalline stability of B was observed by a slight curve along with a bunch of high-intensity peaks in the diffraction range of 20° to 40°. Peak intensities in XRD analysis are indicative of the compositional concentration and existence of essential minerals, i.e., Ca,

K, Si, Mg, P, etc., in their bounded crystalline form as calcite, sylvite, dolomite, apatite, etc. The predominant diffraction pattern of quartz is indicated by the presence of strong intensity peaks at 26.5°, 21.9°, and 27.7° in all diffraction spectra that too is in the agreement with JCPDS file no. 00-016-1157 according to Mallakpour and Naghdi, 2016). On the contrary, the low-intensity peaks of sylvite and calcite at 28.2°, 40°, 50°, 39.4°, and 30.3° represent low compositional concentrations of K and Ca (Kumar et al., 2021), which was also corroborated by the resulting EDS plots. The peak for quartz was more intense in the C sample, followed by COMBI, and least in the case of the B sample, which shows that kitchen waste and fruit peels (KWFPs)-derived C is high in SiO₂, while agro-waste-derived biochar contains the least among all. Meanwhile, the peak intensity of quartz in COMBI was dependent on the ratio of B and KWFPs, possessing a low SiO₂ concentration in COMBI. Similar to quartz, the compositional concentration of K and Ca attributed to the peak intensity of sylvite and calcite varied from high concentrations that adhered to the C sample to low concentrations, which were observed in the B sample. Besides them, the existence of phosphate mineral was confirmed with the apatite peak of C and COMBI samples at a diffraction angle of 45.7° which was in consistent with the JCPDS file No. 076-0694 (Rujitanapanich et al., 2014; Das et al., 2021). However, no diffraction peak for apatite was observed in the B sample. Furthermore, B and COMBI samples were observed with a peak having variable intensities at a diffraction angle of 22.4°, which was assigned to the cellulosic crystallinity of the material (Mohammadpour et al., 2024). The variable intensities of the cellulosic peak between B and COMBI samples were consistent with the fixed carbon content of the materials. However, the absence of a peak in the C sample indicated a significant loss in the crystalline structure of cellulose in the material. The reason behind its significant loss could be a thorough breakdown and conversion of cellulosic feedstock material to high-value humic compounds (Rijo et al., 2024).

4. RSM analysis

The coded polynomial equation given below is used to evaluate the dependency of response variables on independent variables in the context of their fitness, either in a linear or quadratic model. The main goal of using a higher-degree polynomial model is to find the optimal response region in which all four parameters act more efficiently and rapidly to achieve maximum removal efficiency.

$$\begin{aligned} \text{Removal efficiency \%} = & 98.63 - 1.08 A - 0.9492 B + 0.7583 C \\ & - 0.1600 D - 0.8525 AB - 0.5250 AC + 1.48 AD + 0.7000 BC \\ & + 0.2500 BD + 0.0000 CD - 1.12 A^2 + 0.9817 B^2 - 0.6546 C^2 \\ & - 0.7271 D^2 \end{aligned}$$

This equation represents the correlation coefficient of each coded parameter, which, by comparing their values, can be used to identify their relative impacts on each other as well as on the response variable. A negative correlation value sticks to the antagonistic impact of a parameter towards others, whereas a positive value indicates synergistic impacts (Punia & Singh, 2024; Shah et al., 2022). Accordingly, values of A, B, D, AB, AC, A², C², and D² show antagonistic impacts, while values associated with C, AD, BC, BD, CD, and B² exhibit synergistic impacts.

4.1. Test of significance and analysis of variance (ANOVA) analysis

There are many methods to measure the effectiveness of a model based on hypothesis testing regarding model variables. But the first thing before initiating any of these tests is to satisfy the normality assumption for the response variable, in which an error term is required to be tested for its normally independent distribution with a zero mean and a variance of s². For this model, the normal residual plot represented by fig. S3 (a) in Supporting Information, is approximately distributed

along a straight line that is a depiction of error term normality satisfaction, which further concludes that the observed response variable y_i is also normally and independently distributed.

Moreover the statistical fitness and relevance of the model and variables are suggested by the resulting p-values and F-values, which have a confidence level of 95% and a significant value of $p < 0.05$. Residual plots and coefficients of determination were used to evaluate the suitability and quality of fit for the model. The difference between observed and predicted R^2 values gives an insight into response variability that can be further explained through independent variables and their relative interactions. A higher R^2 value represents less variability and a higher accuracy of the polynomial model. By looking at Table S4 of Supporting Information, the fit statistic was reported to have a higher R^2 value of 0.96, which signifies the absolute accuracy of the model. The predicted and adjusted R^2 values of 0.78 and 0.92 displayed a reasonable difference of less than 0.2 and exhibited a satisfactory adjustment of the second-order quadratic model with the experimental statistics. Meanwhile, the ANOVA table listed a significant value of <0.0001 for the coded parameters A, B, C and AD, exhibiting remarkably high fitness of the quadratic model to the experimental results. The observed F values of independent variables were also high compared to the F critical value of 3.36 except D, BD and CD. Both the conditions regarding p values and F values in the cases of A, B, C, AB, AC, AD, BC, A^2 , B^2 , C^2 , and D^2 suggested significant evidence of rejecting the null hypothesis (H_0), which reveals that each of the independent variables pH (A), adsorbent dose (B), adsorbate concentration (C), and contact time (D) contributes significantly to the quadratic model individually as well as interactively. A higher adequate precision of 16.31 in the fit statistic for this model exhibits its desirable value, i.e., >4 , implies an adequate signal-to-noise ratio, whereas the mean and standard deviation displayed a value of 97.96 ± 0.49 . The overall fit statistic and ANOVA findings for this model suggest that it can be utilized to investigate the design space.

4.2. Optimization of independent variables for efficient removal of Lambda-cyhalothrin

The goal of using the RSM approach in LC removal is to find the optimum value of four independent variables, i.e., pH, adsorbent dose, adsorbate conc., and contact time, to maximize their interactions and combined effects on the response variable (Swamy et al., 2014; Das & Mishra, 2017). The maximum and minimum ranges of removal efficiency varies from 99.99% to 94.8%. Among this variation, the highest removal efficiency of 99.99% was observed at an acidic pH value of 2, 0.01 g of adsorbent dose, 50 g/l of adsorbate conc., and 140 min of contact time. In contrast, the minimum removal of LC was of 94.8% at a maximum pH value of 12, following a middle concentration and dose range of adsorbate along with adsorbent (1.5 g and 50 g/l), and a lowest contact time of 40 min. Seeing the experimentally observed data of response variable in Table S3 of supporting information, it is estimated that among four independent variables pH, adsorbent dose and adsorbate conc. exhibits a significant influence on the output of removal efficiency, which is justified by their lowest p-value, the highest F value, and a higher coefficient of determination ($R^2 = 0.96$) represented in the ANOVA (Table S4 of Supporting Information). A p-value of <0.0001 for all three independent variables individually as well as in combined form demonstrates their predominant effects on the removal of LC. However the fourth independent variable D coded for contact time is associated with a significance level of $p \geq 0.1$, which is subjected to follow null hypothesis i.e. owing negligible influence on response variable as a factor solely and in combination with others. The variable parameters including pH, adsorbent dose and contact time is linked with a negative correlation of -1.084 , -0.9491 and -0.16 , represent their antagonist behaviour as a result of their individual and inter parametric interactions on LC removal efficiency. Contrary to the above factors, the third one i.e. adsorbate conc. remarked with a +ve correlation of 0.7583, creating synergistic effects in its combined form with other

variables that can also be seen using contour plots.

The ramp plot represented by fig. S3 (b) in Supporting Information, in numerical optimization is used to analyze the obtained results as a consequence of the optimization process to achieve the maximum goal. The ramp plot shows individual factor graphs in which red colour dots indicates the factor setting that resulted in a desirable solution with a maximized desirability value close to 1. Here, in this case, the obtained data was optimized creating a desirability ramp plot of 100% LC removal efficiency of COMBI that can be achieved keeping the pH value, adsorbent dose, adsorbate conc., and contact time at 5, 2.8 g, 71 g/l and 104 min respectively. The validity of these desired optimum values was evaluated experimentally by performing a run in triplicates and the obtained result was compared with the removal efficiency given by the software. It can be seen from Table S5 (listed in Supporting Information) that the value is quite close to the software obtained value with a minimal difference of 0.70.

4.3. Individual effects of independent variables on removal efficiency of Lambda-cyhalothrin

Figure S3 (c) in Supporting Information represent the random variability of response when pH and adsorbate conc. change from their lowest values of 2 and 20 g/l to their highest possible values of 12 and 80 g/l. A 99.99% removal efficacy was observed in the acidic and near-neutral regions with an adsorbate conc. of 50 g/l, whereas the alkaline region with a higher volume of adsorbate conc. adhered to the lowest removal efficiency of pyrethroid insecticide. Depending on the pH of the experimental run, the type of interaction between COMBI and lambda-cyhalothrin varies between electrostatic and hydrogen bonding. COMBI as a result of surface carboxylic ($-\text{COOH}$), ketonic ($-\text{C}=\text{O}$) and ether ($\text{R}-\text{O}-\text{R}$) groups possess a positive charge under acidic pH, which eventually binds with the negatively charged cyanide group of Lambda-cyhalothrin, exhibiting a strong electrostatic interaction (Yang et al., 2004; Suo et al., 2019; Zahoor et al.). Furthermore, the presence of hydroxyl group (OH) as a dominant functional group in COMBI, demonstrate the reason behind weak intermolecular hydrogen bonding between co-composted-biochar and molecule of LC, alongwith electrostatic interactions, resulting in a higher removal efficiency at low pH (Chandi et al., 2024). Conversely, a higher pH is associated with comparatively lower removal efficiency, which was supposed to be linked with the pK_a value of LC, i.e. > 9 , allowing its dissociation into a negatively charged ionic form, further creating a repulsive force between deprotonated groups of COMBI and anionic form of LC molecules (Alkhatib et al., 2023).

A similar trend was detected in the removal efficiency when adsorbate conc. varies from lowest to highest value. The LC removal efficiency of COMBI increases first along with the increasing concentration of adsorbate from 20 to 70 g/l, after that the increment become plateaued probably due to the non-availability or saturation of adsorbent sites (Fan et al., 2017; Gale et al., 2021). Additionally, this variation in removal efficiency of COMBI with adsorbate concentration is strongly supported by the outcome of adsorption isotherm (directed to Fig. 3 and Table S6 of Supporting Information), revealing a finite number of active sites for adsorption in COMBI. Likewise the above two variables, adsorbent dose and contact time too act as a limiting factor for the removal efficiency of LC. A systematic descending pattern can be observed in both cases, wherein a lower value of both adsorbent dose of 0.01 g and 40 min of contact time exhibits a higher removal efficiency and a decrement can be seen when the values of both factors went up to the final limit of 3 g and 240 min. The responsible reason behind reduction of COMBI's removal efficiency against LC with increasing adsorbent dose is possibly associated with intra-particle interaction resulting in aggregation of biochar's active sites that likely cause hindrance in adsorption of LC over surface area of co-composted-biochar (Phuong et al., 2019). Same as adsorbent dose, when contact time increases the removal rate goes up but after reaching an equilibrium state there is no further increment

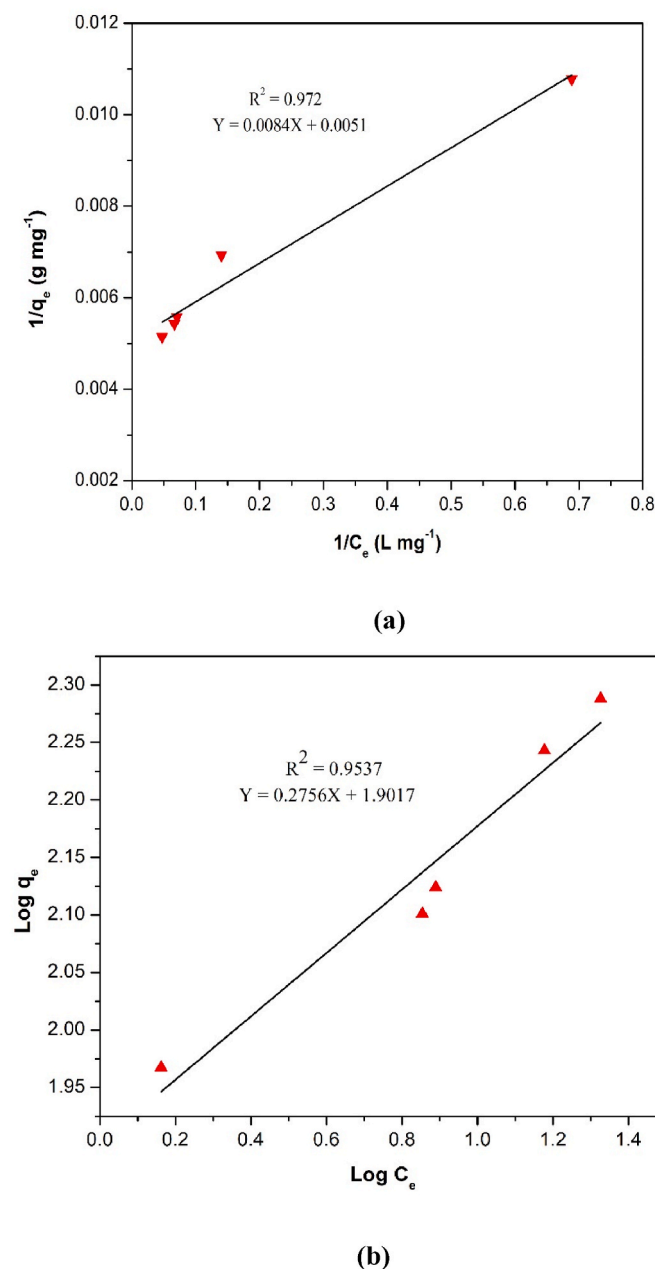


Fig. 3. (a) Langmuir isotherm (b) Freundlich isotherm for adsorption of LC on COMBI surface.

detected, which signifies a contact time between 40 and 140 min as its optimal range.

4.4. 2D Contour graphs and 3D surface plots for Lambda-cyhalothrin removal efficiency

The visualization of the interaction between removal efficiency and the combined effects of predictor variables is represented using 2D contour graphs along with their companion 3D surface plots. Since the number of independent variables is four, each of the contour plots will be held constant for two variables, while the other two will be kept at various levels to get the combined effect on the response variable. The response surface also varies accordingly with the levels of independent variables. The analysed optimum parameters and their concurrent effect on removal efficiency are represented in Fig. S4 of Supporting Information. These contour plots show the relationship between pH, contact

time, concentration and dose settings selected to remove LC, the darker red region represents a higher removal efficiency (%), while the lighter and greener region is associated with comparatively lower removal efficiency. Among these contour plots of AB, AD, BC, BD, and CD, the concurrent effect of pH, with adsorbent dose in AB, adsorbate conc. and adsorbent dose in BC, adsorbent dose and contact time in BD plots were observed with the majority of dark red color covering a hefty portion of plot's area, depicted that these variables in combination showed an influential synergistic effect on LC removal when applied in their optimum value range under enhanced conditions.

5. Adsorption isotherms

The adsorption isotherms was applied for a variable concentration of LC ranging between 20 and 60 g/l by keeping other parameters constant with an equalized values of 2 for pH, 0.01 g for adsorbent dose and a targeted value of 140 min for the contact time. Consistently, for the sorption experiment, two parametric Langmuir and Freundlich isotherm models were applied in order to investigate the interaction and adsorption behaviour of lambda cyhalthrin on the surface of co-composted-biochar (Srikhaow et al., 2023; Abdelhameed et al., 2020). Among these two applied isotherms, the Langmuir model support the assumption that adsorption takes place on adsorbent surface which are homogenously covered with some finite number of active sites, making it a strict monolayer adsorption (Singh & Rawat, 1994; Sharma et al., 2023). The mathematical formulation and its linear form is illustrated using equations (2) and (3).

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L C_e} \quad (3)$$

Where, K_L demonstrate the Langmuir constant in (L mg^{-1}) , $q_{\max}$ represent maximum adsorption capacity (mg g^{-1}) , q_e represent equilibrium adsorption capacity (mg g^{-1}) , and lastly C_i and C_e shows initial and equilibrium concentration of adsorbate in (mg l^{-1}) .

Contrarily, the Freundlich isotherm consider the fact that adsorption occurs on heterogenous surface of adsorbent material, resulting in a multilayer adsorption process. The empirical formula and linear form of Freundlich isotherm is displayed in equations (4) and (5).

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

Here, K_f (mg g^{-1}) is the adsorption coefficient which is also known as Freundlich constant while $1/n$ represent adsorption intensity measure in (l mg^{-1}) . It has been further stated that the value of $1/n$ helps in identifying the type of isotherm either it is desirable when the value is greater than zero ($1/n > 0$), undesirable when it is greater than one ($1/n > 1$) or irreversible during the condition when the value tends to be lower than zero ($1/n < 0$) (Ahsan et al., 2018; Haq et al., 2022).

The resultant data set and graphs of respective isotherm models are delineated in Table S6 of Supporting Information and Fig. 3. By observing Fig. 3, it can be concluded that the best fitted isotherm for the concerned adsorption process is Langmuir isotherm model. The displayed correlation coefficient (R^2) in Fig. 3 and Table S6 of Supporting Information, of Langmuir isotherm is 0.97 which is substantially greater than the R^2 value (0.95) of Freundlich isotherm, indicating the adsorption of LC on active sites of COMBI is entirely formulated of homogenous monolayer interaction with almost negligible interlinking of adsorbate molecules. Moreover, a high $q_{\max}$ value of 197.2 mg/gm is also associated with Langmuir model which is notably a sign of high adsorption capacity of COMBI. Also the R_L value follows the condition i.

$e. 0 < 0.32 < 1$, for Langumir isotherm, depicting the adsorption process of LC molecules on COMBI is favorable.

6. Adsorption mechanism

According to Srikhaow et al. (2023); Alkhatib et al. (2023); Li et al. (2022); Chandi et al. (2024), the adsorption mechanism between pesticide and biochar is primarily determined by specific intermolecular interactions such as electrostatic attraction, van der Waals interaction, hydrogen bonding, π - π EDA association, hydrophobic interaction, and surface diffusion. To determine the responsible interaction of current experimentation, the FTIR spectra of COMBI before and after removal was analysed. The after-removal analysis revealed a strengthening in the peak intensity of hydroxyl (-OH) bond and carboxylate (C-O-O) stretching in the FTIR spectrum (represented in Fig. S5 of Supporting Information), which could be an indicator of intermolecular hydrogen bonding between the hydrogen donor phenolic and carboxylic group of COMBI and nitrogen and oxygen bearing groups of LC (Li et al., 2022; Phuong et al., 2019). Moreover, a clear variation in the peak intensity of aromatic (C=C) and ketonic (C=O) groups of humic and fulvic components in COMBI, reveals the formation of a modest intermolecular π - π EDA association among aromatic rings of composted biochar and LC. In addition to these moderate forces, a substantial electrostatic force of attraction has been determined as a result of interaction between the oxygenated functional groups of COMBI and electronegative halogen and nitrogen groups of LC (Phuong et al., 2019), that prevails strongly and is thus governed as the primary adsorption mechanism for the process of removal.

7. Reusability study of Co-composted-biochar

The reusability experiment of COMBI was performed using 0.1 N HCL as an eluent in four consecutive cycles. Additionally, the removal of LC from simulated water was done under optimal range i.e. by keeping the values of individual parameter akin to the parameteric values of run number 19 (pH-2, adsorbent dose- 0.01 g, adsorbate conc.- 50 g/l and contact time-140 min) which has been recorded with the highest removal efficiency. The results are summarized in Fig. S6 of Supporting Information, showing a gradual decrease in the removal efficiency of COMBI from 99.9% to 79.7% across the four cycles. The reason behind might be the non-availability of active sites during adsorption which can be understood by the fact that the sites are still occupied by the adsorbate molecules making them less prone towards adsorption of further molecules (Dbik et al., 2022).

8. Conclusion

The results of comparative analysis between B, C, and COMBI for various qualitative and quantitative characteristics revealed a significant variation among them. COMBI was recorded with an efficient interaction between biochar's surface and organic components of compost material which was supported by the fact that a high crystalline stability, abundance of oxygen comprised functional groups, and an increased pore volume was detected in the observed data of XRD, FTIR, SEM, and BET analyzer. An optimized adsorption experiment using the RSM-BBD method was successfully conducted for COMBI towards LC elimination, which was notably discovered with a promising removal efficacy of more than 95%. The predictor factors were adjusted for greater attenuation of COMBI's LC removal efficiency when subjected to a lower pH value of 2, a medium range of 50 g/l of adsorbate concentration, 0.01 g of adsorbent dose, and a minimum contact period of 120 min. The purpose of this experiment was to discover how effectively a composite type of bio-adsorbent works as a remediation tool against pyrethroid pesticides. COMBI, a synergistic combination of biochar and compost, eliminates a substantial amount of LC, making it a viable and cost-effective remediation technique for other organic pollutants as

well.

CRedit authorship contribution statement

Vibhuti Sharma: Writing – original draft, Software, Methodology, Investigation, Data curation, Conceptualization. **Ashish Solanki:** Writing – review & editing. **Praveen Sharma:** Validation, Supervision, Resources, Formal analysis. **Dushyant Kumar:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Formal analysis.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2025.125842>.

Data availability

Data will be made available on request.

References

- Abdelhameed, R.M., Abdel-Gawad, H., Hegazi, B., 2020. Effective adsorption of prothiofos (O-2, 4-dichlorophenyl O-ethyl S-propyl phosphorodithioate) from water using activated agricultural waste microstructure. *J. Environ. Chem. Eng.* 8 (3), 103768. <https://doi.org/10.1016/j.jece.2020.103768>.
- Ahamad, A., Kumar, J., 2023. Pyrethroid pesticides: an overview on classification, toxicological assessment and monitoring. *Journal of Hazardous Materials Advances*, 100284. <https://doi.org/10.1016/j.hazadv.2023.100284>.
- Ahsan, M.A., Katla, S.K., Islam, M.T., Hernandez-Viezcas, J.A., Martinez, L.M., Díaz-Moreno, C.A., et al., 2018. Adsorptive removal of methylene blue, tetracycline and Cr (VI) from water using sulfonated tea waste. *Environ. Technol. Innovat.* 11, 23–40. <https://doi.org/10.1016/j.eti.2018.04.003>.
- Alkhatib, F., Ibarhiam, S.F., Alrefaei, A.F., Alrefaei, S.H., Pashameah, R., Habeebullah, T. M., et al., 2023. Efficient removal of deltamethrin from aqueous solutions using a novel Lanthanum metal-organic framework: adsorption models and optimization via box-behnken design. *ACS Omega* 8 (35), 32130–32145. <https://pubs.acs.org/doi/10.1021/acsomega.3c04481>.
- Alrawe, S.A., Alzubaidy, M.H., 2022. Acute and Sub-acute Toxicity Effects of Lambda-Cyhalothrin in Chicks.
- Al-Sarar, A.S., Abobakr, Y., Bayoumi, A.E., Hussein, H.I., Al-Ghothemi, M., 2014. Reproductive toxicity and histopathological changes induced by lambda-cyhalothrin in male mice. *Environ. Toxicol.* 29 (7), 750–762. <https://doi.org/10.1002/tox.21802>.
- Amweg, E.L., Weston, D.P., Ureda, N.M., 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. *Environ. Toxicol. Chem.: Int. J.* 24 (4), 966–972. <https://doi.org/10.1897/04-146R1.1>.
- Ananda Gowda, S.R., Somashekar, R.K., 2012. Evaluation of pesticide residues in farmgate samples of vegetables in Karnataka, India. *Bull. Environ. Contam. Toxicol.* 89, 626–632. <https://doi.org/10.1007/s00128-012-0737-1>.
- Andrade, F.H., Figueiroa, F.C., Bersano, P.R., Bissacot, D.Z., Rocha, N.S., 2010. Malignant mammary tumor in female dogs: environmental contaminants. *Diagn. Pathol.* 5, 1–5. <https://doi.org/10.1186/1746-1596-5-45>.
- Asad, A., Sameoto, D., Sadzadeh, M., 2020. Overview of membrane technology. In: *Nanocomposite Membranes for Water and Gas Separation*. Elsevier, pp. 1–28. <https://doi.org/10.1016/B978-0-12-816710-6.00001-8>.

- Azeem, M., Hayat, R., Hussain, Q., Ahmed, M., Imran, M., Crowley, D., 2016. Effect of biochar amendment on soil microbial biomass, abundance and enzyme activity in the mash bean field. *J. Biodivers. Environ. Sci. (JBES)* 8 (6), 1–13.
- Baharum, N.A., Nasir, H.M., Ishak, M.Y., Isa, N.M., Hassan, M.A., Aris, A.Z., 2020. Highly efficient removal of diazinon pesticide from aqueous solutions by using coconut shell-modified biochar. *Arab. J. Chem.* 13 (7), 6106–6121. <https://doi.org/10.1016/j.arabjch.2020.05.011>.
- Bedi, J.S., Gill, J.P.S., Aulakh, R.S., Kaur, P., 2015. Pesticide residues in bovine milk in Punjab, India: spatial variation and risk assessment to human health. *Arch. Environ. Contam. Toxicol.* 69, 230–240. <https://doi.org/10.1007/s00244-015-0163-6>.
- Bradberry, S.M., Cage, S.A., Proudfoot, A.T., Vale, J.A., 2005. Poisoning due to pyrethroids. *Toxicol. Rev.* 24, 93–106. <https://doi.org/10.2165/00139709-200524020-00003>.
- Brander, S.M., He, G., Smalling, K.L., Denison, M.S., Cherr, G.N., 2012. The *in vivo* estrogenic and *in vitro* anti-estrogenic activity of permethrin and bifenthrin. *Environ. Toxicol. Chem.* 31 (12), 2848–2855. <https://doi.org/10.1002/etc.2019>.
- Brtnicky, M., Dokulilova, T., Holatko, J., Pecina, V., Kintl, A., Latal, O., et al., 2019. Long-term effects of biochar-based organic amendments on soil microbial parameters. *Agronomy* 9 (11), 747. <https://doi.org/10.3390/agronomy9110747>.
- 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, 1–12. <https://doi.org/10.1007/s11270-016-2894-z>.
- Chandi, K., Udomkun, P., Boonupara, T., Kaewlom, P., 2024. Enhancing soil health, microbial count, and hydrophilic methoxymethyl and hydrophobic lambda-cyhalothrin remediation with biochar and nano-biochar. *Sci. Rep.* 14 (1), 19551. <https://doi.org/10.1038/s41598-024-56745-8>.
- Chen, X., Zhou, Q., Liu, F., Peng, Q., Teng, P., 2019. Removal of nine pesticide residues from water and soil by biosorption coupled with degradation on biosorbent immobilized laccase. *Chemosphere* 233, 49–56. <https://doi.org/10.1016/j.chemosphere.2019.05.144>.
- Chen, H., Wang, X., Liu, P., Jia, Q., Han, H., Jiang, C., Qiu, J., 2021. Determination of three typical metabolites of pyrethroid pesticides in tea using a modified QuEChERS sample preparation by ultra-high performance liquid chromatography tandem mass spectrometry. *Foods* 10 (1), 189. <https://doi.org/10.3390/foods10010189>.
- Corcellas, C., Eljarrat, E., Barceló, D., 2015. First report of pyrethroid bioaccumulation in wild river fish: a case study in Iberian river basins (Spain). *Environ. Int.* 75, 110–116. <https://doi.org/10.1016/j.envint.2014.11.007>.
- Cruz, G.J., Mondal, D., Rimaycuna, J., Soukup, K., Gómez, M.M., Solís, J.L., Lang, J., 2020. Agrowaste derived biochars impregnated with ZnO for removal of arsenic and lead in water. *J. Environ. Chem. Eng.* 8 (3), 103800. <https://doi.org/10.1016/j.jece.2020.103800>.
- Das, S., Mishra, S., 2017. Box-Behnken statistical design to optimize preparation of activated carbon from Limonia acidissima shell with desirability approach. *J. Environ. Chem. Eng.* 5 (1), 588–600. <https://doi.org/10.1016/j.jece.2016.12.034>.
- Das, S.K., Ghosh, G.K., Avasthe, R., Sinha, K., 2021. Morpho-mineralogical exploration of crop, weed and tree derived biochar. *J. Hazard Mater.* 407, 124370. <https://doi.org/10.1016/j.jhazmat.2020.124370>.
- Dbik, A., El Messaoudi, N., Bentahar, S., El Khomri, M., Lacherai, A., Faska, N., 2022. Optimization of methylene blue adsorption on agricultural solid waste using box-behnken design (BBD) combined with response surface methodology (RSM) modeling. *Biointerface Res. Appl. Chem* 12 (4), 4567–4583. <https://doi.org/10.33263/BRIAC124.45674583>.
- De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M., 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review. *Sustainable Materials and Technologies* 9, 10–40. <https://doi.org/10.1016/j.susmat.2016.06.002>.
- El-Saeid, M.H., Khan, H.A., 2015. Determination of pyrethroid insecticides in crude and canned vegetable samples by supercritical fluid chromatography. *Int. J. Food Prop.* 18 (5), 1119–1127. <https://doi.org/10.1080/10942912.2013.864672>.
- Fan, S., tom, Y., Wang, Z., Tang, J., Tang, J., Li, X., 2017. Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: adsorption kinetics, equilibrium, thermodynamics and mechanism. *J. Environ. Chem. Eng.* 5 (1), 601–611. <https://doi.org/10.1016/j.jece.2016.12.019>.
- Feng, X.F., Jin, W.G., 2007. Analysis of pesticide contamination in vegetables in Fuzhou City. *Acta Agric Jiangxi* 2006.
- Gale, M., Nguyen, T., Moreno, M., Gillardi-AbdulAziz, K.L., 2021. Physicochemical properties of biochar and activated carbon from biomass residue: influence of process conditions to adsorbent properties. *ACS Omega* 6 (15), 10224–10233. <https://doi.org/10.1021/acsomega.1c00530>.
- Gao, Z.X., Ao, K.H., Li, B., Bao, R.H., Zeng, Q.H., Deng, C.Y., 2012. Determination of tetramethrin and cyhalothrin residues in mutton tissues by RP-HPLC with solid-phase extraction. *Anal. Abstr.* 31 (5), 116–119.
- Gong, D.C., 2013. Pyrethroids Pesticides Residues and Their Behavior in a Multimedium Environment of Liangtan River Basin, vol. 93. School of Environment and Civil Engineering, Chongqing University, Chongqing.
- Hagemann, N., Joseph, S., Schmidt, H.P., Kammann, C.I., Harter, J., Borch, T., et al., 2017. Organic coating on biochar explains its nutrient retention and stimulation of soil fertility. *Nat. Commun.* 8 (1), 1089. <https://doi.org/10.1038/s41467-017-01123-0>.
- Hagemann, N., Subdiaga, E., Orsetti, S., de la Rosa, J.M., Knicker, H., Schmidt, H.P., Kappler, A., Behrens, S., 2018. Effect of biochar amendment on compost organic matter composition following aerobic composting of manure. *Sci. Total Environ.* 613, 20–29. <https://doi.org/10.1016/j.scitotenv.2017.08.161>.
- Hag, A.U., Saeed, M., Muneer, M., Jamal, M.A., Maqbool, T., Tahir, T., 2022. Biosorption of metribuzin pesticide by Cucumber (*Cucumis sativus*) peels-zinc oxide nanoparticles composite. *Sci. Rep.* 12 (1), 5840. <https://doi.org/10.1038/s41598-022-09860-z>.
- Hung, C.Y., Tsai, W.T., Chen, J.W., Lin, Y.Q., Chang, Y.M., 2017. Characterization of biochar prepared from biogas digestate. *Waste Manag.* 66, 53–60. <https://doi.org/10.1016/j.wasman.2017.04.034>.
- Kajama, M.N., Nwogu, N.C., Gobina, E., 2015. Hydrogen permeation using nanostructured silica membranes. *Sustain Dev Plan* 7 (193), 447–456. <https://doi.org/10.2495/sdp150381>.
- Kaur, P., Singh, S., Verma, G., 2018. Facile synthesis of mesoporous carbon material from treated kitchen waste for energy applications. *Materials for Renewable and Sustainable Energy* 7, 1–10. <https://doi.org/10.1007/s40243-018-0116-x>.
- Keilweite, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* 44 (4), 1247–1253. <https://doi.org/10.1021/es9031419>.
- Kumar, A., Bhattacharya, T., Shaikh, W.A., Roy, A., Mukherjee, S., Kumar, M., 2021. Performance evaluation of crop residue and kitchen waste-derived biochar for eco-efficient removal of arsenic from soils of the Indo-Gangetic plain: a step towards sustainable pollution management. *Environ. Res.* 200, 111758. <https://doi.org/10.1016/j.envres.2021.111758>.
- Li, X., Xu, J., Luo, X., Shi, J., 2022. Efficient adsorption of dyes from aqueous solution using a novel functionalized magnetic biochar: synthesis, kinetics, isotherms, adsorption mechanism, and reusability. *Bioresour. Technol.* 360, 127526. <https://doi.org/10.1016/j.biortech.2022.127526>.
- Liu, H., Charrua, A.B., Weng, C.H., Yuan, X., Ding, F., 2015. Characterization of biochars derived from agriculture wastes and their adsorptive removal of atrazine from aqueous solution: a comparative study. *Bioresour. Technol.* 198, 55–62. <https://doi.org/10.1016/j.biortech.2015.08.129>.
- Ma, J., Zhou, B., Zhang, H., Zhang, W., Wang, Z., 2019. Activated municipal waste sludge biochar supported by nanoscale Fe/Cu composites for tetracycline removal from water. *Chem. Eng. Res. Des.* 149, 209–219. <https://doi.org/10.1016/j.cherd.2019.07.013>.
- Mahboob, S., Niazi, F., AlGhanim, K., Sultana, S., Al-Misned, F., Ahmed, Z., 2015. Health risks associated with pesticide residues in water, sediments and the muscle tissues of Catla catla at Head Balloki on the River Ravi. *Environ. Monit. Assess.* 187, 1–10. <https://doi.org/10.1007/s10661-015-4285-0>.
- Mallakpour, S., Naghdi, M., 2016. Application of SiO 2 nanoparticles with double layer coverage consist of citric acid and l (+)-ascorbic acid for the production of poly (vinyl chloride)/SiO 2 nanocomposite films with enhanced optical and thermal properties. *Polym. Bull.* 73, 1701–1717. <https://doi.org/10.1007/s00289-015-1572-4>.
- Merlin, N., Nogueira, B.A., Lima, V.A.D., Santos, L.M.D., 2014. Application of fourier transform infrared spectroscopy, chemical and chemometrics analyses to the characterization of agro-industrial waste. *Quim. Nova* 37, 1584–1588. <https://doi.org/10.5935/0100-4042.20140259>.
- Mohammadpour, S., Moghadam, P.N., Gharbani, P., 2024. Preparation, characterization, and photocatalytic performance of a PVDF/cellulose membrane modified with nano Fe 3 O 4 for removal of methylene blue using RSM under visible light. *RSC Adv.* 14 (13), 8801–8809. <https://doi.org/10.1039/D3RA08599F>.
- Mojiri, A., Zhou, J.L., Robinson, B., Ohashi, A., Ozaki, N., Kindaichi, T., et al., 2020. Pesticides in aquatic environments and their removal by adsorption methods. *Chemosphere* 253, 126646. <https://doi.org/10.1016/j.chemosphere.2020.126646>.
- Mukome, F.N., Zhang, X., Silva, L.C., Six, J., Parikh, S.J., 2013. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *J. Agric. Food Chem.* 61 (9), 2196–2204.
- Navaratna, D., Shu, L., Jegatheesan, V., 2016. Evaluation of herbicide (persistent pollutant) removal mechanisms through hybrid membrane bioreactors. *Bioresour. Technol.* 200, 795–803. <https://doi.org/10.1016/j.biortech.2015.10.041>.
- Özçimen, D., Ersoy-Meriçboyu, A., 2010. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renew. Energy* 35 (6), 1319–1324. <https://doi.org/10.1016/j.renene.2009.11.042>.
- Pandit, N.R., Schmidt, H.P., Mulder, J., Hale, S.E., Husson, O., Cornelissen, G., 2020. Nutrient effect of various composting methods with and without biochar on soil fertility and maize growth. *Arch. Agron Soil Sci.* <https://doi.org/10.1080/03650340.2019.1610168>.
- Phuong, D.T.M., Loc, N.X., Miyaniishi, T., 2019. Efficiency of dye adsorption by biochars produced from residues of two rice varieties, Japanese Koshihikari and Vietnamese IR50404. *Desalination Water Treat.* 165, 333–351. <https://doi.org/10.5004/dwt.2019.24496>.
- Prado-Lu, D., Leilanie, J., 2015. Insecticide residues in soil, water, and eggplant fruits and farmers' health effects due to exposure to pesticides. *Environ. Health Prev. Med.* 20 (1), 53–62. <https://doi.org/10.1007/s12199-014-0425-3>.
- Prost, K., Borchard, N., Siemens, J., Kautz, T., Séquaris, J.M., Möller, A., Amelung, W., 2013. Biochar affected by composting with farmyard manure. *J. Environ. Qual.* 42 (1), 164–172. <https://doi.org/10.2134/jeq2012.0064>.
- Punia, P., Singh, L., 2024. Optimization of alkali pre-treatment of sweet sorghum [Sorghum bicolor (L.) Moench] residue to improve enzymatic hydrolysis for fermentable sugars. *Waste Management Bulletin* 2 (1), 131–141. <https://doi.org/10.1016/j.wmb.2023.12.007>.
- Rehman, H., Rehman, Z., Das, T.K., Rehman, M., Khan, B.A., Nandi, S., et al., 2024. Toxicity evaluation and degradation of cypermethrin-contaminated soil using biochar and *Bacillus cereus* amendments. *Sci. Rep.* 14 (1), 1–15. <https://doi.org/10.1038/s41598-024-81588-4>.
- Rijo, B., Nobre, C., Brito, P., Ferreira, P., 2024. An overview of the thermochemical valorization of sewage sludge: principles and current challenges. *Energies* 17 (10), 2417. <https://doi.org/10.3390/en17102417>.
- Rujitanapanich, S., Kumpapan, P., Wanjanai, P., 2014. Synthesis of hydroxyapatite from oyster shell via precipitation. *Energy Proc.* 56, 112–117. <https://doi.org/10.1016/j.egypro.2014.07.138>.

- Saleh, I.A., Zouari, N., Al-Ghouti, M.A., 2020. Removal of pesticides from water and wastewater: chemical, physical and biological treatment approaches. *Environ. Technol. Innovat.* 19, 101026. <https://doi.org/10.1016/j.eti.2020.101026>.
- Sánchez-Monedero, M.A., Sánchez-García, M., Alburquerque, J.A., Cayuela, M.L., 2019. Biochar reduces volatile organic compounds generated during chicken manure composting. *Bioresour. Technol.* 288, 121584. <https://doi.org/10.1016/j.biortech.2019.121584>.
- Sankar, P., Telang, A.G., Manimaran, A., 2012. Protective effect of curcumin on cypermethrin-induced oxidative stress in Wistar rats. *Exp. Toxicol. Pathol.* 64 (5), 487–493. <https://doi.org/10.1016/j.etp.2010.11.003>.
- Schimmelpfennig, S., Glaser, B., 2012. One step forward toward characterization: some important material properties to distinguish biochars. *J. Environ. Qual.* 41 (4), 1001–1013. <https://doi.org/10.2134/jeq2011.0146>.
- Shah, S.W.A., Rehman, M.U., Arslan, M., Abbasi, S.A., Hayat, A., Anwar, S., et al., 2022. Response surface methodology for optimization of operational parameters to remove ciprofloxacin from contaminated water in the presence of a bacterial consortium. *ACS Omega* 7 (31), 27450–27457. <https://doi.org/10.1021/acsomega.2c02448>.
- Sharma, A., Mittal, R., Sharma, P., Pal, K., Mona, S., 2023. Sustainable approach for adsorptive removal of cationic and anionic dyes by titanium oxide nanoparticles synthesized biogenically using algal extract of *Spirulina*. *Nanotechnology* 34 (48), 485301. <https://doi.org/10.1088/1361-6528/acf37e>.
- Singh, B.K., Rawat, N.S., 1994. Comparative sorption kinetic studies of phenolic compounds on fly ash and impregnated fly ash. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental AND Clean Technology* 61 (1), 57–65. <https://doi.org/10.1002/jctb.280610109>.
- Singh, B., Singh, B.P., Cowie, A.L., 2010. Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Res.* 48 (7), 516–525. <https://doi.org/10.1071/SR10058>.
- Som, A.M., Wang, Z., Al-Tabbaa, A., 2012. Palm frond biochar production and characterisation. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh* 103 (1), 39–50. <https://doi.org/10.1017/S1755691012000035>.
- Srikhaow, A., Win, E.E., Amornsakchai, T., Kiatsiriroat, T., Kajitvichyanukul, P., Smith, S.M., 2023. Biochar derived from pineapple leaf non-fibrous materials and its adsorption capability for pesticides. *ACS Omega* 8 (29), 26147–26157. <https://pubs.acs.org/doi/10.1021/acsomega.3c02328>.
- Suo, F., You, X., Ma, Y., Li, Y., 2019. Rapid removal of triazine pesticides by P doped biochar and the adsorption mechanism. *Chemosphere* 235, 918–925. <https://doi.org/10.1016/j.chemosphere.2019.06.158>.
- Swamy, G.J., Sangamithra, A., Chandrasekar, V., 2014. Response surface modeling and process optimization of aqueous extraction of natural pigments from *Beta vulgaris* using Box–Behnken design of experiments. *Dyes Pigments* 111, 64–74. <https://doi.org/10.1016/j.dyepig.2014.05.028>.
- Taha, S.M., Amer, M.E., Elmarsafy, A.E., Elkady, M.Y., 2014. Adsorption of 15 different pesticides on untreated and phosphoric acid treated biochar and charcoal from water. *J. Environ. Chem. Eng.* 2 (4), 2013–2025. <https://doi.org/10.1016/j.jece.2014.09.001>.
- Tang, W., Wang, D.I., Wang, J., Wu, Z., Li, L., Huang, M., et al., 2018. Pyrethroid pesticide residues in the global environment: an overview. *Chemosphere* 191, 990–1007. <https://doi.org/10.1016/j.chemosphere.2017.10.115>.
- Tulun, Ş., Akgül, G., Alver, A., Çelebi, H., 2021. Adaptive neuro-fuzzy interference system modelling for chlorpyrifos removal with walnut shell biochar. *Arab. J. Chem.* 14 (12), 103443. <https://doi.org/10.1016/j.arabjc.2021.103443>.
- Vaz-Moreira, I., Silva, M.E., Manaia, C.M., Nunes, O.C., 2008. Diversity of bacterial isolates from commercial and homemade composts. *Microb. Ecol.* 55, 714–722. <https://doi.org/10.1007/s00248-007-9314-2>.
- Werner, I., Moran, K., 2008. Effects of pyrethroid insecticides on aquatic organisms. *Synthetic pyrethroids: Occurrence and behavior in aquatic environments* 991, 310–335.
- Wolansky, M.J., Tornero-Velez, R., 2013. Critical consideration of the multiplicity of experimental and organismic determinants of pyrethroid neurotoxicity: a proof of concept. *J. Toxicol. Environ. Health, Part A* 16 (8), 453–490. <https://doi.org/10.1080/10937404.2013.853607>.
- Yang, Y., Chun, Y., Sheng, G., Huang, M., 2004. pH-dependence of pesticide adsorption by wheat-residue-derived black carbon. *Langmuir* 20 (16), 6736–6741. <https://doi.org/10.1021/la049363t>.
- Yang, X., Zhang, S., Ju, M., Liu, L., 2019. Preparation and modification of biochar materials and their application in soil remediation. *Appl. Sci.* 9 (7), 1365. <https://doi.org/10.3390/app9071365>.
- Yang, C., Lim, W., Song, G., 2020. Mediation of oxidative stress toxicity induced by pyrethroid pesticides in fish. *Comp. Biochem. Physiol. C Toxicol. Pharmacol.* 234, 108758. <https://doi.org/10.1016/j.cbpc.2020.108758>.
- Ye, S., Zeng, G., Wu, H., Liang, J., Zhang, C., Dai, J., et al., 2019. The effects of activated biochar addition on remediation efficiency of co-composting with contaminated wetland soil. *Resour. Conserv. Recycl.* 140, 278–285. <https://doi.org/10.1016/j.resconrec.2018.10.004>.
- Zahoora, M., Ullahb, A., Ikramb, J., Umarc, M. N., & Ullahd, R. Separation of organic pesticide (insecticide): lambda-cyhalothrin from wastewater using magnetic carbon nanocomposites. <https://doi.org/10.5004/dwt.2023.29588>.
- Zhao, L.N., 2014. Residue and Risk Assessment of 7 Kinds of Pyrethroids in Water Environment in the Pearl River Delta. Shanghai Ocean University. <https://www.fao.org/faostat/en/#search/Insecticides%20%E2%80%93%20Pyrethroids>.
- Zhuan, R., Wang, J., 2020. Degradation of diclofenac in aqueous solution by ionizing radiation in the presence of humic acid. *Separ. Purif. Technol.* 234, 116079. <https://doi.org/10.1016/j.seppur.2019.116079>.