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Potato peel biochar: A sustainable material for the removal of pesticides and soil amendment for crop productivity

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ABSTRACT

This study illustrated the removal of Chlorpyrifos, an organophosphate pesticide, by potato peel biochar. Potato peel biochar was prepared using peels of potato collected from different points (canteens and housing complexes) at Haldia (West Bengal). In batch assay, the biochar adsorbed the chlorpyrifos on its surface almost 93% in 24 hours. The parameters (temperature, pH and biochar amount) were optimized by experiments. Results confirmed the effective removal of pesticide removal by biochar at 30 and 40ºC. The pH 4.5, 7.5 and 8.5 were best at both temperatures. Based on the optimization results and for broad application of the prepared biochar at various geographical regions, we selected pH 7.5 and 35±2ºC. Results showed maximum uptake of chlorpyrifos (5 mg/mL) using 10 mg biochar at pH 7.5 and 35±2ºC. Experiments on plant system, Vigna radiata showed enhanced seedlings' growth when the soil was amended with the prepared biochar. Biochar helps in pesticide removal and has essential minerals that help plant growth. Therefore, this study shows the potential use of this bacterium to help amend the soil for pesticide degradation and soil fertility enhancement.

Keywords: Biochar; Chlorpyrifos; Pesticide; Potato peel; *Vigna radiata*

INTRODUCTION

The slow pyrolysis of biowastes produces biochar in an oxygen-limited environment in a muffle furnace and is a black residue consisting of carbon and ashes (Yang *et al.,* 2018)**.** Biochar is a compound that helps to enrich the balance of nutrition and carbon compounds in the soil (Jatav *et al.,* 2021; Cheng *et al.,* 2024). Biochar is an essential sorbent for a different group of pesticides; the sorbent power of biochar for pesticides depends on the physicochemical properties, i.e., organic carbon contents, porous structure and ionic interaction, and specific surface area (Khorram *et al.,* 2016)**.** Biochar can modify soil physiochemical structure and change the negative and positive effects on the structure of the microbe's community and function (Zhu *et al.,* 2017)**.** Biochar is a high-carbon compound that can reduce the leaching of pesticides in the soil and enhance pesticide adsorption capacity by enticing pesticides into the micropore and deformity of pore biochar particles (Khorram *et al.,* 2016)**.** Biochar is a subtle grain, highly porous charcoal separated, and the nutritional value of soil increases with amending biochar to soil (Hunt *et al.,* 2010**.** Nitrogen, Phosphorus, and potassium in biochar and some elementary cations (calcium and magnesium) are indispensable for plant growth (Rawat *et al.,* 2019)**.**

Pesticides have been used for decades to protect crops from insects and microbes (Verma *et al.,* 2015). Pesticide pollution has become a significant issue all over the world. Only 0.1 per cent of pesticides reached the target organisms, and the residuum percentage contaminated the neighbouring environment (Gill and Garg, 2014)**.** Pesticides not only kill the target organism but also kill the nontarget organism. That was an essential role of an ecosystem. Organophosphate pesticides are used worldwide for gardening and agriculture purposes to control pests. Chlorpyrifos is one type of organophosphate pesticide. Chlorpyrifos can leach into water bodies from farmland (Wołejko *et al.,* 2022)**,** which must be toxic to various organisms in the water. Chlorpyrifos block the transmission of the signal from one nerve to another nerve by phosphorylation of cholinesterase. Phosphorylated cholinesterase cannot break acetylcholine, which is why acetylcholine concentration improves and becomes the reason for the death of insects (Karanth and Pope, 2000)**.** Chlorpyrifos can

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enter the human body through various routes, such as ingestion, inhalation, or dermal absorption**.** Continuous exposure of pesticides into the body causes various diseases, i.e., neurological, psychological, and behavioural dysfunction, immune system dysfunction, dysfunction of the reproductive system, cancers, headaches, and impaired retention**.** Neuro-degradation diseases such as Alzheimer's disease and Parkinson's have become common in persons exposed to pesticides occupationally (Sbabbir *et al.,* 2018)**.** Additionally, this compound adds its more toxic metabolites to nature after degradation. The pesticide chlorpyrifos degrades to give metabolites such as 3, 5, and 6-trichloro-2-pyridimol (TCP) more toxic than its parental form. TCP degradation is very slow since it is highly persistent in the soil.

Among various approaches, microbial degradation of critical pesticide residues in soil and water can be most effectively used, reducing the environment's hazardous conditions. Recently, biochar has become the most applied substance in soil for enhancing soil fertility and removal of toxic chemicals. Pyrolysis of organic wastes in the absence of oxygen helps in biochar formation. Biochar has several applications, including removing toxic compounds from the environment (Singh *et al.,* 2022; Manda Zhao l *et al.,* 2017; Zhao *et al.,* 2018). The enhancement of crop productivity in the field having biochar is due to a decrease in nitrogen uptake and enrichment of soil with various minerals of biochar. Prevention of leeching of valuable minerals by biochar also leads to soil fertility (Calderón *et al.,* 2015; Singh *et al.,* 2022). Previous scientific reports described that the microbes growing on biochar surfaces have the necessary enzymatic machinery to absorb and assimilate biochar for growth. The present work evaluated the removal of chlorpyrifos, an organophosphate pesticide, using biochar formed by pyrolysis of potato peel. Growth enhancement of Vigna radiata (moong bean) is also tested in pots having garden soil mixed with biochar.

MATERIALS AND METHODS

Materials

Potato peels were collected from various canteens (schools, colleges, hospitals and industries) and housing complexes in Haldia, Purba Medinipur. Noorani 505, having Chlorofyrifos 50 % EC (Anu product, India), was selected based on an initial market survey in Haldia. GC-MS analysis determined the formulation of this pesticide (Shabbir *et al.,* 2018). *A Vigna radiata (*moong bin*)* seed *was* procured from a local market in Haldia. All other required chemicals were bought from Hi Media, India, and are of analytical grade.

Biochar from Potato Peel

The potato peel collected was from various canteens and housing complexes under Haldia municipality. The peels were washed with running tap water to remove adhered impurities, followed by distilled water, and finally dried under direct sunlight to get the peels thoroughly dried. The dried potato peels were made into fine powder and subjected to slow pyrolysis in a muffle furnace under oxygen-limited conditions at 700°C to 900°C for 2 hours.

Proximate analysis

A proximate analysis of biochar was assayed. The parameters quantified were moisture content, ash content, volatile matter, fixed carbon, and higher heating value (Yang *et al.,* 2018). This biochar was analyzed using a ZEISS- Scanning Electron Microscope (SEM), FTIR, X-ray diffraction (XRD) and Energy Dispersive X-ray spectroscopy (EDS) and reported in our previous paper to get deep inside its morphology and minerals (Singh *et al.,* 2022).

Chlorpyrifos removal by Potato biochar

Firstly, a stock chlorpyrifos (100 mg/ml) was made from the pesticide formulation Noorani 505 in phosphate buffer (pH 7.0). Optimization of parameters like pH (4.5 – 9.0), temperature (30 and 40ºC) and potato biochar (10-20 mg/mL) with a fixed concentration of chlorpyrifos (5mg/mL) was studied to have the best result using minimal biochar. The reaction mixture contained biochar uniformly dissolved in buffer and chlorpyrifos in a 1.5 ml Eppendorf tube. The experimental sets were incubated at two definite temperatures in a static incubator. At every 30-minute interval, the reading was recorded. After incubation, the reaction mixture was centrifuged at 5000 rpm for 10 minutes, and the soup was collected in a new tube. The soup contained the residual chlorpyrifos after the treatment period. The soup was subjected to a

UV-Vis Spectroscopic study (Shimadzu, UV-1700). The soup was subjected to a UV-vis spectrophotometer for a record of absorbance spectra between 200 and 300 nm. The absorbance maximum of Chlorpyrifos at 290 nm was considered to quantify residual Chlorpyrifos (Shabbir *et al.,* 2018). The amount of pesticide adsorbed on the biochar surface (removal %) was calculated according to the equation given below:

$$\text{Removal (\%)} = [(a-b)/a)] \times 100$$

Where, a, absorbance of the reaction mixture at 0 h and b, absorbance of the reaction mixture at time 't' (0.5-24 h)

Effect of biochar-treated pesticides on *V. radiata* (moong bin)

The experiment was planned to study the effects of biochar-treated pesticides on moong bin growth parameters in pot culture. The seeds of the moong bin were precisely washed first with tap water and next with sterile distilled water. Finally, seeds were soaked in water for overnight and were sown in a pot full of sterile soil. The soil has been mixed uniformly with biochar and negative control (no biochar). The pots were incubated in a plant growth chamber under an ambient environment (12/12 light/dark and room temperature). After germinating the seeds, pesticide solution was sprayed regularly on the definite sets (Table 1). The seedlings of moong beans were allowed to be nurtured for 10 days, and data were recorded after that.

Table 1: Experimental sets for studying the effect of biochar and pesticide on moong bean

Sl. No	Biochar	Tape water	Pesticide
1	-	+	-
2	-	+	+
3	+	+	-
4	+	+	+

Statistical Analysis

All experiments were conducted at least thrice, and the recorded data were denoted as the values' mean and standard deviation (STDV).

RESULTS AND DISCUSSION

The rapid increase in world population necessitates a high output of agricultural products to support any nation. Effective farming techniques help in the proper handling of pre- and post-farming. Pesticides help prevent pests and insects from damaging crops, reducing crop loss. Additionally, the byproducts of these pesticides in soil can affect non-target species, including humans. Soil microbiota is also affected by the high dose of such chemicals on crops. Biochar can sustainably control the environment. It helps increase soil fertility and, most importantly, removes toxic chemicals. In the present study, biochar developed by slow pyrolysis of potato peels demonstrated effective chlorpyrifos removal in an aqueous environment (Singh *et al.,* 2022).

Proximate Analysis

The proximate analysis of potato peel biochar showed 5.2% moisture content, 17% ash content, and 55.8% fixed carbon, and this biochar has 25% HHV (Singh *et al.,* 2022). SEM images of the biochar surface showed shrinkage and cracking with porosity, which were highly heterogeneous. The structures help in the effective adsorption of pesticides. The minerals in the biochar were Magnesium, Calcium, Sodium, and a trace amount of Zinc, Aluminium, and Silicon (Singh *et al.,* 2022).

Biochar as an effective Chlorpyrifos removal

The most popular brand formulation, Noorani 505, was selected with Chlorpyrifos (50 % EC). Chlorpyrifos is an organophosphate compound having a molecular weight of 350.575g/mol and formula $C_9H_{11}Cl_3NO_3PS$. A stock of Chlorpyrifos (100 mg/mL) was prepared in PBS-phosphate buffer (Hi Media, India). UV-vis study showed a significant peak at 290 nm (Singh *et al.,* 2022).

The Chlorpyrifos in the aqueous phase was studied using the UV-Vis spectrophotometer by recording the absorbance maxima at 290 nm to detect residual pesticide in the sample solution after treatment with an appropriate amount of biochar for a definite period. The result indicated that about 80% of Chlorpyrifos removal by biochar (10 mg) was in 5 hours; after

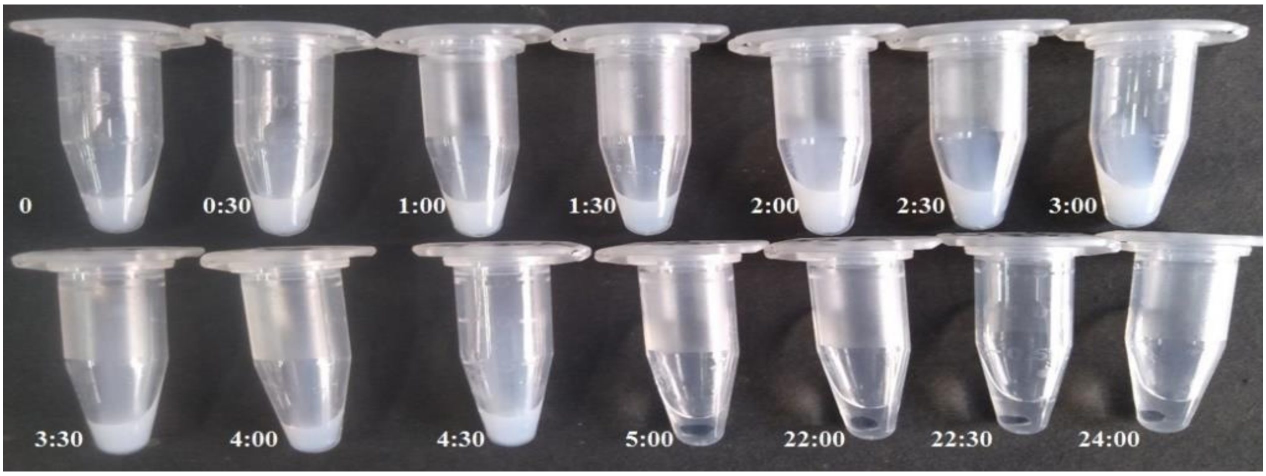

Figure 1 shows the removal of pesticides using biochar at different time points (0-24 hours). Biochar, 10 mg; Chlorpyrifos, 5 mg/mL in Phosphate buffer, pH 7.5

that, the rate decreased and became saturated after 22 hours. A quantitative estimation of pesticide removal was found to be 93.05 % after 5 h, and it remains the same up to 24 h at pH 7.0 and room temperature (Figure 1).

The role of pH in controlling the removal efficiency of pesticides depends on the chemical and physical nature of the biochar used in the medium. It was reported that soil pH is an essential factor in the uptake of pesticides by biochar. Therefore, at 30 and 40 ^{0}C temperatures and three biochar concentrations (10, 15 and 20 mg/mL) with 5 mg/mL chlorpyrifos, the experiment was set to determine the removal efficacy of chlorpyrifos at different pH (4.5-9). Figures 2 a and b demonstrate the removal efficacy after 24 hours of treatment. At 30 ^{0}C, biochar maximum removal was recorded at pH 4.5 and 20 mg/mL, followed by pH 7.5 (with 20 mg/mL biochar). Similarly, data was recorded for 40 ^{0}C, which showed biochar maximum removal at pH 8.5 and 10 mg/mL biochar, followed by pH 4.5 (with 20 mg/mL biochar).

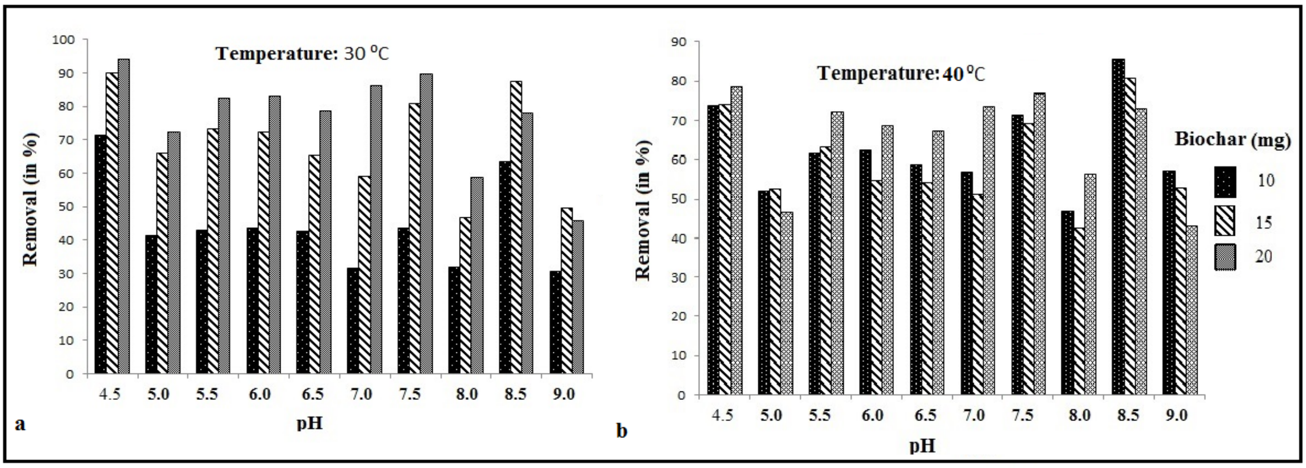

Figure 2: Histogram showing Chlorpyrifos (5 mg/mL) removal by different concentrations of biochar (10, 15 and 20 mg/mL) at different pH (4.5-9.0).

Based on the initial results, a final experiment was conducted using 10 mg/mL biochar and 5mg/mL Chlorpyrifos at 37ºC at different time frames at pH 7.5. Figure 3 shows the maximum uptake of Chlorpyrifos after 5 hours of the treatment period. This finding showed the potential use of biochar from food waste to remove pesticides. Tomczyk and coworkers (2020) reported the biochar physiochemical properties and applications. Xu and co-workers (2024) reported mechanism of adsorption of biochar for pesticide.

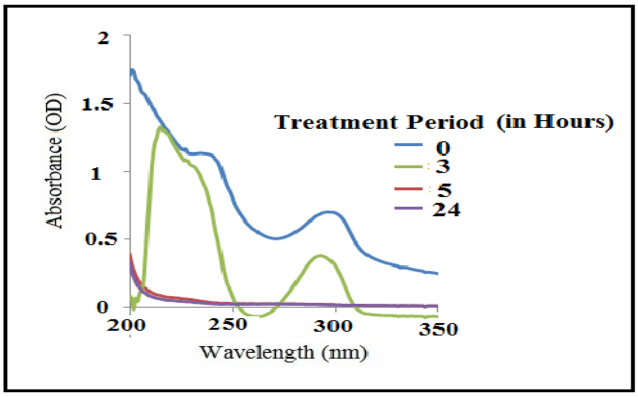

Figure 3: Spectra of Chlorpyrifos (5 mg/mL) in the presence and absence of the biochar (10 mg/mL) in buffer (PB, pH 7.5) for 12 da24 hours.

Impact of biochar to plant system

V. radiata was selected to assess the potential application of biochar mixed in soil to enhance pesticide removal and crop productivity. The experiment setup was established, as shown in Table 1 (materials and methods section). The random seedlings were selected, and morphological data were recorded from each set (Table 2). Figure 4 shows the comparison of the seedlings' growth with different treatments. Set 4, soil amended with biochar and seedlings sprayed with pesticide showed maximum growth, indicating a positive response of biochar in adsorbing pesticides and slowing microbial growth, which helped in pesticide mineralisation. This established no negative effect of the biochar on plant growth. The result also corroborates our previous report (Singh *et al.,* 2022). Similar works also been reported by authors showing biochar as soil fertility enhancer (Hong-Zhao *et al.,* 2019; Nepal;). This biochar can be formulated with nanoparticles and applied to the crop plants for better growth. Nanomaterials have potential in enhancing plant growth and fruiting (Tiwari, 2022).

Table 2: Measurement of morphological traits of *Vigna radiata* seedlings grown in pots for 10 days. The experimental sets represent 1, Control (only tap water), 2, Chlorpyrifos (5mg/mL), 3, Biochar (10mg/g soil) and 4, Biochar (10mg/g soil) and Chlorpyrifos (5mg/mL). Data represented here in Mean±STDEV

Set	Shoot length (cm)	Root length (cm)	No. of rootlets	Fresh weight (gm)	Dry weight (gm)
1	14.5±0.71	5.45±0.07	14.5±0.71	0.91±0.01	0.14±0.015
2	16.3±0.42	6.5±0.71	11.5±0.75	1.12±0.01	0.17±0.015
3	18.5±0.71	8.9±0.14	16.5±0.71	1.32±0.03	0.205±0.01
4	20.25±0.35	10.1±0.14	18.5±0.73	1.535±0.04	0.24±0.015

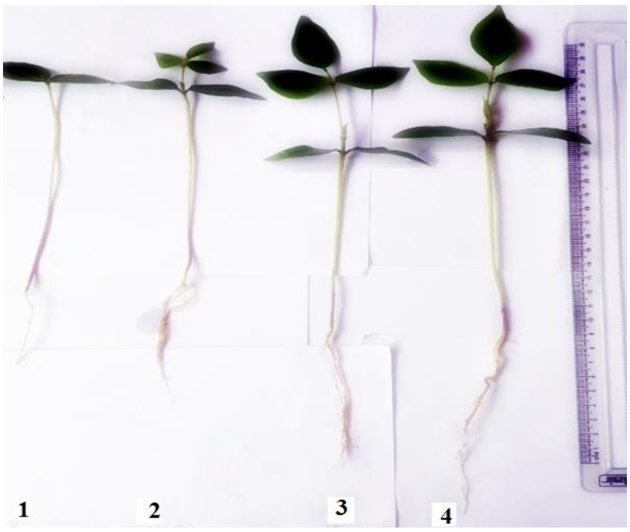

Figure 4 Morphology of *V. radiata* (moong bean) 10 days seedlings grown in the presence and absence of biochar-amended garden soil in pot culture

CONCLUSIONS

Pesticide use is an indispensable farming practice that decreases the loss in crop yields by avoiding the propagation of pests and pathogens, together with rodents. Due to the excess of these substances in the ecosystem, injuries occur to non-target organisms. Here, biochar made from the peel of potato has shown:

i., high efficacy in the removal of Chlorpyrifos from commercial pesticide formulations Noorani 505 (Anu product Pvt. Ltd).
ii., pH 4.5, the biochar activity was found to be maximum, followed by 7.5 and 8.5.
iii., biochar also enhanced moong bean plants when grown on soil amended with it. The nutrients in biochar are utilized during the growth period and do not cause any inhibitory effects.

CONFLICT OF INTERESTS

There is no conflict of interest among the authors.

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