RGU Journal of Social Science and Research, Vol. 1, Issue. 4 (2025)
(Special Issue on Sustainability and Social Entrepreneurship)
e-ISSN: 3049-3366
DOI: 10.3254/rgujssr.v1i3.86

Effectiveness of iron Nanoparticle-Functionalized biochar in the stabilization and breakdown of polycyclic aromatic hydrocarbons in contaminated soil: A comprehensive environmental and agronomic evaluation

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ARTICLE INFO

Keyword:
: Biochar, Nanoparticles, Polycyclic aromatic hydrocarbons, Rice cultivation, Soil remediation, Pyrolysis

ABSTRACT

Biochar (BC), a carbon-rich material generated from biomass pyrolysis, has gained significant attention for its capacity to immobilize and remove environmental pollutants. Although biochar interacts extensively with plant roots and rhizosphere microbes, limited information exists on its nanoscale modifications and their influence on contaminant bioavailability. Polycyclic aromatic hydrocarbons (PAHs) represent persistent soil pollutants that impair crop establishment and productivity. This study evaluates the efficiency of iron nanoparticle-coated biochar (Fe-BC) in stabilizing and degrading PAHs in soil and its subsequent effects on rice plant growth. Results demonstrate that Fe-BC effectively reduces PAH bioavailability and enhances early rice plant growth by mitigating toxicity and improving soil physicochemical conditions.

1. Introduction

Biochar, a highly porous carbon with numerous practical uses, is produced by pyrolyzing organic biomass.In order to produce biochar, organic biomass or agricultural leftovers must be heated to high temperatures in a low-oxygen atmosphere. This process turns the biomass into carbon-rich charcoal (Pandao et al.,2023).One popular method for producing biochar is thermochemical conversion. Pyrolysis, hydrothermal carbonization, gasification, and torrefaction are examples of thermochemical conversion processes (Yaashikaa et al.,2020).The physicochemical characteristics and structure of biochar, such as elemental components, pore structure, surface area, and functional groups, are influenced by the temperature during pyrolysis (Dhyani et al., 2018).Different characterization techniques, such as SEM for biochar morphology and FTIR for functional group determination, can be used to identify different biochar qualities (Braghiroli et al.,2019).Biochar has been made from a variety of agricultural leftovers, including corn cob, rice straw, wheat straw, waste wood, and sugar beet tailings. Cellulose, hemicellulose, and lignin make up the majority of these biomasses. In agricultural fields, biochar has also been used to remove soil contaminants (Yaashikaa et al.,2020).

Various hazardous pollutants, including heavy metals, organic contaminants, and excess nutrients, have unexpectedly been produced due to the quick expansion of agriculture and industry (Liu et al., 2020). In order to increase the adsorption capacity

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of biochar, different surface modifications have been reported. These include changing the surface charge of biochar with metal nanoparticles (Fe2O3, La2O3, Al2O3, ZnO, etc.), increasing the specific surface areas with activating agents (ZnCl2, H2SO4, and NaOH, etc.), and supporting the metal (oxides) (Fe°, Fe3O4, MgO, and CaO, etc.) that can react with pollutants(Ahmed et al., 2016; Sizmur et al., 2017; Oliveira et al., 2017; Saifullah et al., 2018; Wahi et al., 2017; Cha et al., 2016).During the composting process, inorganic additions can enhance the substrates' chemical and physical characteristics. Certain materials, such clays and nanoclays, have the ability to replicate the organo-mineral interactions that occur between soil clays and organic matter, preventing C mineralization and lowering CO2 emissions. (Sakiewicz et al. 2015; Chowdhury et al. 2016). The use of additives in composting mixtures has the potential to boost soil carbon stocks while also improving compost stability (Barthod et al., 2018; Medina et al., 2020). The chosen additives should either increase the pool of C with slow turnover or create organo-mineral interactions that shield C from decomposition by matching the natural interactions between SOM (Soil organic matter) and fine mineral particles in order to stabilize compost-derived C and increase its MRT (Mean residence times) in soils (Cotrufo et al. 2019).The half-life and mean residence time of organic matter in compost-amended soils under incubation conditions are doubled when biochar and nanoparticles are added to the compost. This might significantly boost the advantages of applying compost to soils since the beneficial, if short-term impacts on soil fertility and carbon storage could continue longer (Medina et al., 2025).Soil quality can be enhanced by adding biochar. Due to its strong adsorptive ability and potential to improve PAH (Polycyclic aromatic hydrocarbon) biodegradation through microbial stimulation, biochar has been used to remediate soils contaminated with PAHs (Bao et al., 2020).According to Han et al. (2017), the degradation of existing PAHs and the number of PAH degraders were greatly enhanced by the addition of agricultural wastes (wheat stalk, mushroom cultivation substrate waste, and cow dung). According to several research (Bengtsson and Zerhouni, 2010; Li et al., 2012; Feng et al., 2014; Koshlaf et al., 2019), appropriate carbon sources could encourage the biodegradation of PAHs in soils by introducing the co-metabolism substrates.Soil functional groups, pore size, pore structure, surface area, and chemical characteristics can all be changed by modified biochar (MB). By affecting the soil's physical and hydraulic characteristics, nutrient profile, gas exchange characteristics, organic matter content, pH, cation exchange capacity (CEC), and biological activities, such as those of bacteria, fungi, and enzymes, these modifications have a substantial impact on soil quality (Fakhar et al., 2025).

2. MATERIALS AND METHODS

2.1. Biochar preparation

Rice straw was used as a raw material for biochar synthesis.Rice straw was collected during the rice harvesting season in Assam. To eliminate any dust that had adhered, the collected straw was rinsed with tap water, excess water drained and was dried in an oven at 80oCfor 12 hours before grinding(Sornpitak&Worasuwannarak, 2019). The dried rice straw material was then placed in heat-resistant ceramic crucibles to produce an oxygen-limited environment during biocharformation before being transferred to a pyrolysis muffle furnace and heated at a temperature of 300°C to 700°C (Lehmann et al.,2009; Schmidt et al., 2015).This technique produced a highly carbonaceous solid residue, which was transformed into the desired end product, biochar.Rice straw-derived (RSD) biochar looks to be a potential way to solve the problem of reduced soil nutrients and carbon storage, as well as increased Green House Gases (GHGs) emissions related with rice straw application from rice paddies. To improve soil quality, RSD biochar produced at 400 °C may be a preferable solution (Wu et al., 2012).

2.2. Selection of Nano metals for the experiment

FeCl3 selected for the experiment.When heated to high temperatures, iron(III) chloride (FeCl3) is largely transformed into various iron

oxides (Fe2O3), (Fe3O4) through a thermal decomposition and oxidation process.A low dose of ZVI (Zero-valent iron) and Fe3O4 NPs boosted plant development in Fe-deficient conditions by reducing oxidative stress and regulating phytohormones in rice plants (Al-Amri et al.,2020).

2.3. Fenano metal particle added with Biochar

$FeCl_3$ was used to coat biochar by following the method of Ahuja et al. (2022). $FeCl_3$ loaded onto biochar at high temperatures, typically in the range of 700-800°C. This process is a method of creating modified biochar.

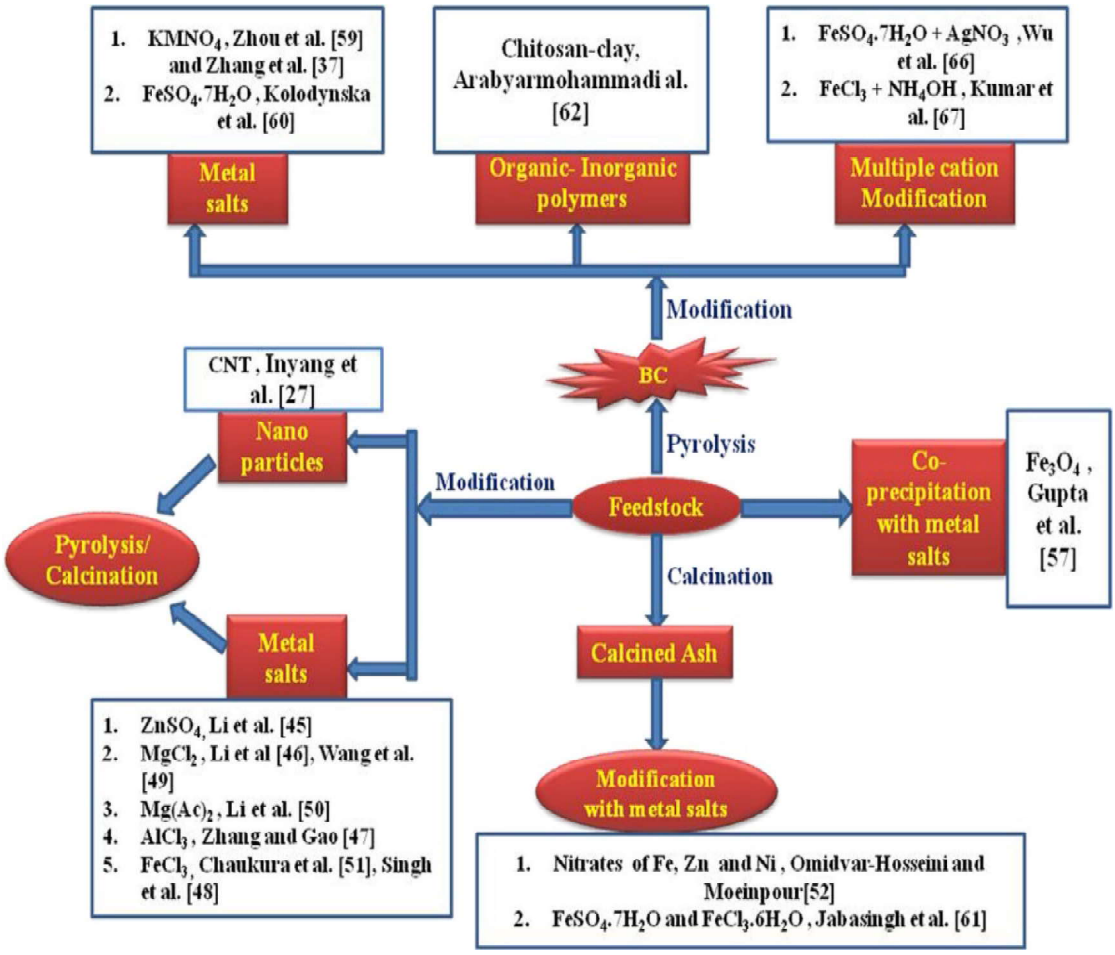


Figure: scheme of preparation of Metal salts/Biochar composite (Adapted from: Ahuja et al., 2012)

2.4. Physical and Chemical Characterization based on methods mentioned by Hadey et al., 2022

(i) Bulk and tapped Density; (ii) Compressibility index; (iii) Combustion indices; (iv) Proximate analysis to obtain the values of ash content; volatile matter (VM) and fixed carbon; (v) Elemental Analysis to determine the C, H, O, and S elemental composition of the feedstock and biochar will be determined following the ASTM E777, E778 standard method; (vi) Fourier Transform Infrared Spectroscopy (FTIR) to determine the functional groups; (vii) SEM/EDS to determine the surface Morphology; (viii) X-Ray Di:raction Analysis to identify the crystalline phases formed for the prepared biochars; (ix) Thermogravimetry (TG) analysis.

2.5. BiocharNano metal composite treatment and Rice plant growth analysis on Polycyclic aromatic hydrocarbon soil

This experiment consists of mainly two

treatments. T1: Growing rice plants without using fertilizer in PAH-contaminated soil, T2: Growing rice plants with Fe-coated biochar composite in PAH-contaminated soil. pH, water-holding capacity, and moisture content of the soil were examined before and after applying the biocharnanometal composite. Growth and density of the cultivation were checked for the effective result every week for two months.According to Kakar et al. (2019), plant height (PH) and tiller number (TN) was measured till the end of the experiment.

3. RESULTS AND DISCUSSION

SEM pictures at high magnification highlight the biochar's porosity, indicating the presence and type of macro- and micro-pores.Using a scanning electron microscope, we can observe the 3D surface of Biochar(Hardie et al, 2014). This is critical because the porous structure determines the biochar's surface area and ability to serve as a substrate for nanoparticles. FTIR & TGA is completed for the confirmation of biochar and metal nanoparticle coating.FTIR spectroscopy helps identify functional groups and structural changes in materials(Xu et al., 2014).

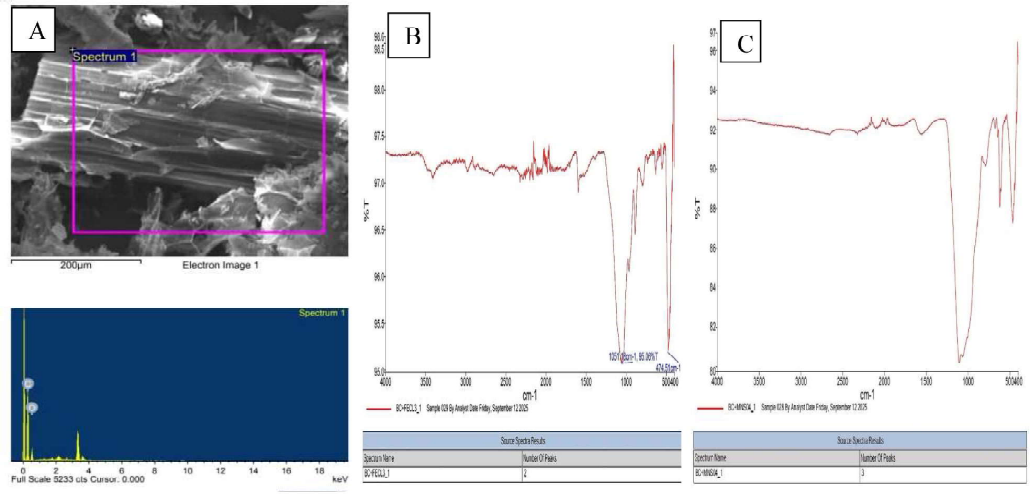


Fig: (A) SEM-EDX of Biochar, (B) FTIR result of Biochar+$FeCl_3$, (C) Fig: FTIR result of Biochar+$MnSO_4$

The untreated contaminated soil contains a high level of bioavailable Naphthalene, which directly inhibits germination and early growth, resulting in poor density and small size.

The Biochar-Fe treated soil successfully eliminated and decreased Naphthalene concentration from the soil solution, significantly lowering its toxicity. This low-stress environment, along with the potential nutrient benefits of Fe, allows the plants to produce healthy roots and shoots, resulting in increased growth and plant density after two weeks

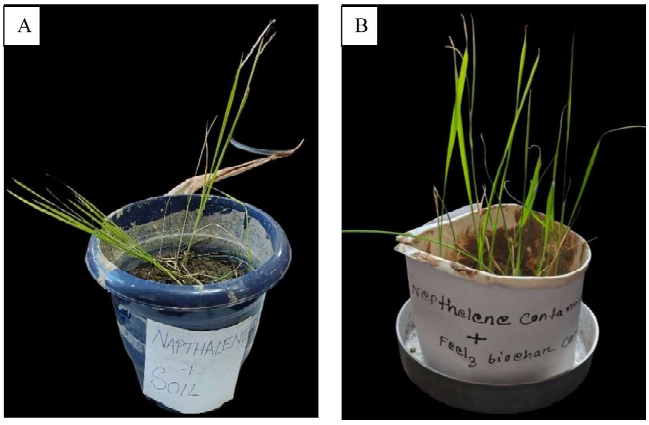


Fig: (A) Growth and density of Rice plant after two weeks in Naphthalene contaminated soil, (B)Growth and density of Rice plant after two weeks in Naphthalene contaminated soil+ Fe Biochar composite

CONCLUSION

Rice straw was pyrolyzed at high temperatures to produce biochar, a carbon-rich substance with a highly porous structure that is critical to its functionality. The Fe-BC composite was generated after being modified with FeCl3 at high temperatures. Comprehensive characterisation techniques were utilized to confirm the successful alteration and structure: Scanning Electron Microscopy (SEM) visually confirmed the biochar's porosity as well as the presence and distribution of the metal nanoparticle coating; Fourier-Transform Infrared Spectroscopy (FTIR) provided chemical evidence of the successful anchoring of Fe components through shifts and the appearance of characteristic Fe-O stretching vibrations; and Thermogravimetric Analysis (TGA) quantified the metallic load and assessed the composite's improved thermal stability. The main finding of the experiment was a significant difference in rice plant growth between the two treatments: the control group (T1), grown in Naphthalene-contaminated soil without treatment, had inhibited germination, low growth, and poor density due to the PAH contaminant's high bioavailability and toxicity. In contrast, the treatment group (T2) that got the Fe-BC composite experienced significantly higher growth and plant density after only two weeks. This observed increase is ascribed to the Fe-BC's dual action. First, the large surface area and porosity of the biochar, along with the Fe coating's enhanced adsorptive activity, efficiently immobilized and degraded the Naphthalene. This significantly lowered the quantity and bioavailability of the toxin in the soil solution, reducing phytotoxicity stress on immature rice plants. Second, the Iron component most likely provided vital micronutrient support or worked as a catalyst for the PAH's microbial or chemical breakdown, so contributing to a healthy growth environment. Thus, the study concludes that Fe-coated rice straw biochar is a highly effective, sustainable, and synergistic soil amendment that addresses both environmental contamination (PAH remediation) and agricultural productivity (early rice plant growth enhancement), making it a promising solution for managing contaminated agricultural lands.

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