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Remediation of Crude Oil Polluted Soil Using Biochar and Nanocomposites Prepared From Bread Fruit Seed Husk

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ABSTRACT: Crude oil contamination presents significant environmental challenges, particularly in soil fertility. This study investigates the use of breadfruit seed husk-derived biochar, combined with iron (FeNPs) and copper (CuNPs) nanoparticles, for degrading total petroleum hydrocarbons (TPH) in contaminated soils. FeNPs and CuNPs were synthesized and characterized using standard methods, including SEM, UV-Vis, and FTIR. The study examined the degradation of TPH in three soil samples (A, B, C) treated with biochar, FeNPs, and CuNPs, both individually and in combination. The FeNPs + Biochar combination achieved the highest TPH degradation (up to 89.03% in soil sample A), significantly outperforming CuNPs + Biochar and biochar alone. Results indicate that FeNPs, through redox reactions, are more effective in breaking down long-chain hydrocarbons than CuNPs, which show lower efficiency due to dependence on specific soil conditions. This study suggests that the combination of biochar and FeNPs offers a promising, eco-friendly approach for the remediation of crude oil-contaminated soils.

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Cleaning is a technique involving the use of organisms to eliminate, change or immobilize environmental contaminants. There are mainly two types of recognized kinds of remediation: in situ and ex situ remedies. Ex situ remediation techniques have the capability of only handling dirt when it has been removed from beneath the earth. The in situ treatment methods, on the other hand, are those that introduce the biological processes to the soil while at the same time leaving the ground intact. Past remediation methods have not been able to address the issue of pollution using heat, chemical, or physical cleaning techniques since the latter method only relocates the pollutants to a higher order-that of air pollution. Perhaps bioremediation technology, which degrades toxins, may replace it, as stated by Rahman *et al.* (2024) and Parul and Ahmed (2023), benefiting both the environment and creating an income generation activity.

During the past two decades, much global concern has been drawn to the pollution of the atmosphere by oil and petrochemical products throughout the world. Like most developing nations, Nigeria is suffering from severe environmental pain emanating from land pollution brought on by indiscriminate dumping of oil and products into the environment (Emoyan *et al.*, 2020; Nkwoada *et al.*, 2018; Udebuani *et al.*, 2011).

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Unfortunately, the conventional methods of removing these pollutants from the environment exacerbate the malaise of environmental pollution. The increasing numbers of chemical agents produced by man into the environment that can cause harm to plants and animals in both terrestrial and aquatic ecosystems; thus, protect the environment from industrial pollution, which constantly threatens both terrestrial and aquatic ecosystems. (Azorji *et al*., 2023; Nwachukwu *et al*., 2020).

Oil pollution-or land contamination by petroleum fuels-can take place when the production of oil is improper; their use was at fault, or when their disposal is inappropriate. Amongst all the organic compounds and waste products harmful to the environment, the oil pollution contains many varieties of organic chemicals. Two such are polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs). The ecosystem suffers much from these contaminated sources as they harm humans, animals, and surroundings. Once they are absorbed to the soil particles, the oil contamination can be persistent on the ground for quite a long time (Gennadiev *et al*., 2015). The removal of such type of contaminants cannot be easily performed because some of the oil mixtures contain a large number of various components, biodegradation of the compounds does not take place at high speed, and some of the chemicals are slightly soluble in soil. Moreover, they are also considered to be a constant source of soil pollution because they drain from the ground, which may be a negative impact on the nearby cities. Some of the most common methods of removal include: booming and skimming, hand removal, mechanical removal, water cleaning, sediment shifting and tilling and soil washing, vapour extraction, encapsulating and other physical methods. Unfortunately, some of these technologies are expensive, pollute the environment, and do not fully clean the area, thus aggravating the problem. Consequently, the objective of this study is to investigate the potential of breadfruit seed husk-derived biochar, combined with iron nanoparticles (FeNPs) and copper nanoparticles (CuNPs) for degradation of total petroleum hydrocarbons (TPH) in oil-contaminated soils

MATERIALS AND METHODS

The husk of breadfruit seeds was collected from the local market at Ideato North L.G.A., Imo State. The collected sample was sundried, cleaned with distilled water, and then crushed using a grinding machine. The soil samples were collected within Ogba town in ONELGA, part of Rivers State. Major concentrations of the sample were obtained from three oil field sites operated by SHELL (sample A), TOTAL (sample B), and AGIP (sample C). The samples were carefully obtained using a shovel at a depth of four feet.

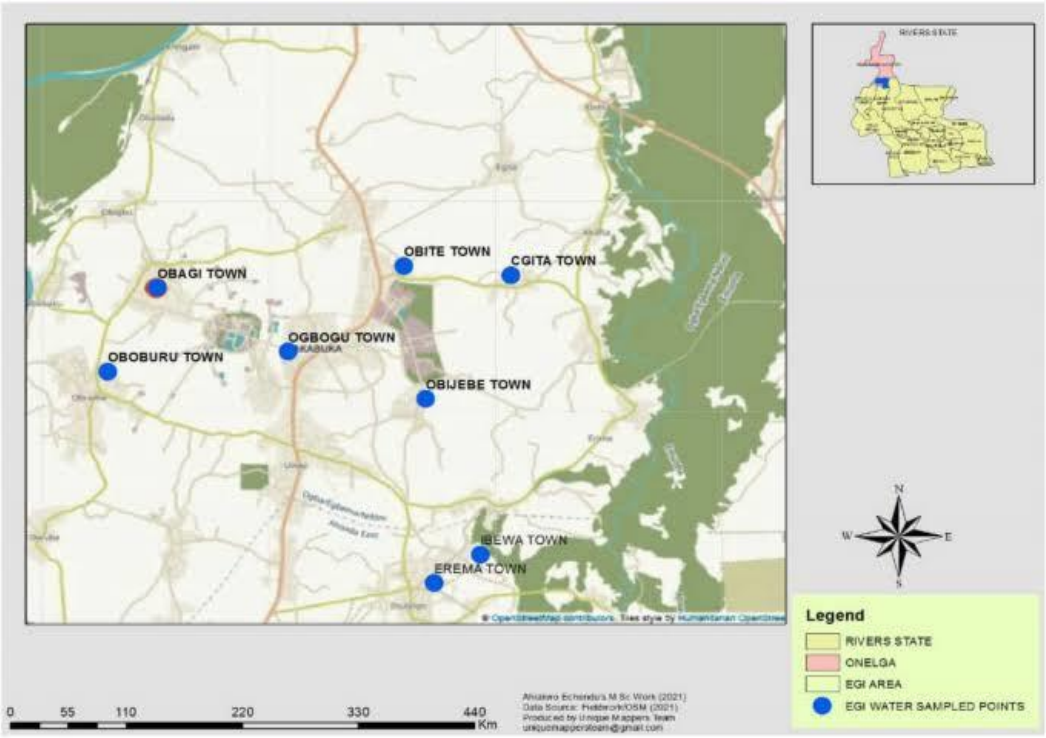

Fig 1: Map of Obagi, Rivers State Showing the Soil Sample Site.

Biochar Conversion: After approximately thirty-five minutes at 150°C in the furnace, the ground biomass was allowed to cool and stored. The carbonized product was then filtered using an industrial sieve with a mesh size of 0.5 mm.

Plant Extraction: A sample of 100 g of breadfruit seed husk was pulverized into fine powder and mixed with 200 mL of ethanol in a conical flask. The process used maceration, with the mixture being soaked for 40-48 hours. Filtration was carried out using filter paper, and the resulting solution was evaporated on a water bath at 78°C until dry. The extracts obtained were kept in a refrigerator at 4°C.

Nanoparticle Synthesis: 2.54 g of $FeCl_2$ was weighed and dissolved in 100 mL of distilled water to create a 0.02 M $FeCl_2$ solution. Similarly, 3.76 g of $CuNO_3$ was weighed and dissolved in 100 mL of distilled water to produce a 0.02 M $CuNO_3$ solution. To stabilize the nanoparticles, 2.5 g of plant extract was dissolved in 200 mL of distilled water and mixed with the nanoparticles at a 0.02 M concentration. The solutions were heated to 90°C until a color change was observed. The resulting solution was filtered through filter paper and then dried in an oven.

UV-Vis Spectroscopic Analysis: UV-Vis spectrophotometric analysis of the synthesized biochar and nanoparticles was performed using an Apel PD30000uV spectrophotometer (2-nm slit width, 10-mm cell) at room temperature. A portion of 0.1 g of the material was dissolved in 10 mL of ethanol. The filtrate was analyzed between 190–800 nm wavelengths.

Fourier Transform Infra-Red Analysis: 0.1 g of the sample was mixed with 0.5 g of potassium bromide and 1 mL of Nujol (a solvent used for sample preparation). The paste was placed in a sample mold for scanning between 600–4000 cm^{-1} using a Buck 530 IR-spectrophotometer.

Scanning Electron Microscopy: A sample of 0.1 g was sprayed with double adhesive on a sample stub coated with 5 nm of gold using a sputter coater (Quorum Technologies, Model Q150R). The sample was examined under SEM, where morphologies of various magnitudes were captured. The sample was then placed in the SEM-EDX machine for minor adjustments.

Particle Size Analysis: Nanoparticle concentration was adjusted to 0.1 mg/mL and filtered through a 0.22 µm syringe filter. Particle size distribution was measured using a Zetasizer Nano (Malvern Instruments, Model ZS-N90) with a sample temperature of 25°C. The system was calibrated using a reference sample, and three successive runs were performed for reproducibility. The average particle size (Z-average) and polydispersity index (PDI) were recorded.

Impregnation of Nanoparticles and Biochar: 2 g each of CuNPs and FeNPs were dissolved in 200 mL of filtered water, and 20 g of biochar was added to the solution. The mixture was left to soak for 24 hours. After filtration and drying in an oven at 80°C, 10 g of dried biochar nanoparticles was added to 50 g of polluted soil and mixed thoroughly.

Total Petroleum Hydrocarbon Analysis: The soil samples were treated with 30 mL of dichloromethane (DCM) as an extracting solvent. The samples were shaken for 20 minutes and allowed to settle for 1 hour. The filtrate was concentrated to 1 mL using evaporation and then analyzed using GC/FID.

Soxhlet Extraction of oil from the soil samples: A 250 mL round-bottom boiling flask was filled with 100 mL of n-hexane. 10 g of soil was placed into the Soxhlet thimble with cotton wool placed beneath it. The device was heated at 60–75°C, and the solvent was refluxed 4–5 times. The oil was separated from the solvent by rotary evaporation at 40–60°C.

Quantification with GC-FID: TPH analysis was performed on a Bucked M910 gas chromatograph interfaced with a flame ionization detector (FID). The analysis used a 15 m RESTEK MXT-1 capillary column with a 250 µm diameter and 0.15 µm film thickness. The injector temperature was maintained at 280°C, and the splitless injection method was used with a sample size of 2 µL. The temperature program was set to increase from 200°C to 330°C at a rate of 30°C/min, with the final temperature held for 5 minutes. Helium was used as the carrier gas at a flow rate of 40 mL/min. TPH concentrations were expressed in µg/mL.

RESULTS AND DISCUSSION

The first step of the study involved synthesizing FeNPs and CuNPs using a breadfruit seed husk extract as a reducing agent. The SEM images in Fig. 2 reveal that both FeNPs and CuNPs have spherical shapes with diameters ranging from 60 nm to 100 nm. These observations are consistent with the work of Amin *et al.* (2022), who also reported similar nanoparticle shapes synthesized from plant-based materials. The spherical shape of nanoparticles is ideal for their interaction with soil particles and

pollutants, as it enhances their surface area and reactivity.

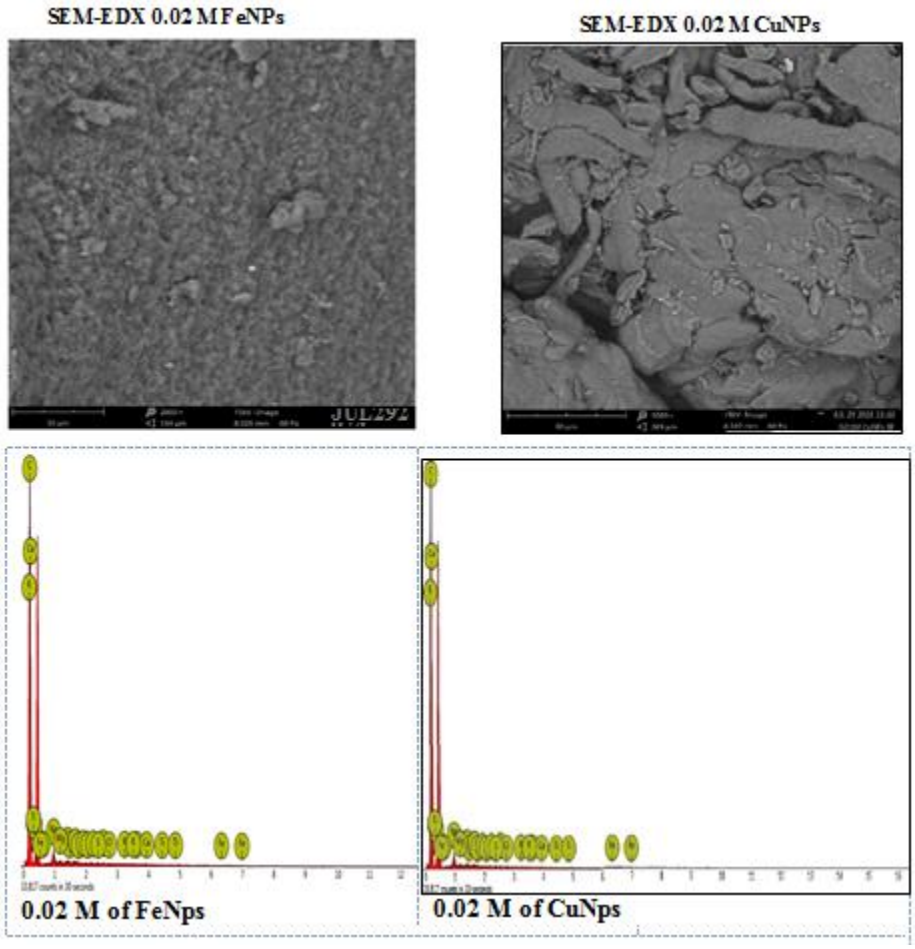

Fig 2: SEM Results of the Synthesized Iron and Copper Nanoparticles

The SEM images indicate significant electrostatic interactions and hydrogen bonding between the plant extract and the metal ions, facilitating the formation of nanoparticles. This suggests that the breadfruit seed husk extract played a vital role in stabilizing the nanoparticles, ensuring that they maintained their intended structure and size. In addition to SEM analysis, UV-Vis spectroscopy was employed to further characterize the synthesized nanoparticles.

The UV-Vis spectrum for FeNPs (Fig. 3) shows an absorption peak around 450 nm, which is characteristic of FeNPs and indicates the successful reduction of Fe^{2+} ions into nanoparticles. This is consistent with other studies, such as that by Kiranmai *et al*. (2017), who observed similar absorption peaks in the UV range for iron nanoparticles synthesized using plant extracts. The maximum absorbance for CuNPs, as shown in Fig. 4, was observed at 250 nm, further supporting the successful synthesis of CuNPs.

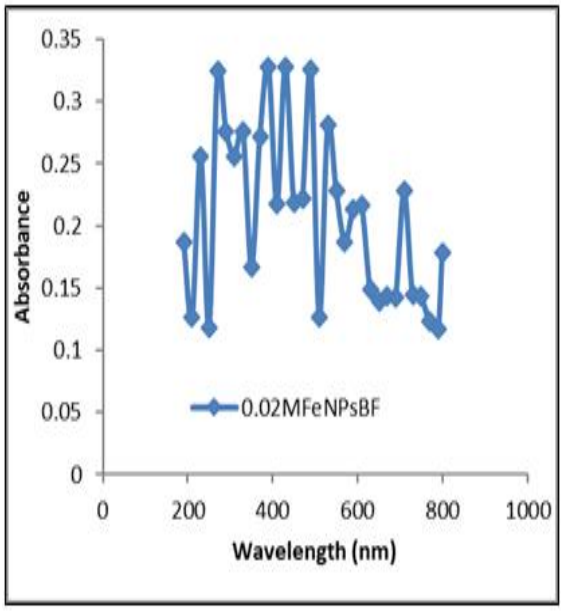

Fig 3: UV-Visible spectrum of FeNPs at 0.02M

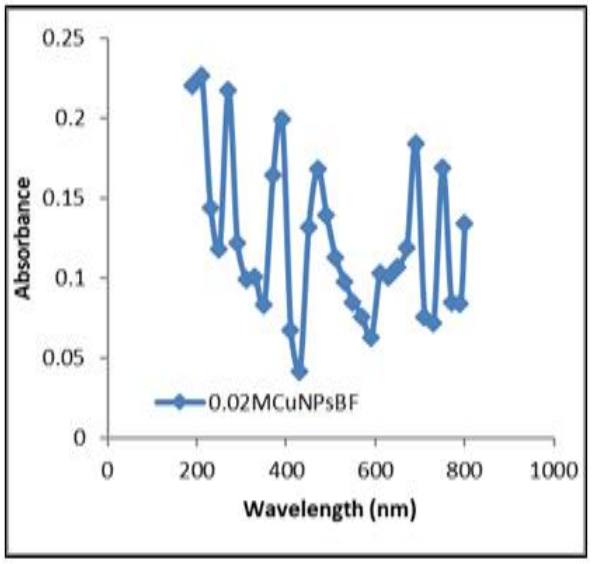

Fig 4: UV-Visible Spectrum CuNPs at 0.02M

This result aligns with previous findings by *Kiranmai et al.* (2017), where absorption peaks were observed at around 270 nm for copper nanoparticles. The differences in absorption peaks between FeNPs and CuNPs suggest that the two nanoparticles may have slightly different properties in terms of their interaction with light, which could influence their reactivity during the hydrocarbon degradation process. FTIR analysis (Fig. 5 and Fig. 6) revealed the presence of polyphenols in the breadfruit husk extract, which acted as reducing and capping agents for the nanoparticles. This confirmed the expected bioactive compounds involved in nanoparticle stabilization, as also noted by Koyyati *et al.* (2016).

Fourier Transform Infrared (FTIR) spectroscopy was used to analyze the functional groups present on the surface of the nanoparticles. The FTIR spectra for FeNPs and CuNPs, shown in Fig. 5 and Fig. 6, reveal the presence of polyphenols and other bioactive compounds from the breadfruit seed husk extract. These compounds likely play a role in capping and stabilizing the nanoparticles. The peaks observed at specific wavelengths indicate the presence of functional groups that are capable of interacting with organic pollutants, further enhancing the nanoparticles' potential for soil remediation. Particle size is a critical factor affecting the reactivity and effectiveness of nanoparticles in environmental applications. The particle size distribution of both FeNPs and CuNPs was determined using a Zetasizer. Table 1 summarizes the particle size analysis (PSA) results. FeNPs had an average particle size of 10.30 nm, while CuNPs had a larger size of 14.30 nm. The polydispersity index (PDI) for both nanoparticles was moderate, indicating a relatively uniform particle size distribution. The smaller size of FeNPs suggests that they may have a larger surface area, which could explain their higher reactivity in hydrocarbon degradation processes.

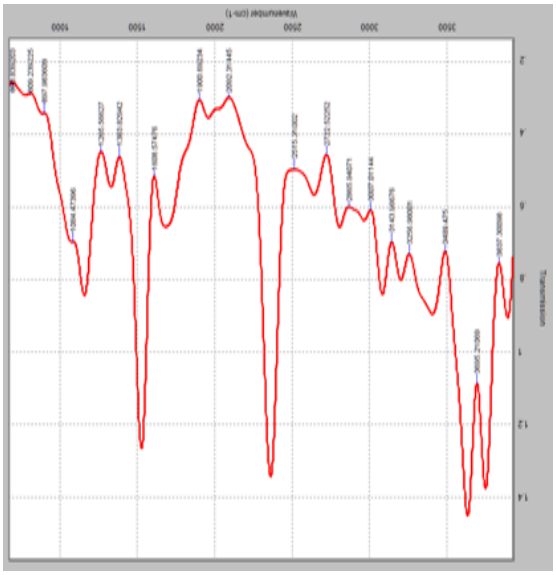

Fig. 5: FTIR analysis of FeNPS

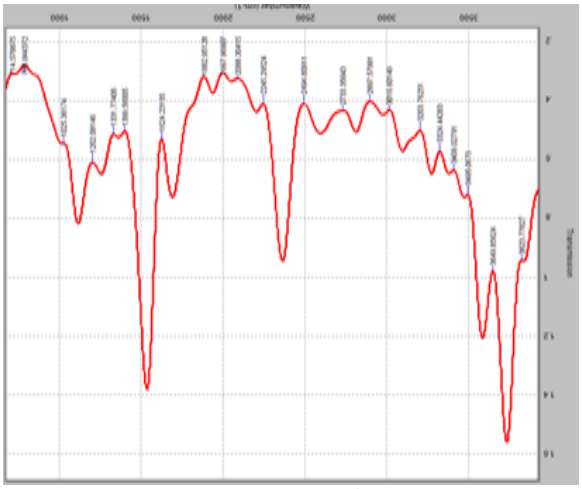

Fig. 6: FTIR analysis of CuNPS

Table 1: Particle size area of FeNps and CuNps

Nanoparticles	PSA (nm)	Polydisperity Index	Length Unit
0.02 M FeNps	10.30	0.628	DV (10.3)
0.02 M CuNps	14.30	0.686	DV (10.3)

The degradation of TPH in soil samples treated with biochar, FeNPs, CuNPs, and combinations of these materials was monitored over a two-week period. Table 2, Table 3, and Table 4 show the TPH degradation trends for soil samples from three different sites (SHELL, TOTAL, and AGIP), treated with biochar, FeNPs + biochar, and CuNPs + biochar. In soil sample A (SHELL), the FeNPs + biochar combination showed the highest TPH degradation,

with a 89.03% reduction (Table 2). This result is significantly higher than the 52.11% degradation observed with CuNPs + biochar, and the 30.38% degradation seen with biochar alone. This demonstrates that FeNPs, when combined with biochar, are highly effective at breaking down petroleum hydrocarbons in contaminated soils.

Table 2: TPH degradation trend in soil sample A (SHELL) within 2 weeks

COMP.	Soil Sample A Initial	Sample A +Biochar (mg/kg)	% Reduction	Sample A + CuNPs +Biochar (mg/kg)	% Reduction	SampleA +FeNPs +Biochar (mg/kg)	% Reduction
C9	3.9520	22.9920	20.88	14.8454	66.94	2.4555	87.11
C12	18.2443	17.8975	40.68	13.4406	80.39	10.7755	100.00
C13	17.2843	10.5730	29.20	15.3607	54.66	14.2879	82.18
C14	21.2587	15.3607	20.21	12.7660	52.48	1.9205	100.00
C18	5.1232	13.8463	27.60	24.8854	74.02	2.0308	77.88
C19	7.0454	25.1232	40.63	12.0886	83.69	12.9609	94.53
C22	33.2479	8.1569	25.54	10.6633	42.79	1.1766	100.12
C25	3.9470	12.8852	21.27	17.0443	54.38	18.2433	75.85
C30	32.7518	11.4521	45.58	0.8491	39.78	1.0676	92.09
C32	19.2832	10.9649	32.24	10.5243	76.30	8.6431	80.54
TOTAL	162.1464	139.2518	30.38	132.4677	52.11	73.5873	89.03

In soil sample B (TOTAL), the degradation efficiency was lower compared to soil sample A, with FeNPs + biochar achieving 78.86% degradation (Table 3), while CuNPs + biochar achieved 44.93% and biochar alone achieved 22.00%. These findings suggest that while FeNPs continue to perform well in hydrocarbon degradation, the composition of the soil, including factors like organic content and microbial activity, may influence the overall efficiency.

Table 3: TPH degradation trend in soil sample B (TOTAL) within 2 weeks

COMP.	Soil sample B Initial	Sample B + Biochar (mg/kg)	% Reduction	Sample B + CuNPs +Biochar (mg/kg)	% Reduction	Sample B + FeNPs + Biochar (mg/kg)	% Reduction
C10	2.9910	6.9366	29.84	5.1191	51.76	3.8433	73.61
C11	18.4576	13.6576	41.77	10.8808	30.00	3.8400	69.92
C12	21.1111	8.6443	14.47	7.2521	29.28	8.7510	82.56
C18	8.6309	10.9227	60.93	8.6452	42.00	8.0043	100.00
C21	12.4886	10.9888	34.36	8.8525	29.30	17.3910	73.60
C19	4.9120	9.6043	65.93	9.6043	60.00	10.5706	79.88
C27	6.8265	5.0176	26.79	4.0580	70.43	1.9243	84.29
C28	20.1686	5.9726	13.94	3.0925	31.81	16.3137	67.44
C33	29.7604	13.7632	24.64	8.7489	59.45	18.2433	88.79
C35	14.4012	28.0525	21.48	23.0441	48.38	12.3700	60.00
C37	2.9931	18.3456	10.00	11.3054	38.00	3.8433	84.15
C10	14.4020	4.9120	20.05	1.9233	48.84	3.8400	70.07
TOTAL	180.1853	136.817	22.00	102.5262	44.937	108.9348	78.86

Table 4: TPH degradation trend in Sample C (AGIP) within 2 weeks

COMP.	Soil Sample C nitial	Sample C +Biochar (mg/kg)	% Reduction	Sample C +CuNPs +Biochar (mg/kg)	% Reduction	Sample C +FeNPs +Biochar (mg/kg)	% Reduction
C10	12.8011	5.8699	26.94	1.9233	36.13	1.9212	22.58
C11	11.9254	3.9520	24.23	2.9920	16.32	7.6822	42.18
C12	26.1321	12.488	9.88	6.7233	39.85	4.9078	66.13
C15	18.2441	8.0043	2.56	7.6747	7.20	6.7521	99.68
C18	18.9857	21.1112	33.15	14.4041	11.33	5.7814	57.88
C21	12.9055	10.5706	13.45	8.9580	26.14	7.8927	87.50
C19	8.9588	3.9550	8.83	1.3878	46.23	2.0678	36.95
C27	11.3195	13.4494	9.84	15.2481	22.40	13.5478	39.36
C28	7.8976	20.2558	11.70	16.3203	14.45	18.2827	48.71
C33	33.0646	13.5520	3.27	10.2356	61.04	7.2555	73.09
C35	28.0525	2.8812	18.88	8.9499	56.19	1.9212	95.85
TOTAL	**195.4208**	**116.0894**	14.79	**94.8171**	30.67	**78.0124**	61.00

Finally, in soil sample C (AGIP), FeNPs + biochar still performed the best, with a 61.00% TPH reduction (Table 4), while CuNPs + biochar resulted in a 30.67% reduction and biochar alone achieved only a 14.79% reduction. These results indicate that the addition of FeNPs continues to provide a significant catalytic effect, particularly in degrading long-chain hydrocarbons. The higher reactivity of FeNPs in redox reactions likely contributes to their superior performance compared to CuNPs, which is consistent with previous studies that highlighted the efficiency of FeNPs in degrading more recalcitrant hydrocarbon fractions.

Conclusion: The breadfruit seed husk extract proved to be an excellent reductant for synthesizing copper (CuNPs) and iron (FeNPs) nanoparticles in a rapid, cost-effective, and environmentally friendly manner. The functional groups in the seed husk extract facilitated the reduction of metal ions into nanoparticles, which were characterized using UV-Vis spectroscopy, FTIR, SEM, and particle size analysis. The incorporation of CuNPs and FeNPs into biochar significantly enhanced hydrocarbon degradation, with FeNPs demonstrating higher efficiency in degrading total petroleum hydrocarbons (TPH) in contaminated soils. The study indicates that biochar, when combined with nanoparticles, promotes microbial and enzymatic activity, accelerating the cleanup of oil-polluted soils. Given its affordability and effectiveness, this approach holds great promise for large-scale remediation projects, particularly in agricultural areas affected by crude oil contamination.

Declaration of Conflict of Interest: The authors declare no conflict of interest

Data Availability Statement: Data are available upon request from the first author

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