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Removal Potentials of Heavy Metals by Cassava Peels, Parts of Pawpaw Plant, Coconut Husk, Guinea Corn Chaff, and Pineapple Peels from Bonny Light Crude Oil Polluted Soil

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ABSTRACT: Removal of environmental contamination such as heavy metals in soil, water and environment is of great importance for human welfare. Hence, the objective of this paper is to comparatively evaluate the removal potentials of heavy metals by cassava peels, parts of pawpaw plant, coconut husk, guinea corn chaff, and pineapple peels from bonny light crude oil polluted soil using appropriate standard methods. Results obtained indicated significantly high levels of heavy metals in the untreated crude oil contaminated soil at weeks 1, 8 and 12. There was a significant ($P<0.05$) decreasing trend in heavy metal levels in the contaminated soil after treatment with the various agro-residues after the 12-week period. The highest reduction of the heavy metals was observed in the test Group treated with a combination of the agro-residues under study; Ni (46.8%), Pb (61%), Cr (46.3%), Cd (34.1%) and As (49.8%) reduction. The results showed that the agro-residues under study can effectively enhance microbial removal of heavy metals in crude oil polluted soil.

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Industrialization and extraction of natural resources has led to environmental degradation in terms of industrial pollution. With industries operating, a 100 per cent pollution-free environment is a myth; it is neither possible nor necessary. There has been a considerable increase in the discharge of industrial waste to the environment, mainly soil and water, which has led to the accumulation of heavy metals. Consequently, contamination of soil, groundwater, sediments, surface water and air with hazardous heavy metals and toxic chemicals is one of the major threats facing the world, as they cannot be broken down to non-toxic forms and therefore have long-lasting effects on the ecosystem (Lahiry, 2017; Girma, 2015). After crude oil spills, heavy metals are bound to soil with large chain hydrocarbon compounds after volatile constituents of the oil have vaporized into the atmosphere (Ekperusi *et al.*, 2016). Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu),

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mercury (Hg), and nickel (Ni) (GWRTAC, 1997). Soils are the major sink for heavy metals released into the environment by various anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova *et al.,* 2006) and their total concentration in soils persists for a long time after their introduction (Adriano, 2003). Changes in their chemical forms (speciation) and bioavailability are, however, possible. Maslin and Maier (2000) noted that the presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity and land tenure problems (Ling *et al*., 2007; McLaughlin *et al*., 2000(a); McLaughlin *et al*., 2000(b)). In the remediation of contaminated soil, much attention is given to the petroleum hydrocarbons and other related compounds while less or none is given to the associated heavy metals in such contaminated environment. Heavy metals due to their non-biodegradable nature can remain bound in soil for a long time, can bioaccumulate into soil biota, leached into underground water and pose a considerable threat to the environment, biodiversity and public health (Ekperusi *et al*., 2016; Ekperusi and Aigbodion, 2015). Bioremediation is an innovative and promising technology available for removal of heavy metals and recovery of the heavy metals in polluted water and lands. Since microorganisms have developed various strategies for their survival in heavy metal-polluted habitats, these organisms are known to develop and adopt different detoxifying mechanisms such as biosorption, bioaccumulation, biotransformation and bio mineralization, which can be exploited for bioremediation either ex situ or in situ (Lin and Lin, 2005; Malik, 2004; Lim *et al*., 2003; Gadd, 2000). Microorganisms take up heavy metals actively (bioaccumulation) and/or passively (adsorption) (Hussein *et al*., 2001). The microbial cell walls, which mainly consist of polysaccharides, lipids and proteins, offer many functional groups that can bind heavy metal ions, and these include carboxylate, hydroxyl, amino and phosphate groups (Scott and Karanjkar, 1992). The control for bioremediation processes is a complex system of many factors that permit optimal microbial growth and activity. These factors include the existence of a microbial population capable of degrading the pollutants, the availability of contaminants to the microbial population, the environment factors (type of soil, temperature, pH, the presence of oxygen and nutrients) (Barh *et al.*, 2015; Naik and Duraphe, 2012). Bioremediation efficiency depends on manipulation of environmental conditions to enhance microbial growth and faster degradation. Nowadays, relative new technologies are present which increase the bioremediation process faster and more fruitful in short time period. Such technologies act on either on three components of bioremediation (microorganisms, pollutants or environment) which are important for this process to occur (Barh *et al.,* 2015). Organic nitrogen-rich nutrients (biostimulation) are an effective means to enhance the bioremediation process and widely available as wastes in the environment; hence, they can serve as "natural waste-to-environmental clean-up. (Bhakta, 2017). Assessment of the levels of heavy metals in crude oil polluted environment before and after engineered remediation is vital in order for environmental managers and scientist to device appropriate protocol for a comprehensive remediation in hydrocarbon polluted soil. This study exploits the potentials for use agro-residues such pawpaw parts (leaves, fruit and root), guinea corn chaff, pineapple peels, coconut husk and cassava peels to enhance removal of heavy metals in crude oil contaminated soils.

Hence, the objective of this paper is to comparatively evaluate the removal potentials of Heavy metals by Cassava peels, parts of pawpaw plant, Coconut husk, Guinea corn chaff, and pineapple peels from Bonny Light Crude Oil Polluted Soil

MATERIALS AND METHODS

Agricultural soil: Agricultural soil used in this study was collected from the Agricultural Garden of the Faculty of Agriculture, University of Port Harcourt. Analysis of the fresh test soil collected showed the following properties: sand – 70%, clay – 9%, silt – 21%, Total Organic Carbon – 3.77g/kg, pH 7.9 and Total Hydrocarbon Content – 122mg/kg. The soil sample was air dried for 7 days and passed through 1.7mm sieve.

Crude oil polluted soil: Bonny light crude oil was used to contaminate 7kg of soil sample to achieve 10% pollution level. The contaminated soil sample was allowed to stay for one week for micro-organisms to acclimatize before application of amendments. Soil remediation lasted for 12 weeks. Mixing and watering of soil was carried out every three days.

Preparation of the Agro wastes: Agro-residues were obtained from various locations: Cassava peels and different parts of pawpaw plant were obtained from

Alakahia in Port Harcourt, Rivers State, Nigeria; Coconut husk was obtained from Rumokoro market in Port Harcourt, Rivers State, Nigeria; Guinea corn chaff and pineapple peels were obtained from Choba market in Obio/Akpor Local Government Area of Rivers State, Nigeria. Agro-residues collected were air dried and later milled into particulates using corn mill Px 2200 China. Coconut husk used was sun dried, cut into bits, and mashed with mortar and pestle to soften them and later ground into particulates. The ground sample was passed through a 2mm sieve.

Preparation of Soil samples and Identification of Heavy Metals: Soil sample was sieved using a 1.7mm sieve and heated in a furnace at 400 °C for 2 h to remove organic matters. The soil sample (1 g) was partially digested with HNO_3–HCl for 2 h at 90 °C and afterward, diluted to 100 mL with de-ionized water, left for 3 h, and then filtered. A flame Atomic Absorption Spectrophotometer (AAS) (UNICAM model) was used to carry out heavy metal analysis as described by Miroslav and Vladimir, (1999). Heavy metals namely Cadmium (Cd), Chromium (Cr), Arsenic (As), Nickel (Ni) and Lead (Pb) were determined.

Experimental Design: The various groups involved in the study are defined as in Table 1.

Table 1. Experimental Groups in the study

Group	Soil quantity & status	Amendment received
CGR1	1kg unpolluted soil	No treatment
CGR2	1kg polluted soil	No treatment
PGR3	1kg polluted soil	0.1kg of prepared cassava peels.
PGR4	1kg polluted soil	0.1kg of prepared coconut husk
PGR5	1kg polluted soil	0.1kg of prepared guinea corn chaff
PGR6	1kg polluted soil	0.1kg of prepared pawpaw substrate
PGR7	1kg polluted soil	0.1kg of prepared pineapple peels
PGR8	1kg polluted soil	0.02kg each of plant materials (cassava peels, coconut husk, guinea corn chaff, pawpaw substrate, pineapple peels)

Statistical analysis of data: All values were expressed as mean ± SD and then subjected to analysis of variance (ANOVA) using the Statistical Package for Social Sciences (SPSS) version 17.0 (SPSS Inc., Chicago Illinois). Statistical significance was considered at P=0.05.

RESULTS AND DISCUSSION

Effects of the various amendments on heavy metal levels in the test soils are shown in Figure 1. Results for Ni, Pb, Cr and Cd in the control and treated soils are shown in Figures 1 - 10. Results for week 8 and week 12 showed significant reduction in Nickel levels; the soil sample treated with a combination of agro-residues showed more significant reduction when compared to the untreated samples. Figure 2 shows the percentage reduction in Nickel at weeks 8 and 12. No Significant ($p \geq 0.05$) reduction in the Lead (Cr), (Cd) and Arsenic (As) concentrations was recorded for the treated polluted soil samples at week 1. However, week 8 and week 12 showed significant reduction in the concentrations of these heavy metals in the soil samples. Arsenic (As) concentration in the treated and untreated soil samples is shown in Fig 5. The results show that there was no significant ($p \geq 0.05$) reduction in the Arsenic (As) concentrations in all the treated polluted soil samples compared to the untreated at week 1. Interestingly however, week 8 recorded significant reduction in the Arsenic (As) concentrations in the soil samples treated with Guinea corn chaff (4.01 mg/kg), Pawpaw parts (4.12 mg/kg), Pineapple peels (4.00 mg/kg) and combined (3.87 mg/kg), indicating further reduction when compared to the untreated samples (6.18 mg/kg). Figure 10 shows the percentage reduction in Arsenic in the treated soil samples at week 8 and week 12. A comprehensive analysis of published data indicates that heavy metals such as arsenic, cadmium, chromium, lead, and mercury, occur naturally and contribute significantly to environmental contamination through anthropogenic activities (He *et al.,* 2005). Crude oil spillage is one of the ways elevated concentrations of heavy metals are introduced into the soil (Osuji and Onojake, 2004). This corroborates the elevated heavy metal levels observed in crude oil polluted soil in the present study. There was a significant increase in heavy metals (As, Cd, Cr, Pb and Ni) at weeks 1, 8 and 12 as compared with the control group (unpolluted sample). Also, this is in agreement with findings by Krishna and Govil (2004) that crude oil pollution of soils result in increased levels of heavy metals. Previous reports had pointed out that these toxic elements may interfere metabolically with nutritionally essential metals such as iron, calcium, copper, and zinc, when these elements find their way to the human body (Abdulla and Chmielnicka, 1990; Wang and Fowler, 2008). The level heavy metals in the test soil and the percentage reduction over the experimental period is shown in Fig 1 – 10. Soil heavy metal content decreased from week

1 to week 12 in the treated crude oil polluted soil. Polluted soil treated with a combination of the various agro-residues in this study recorded the highest reduction in heavy metal levels; Ni had a percentage reduction of 46.8%, Pb (61%, reduction), Cr (46.3% reduction), Cd (4.1% reduction) and As (49.8% reduction) when compared with the polluted but not treated soil samples.

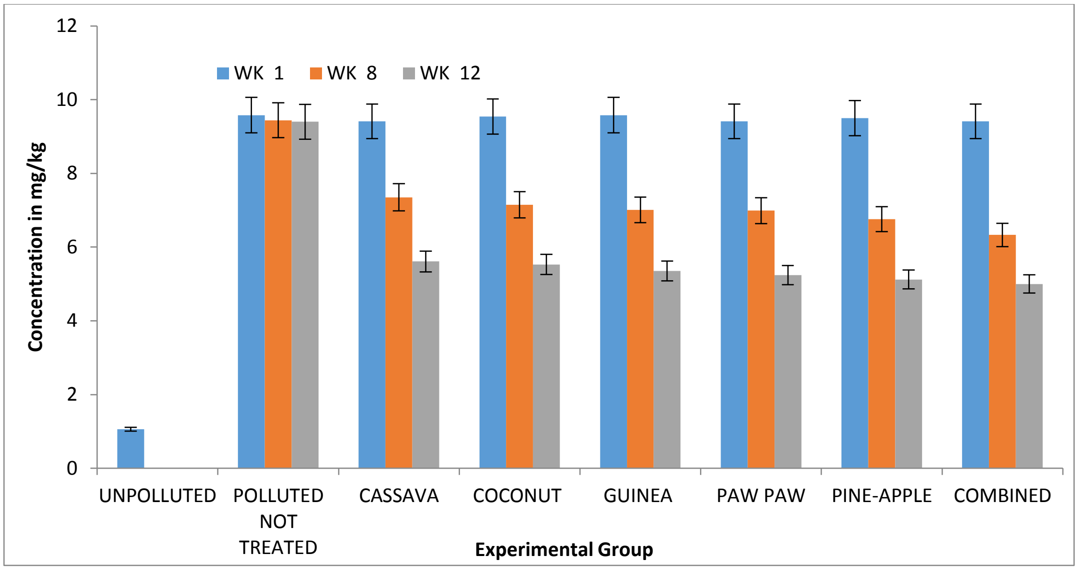

Fig 1. Standard Error Bar showing Nickel (Ni) in treated and untreated crude oil polluted soil

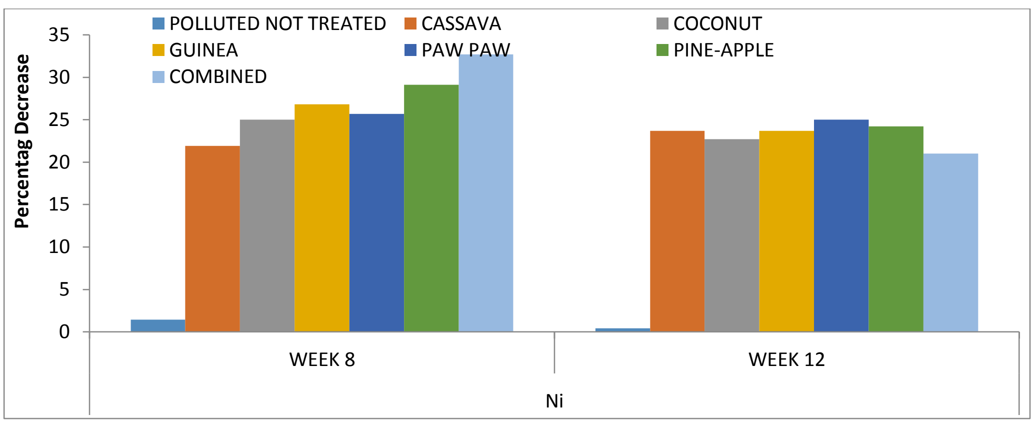

Fig 2. Percent Reduction in Nickel (Ni) - Treated and untreated crude oil polluted soil

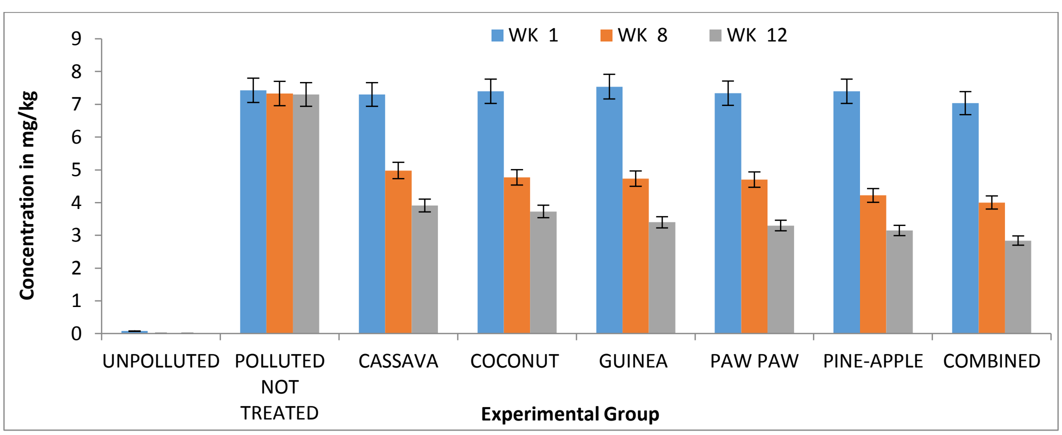

Fig 3. Standard Error Bar showing Lead (Pb) in treated and untreated crude oil polluted soil

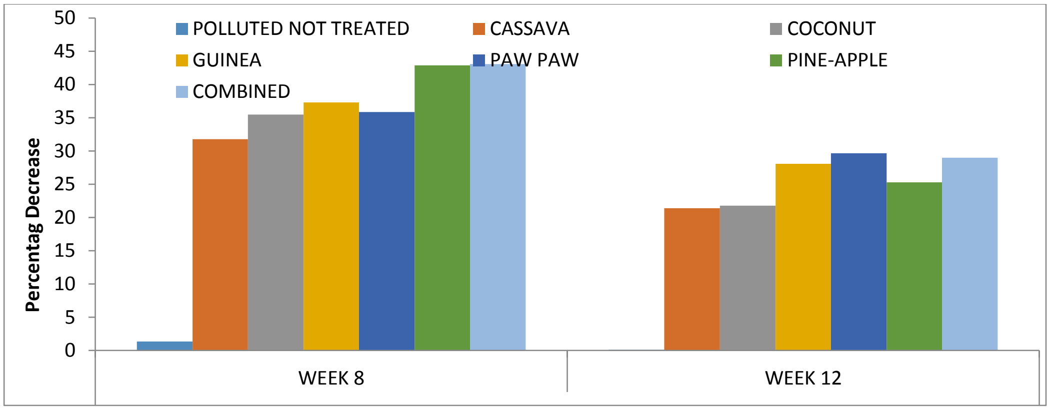

Fig 4. Percent Reduction in Lead (Pb) - Treated and untreated crude oil polluted soil

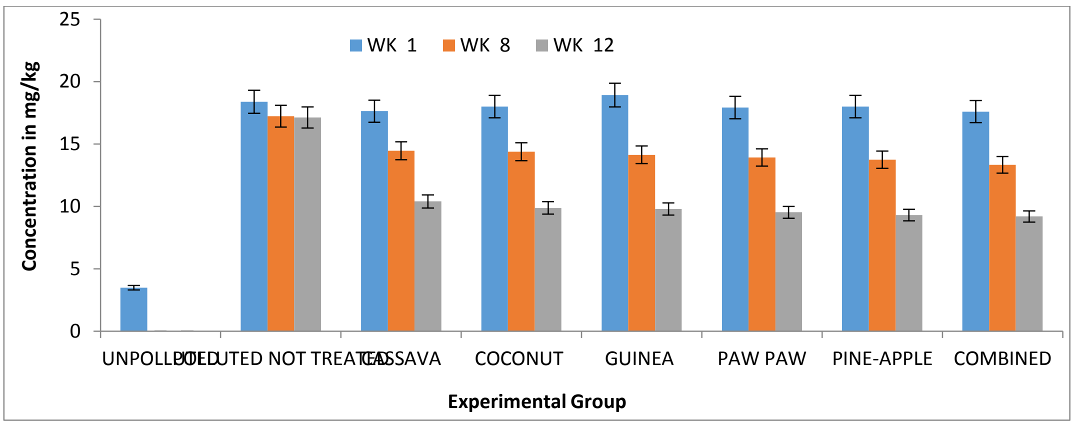

Fig 5. Standard Error Bar showing Chromium (Cr) in treated and untreated crude oil polluted soil

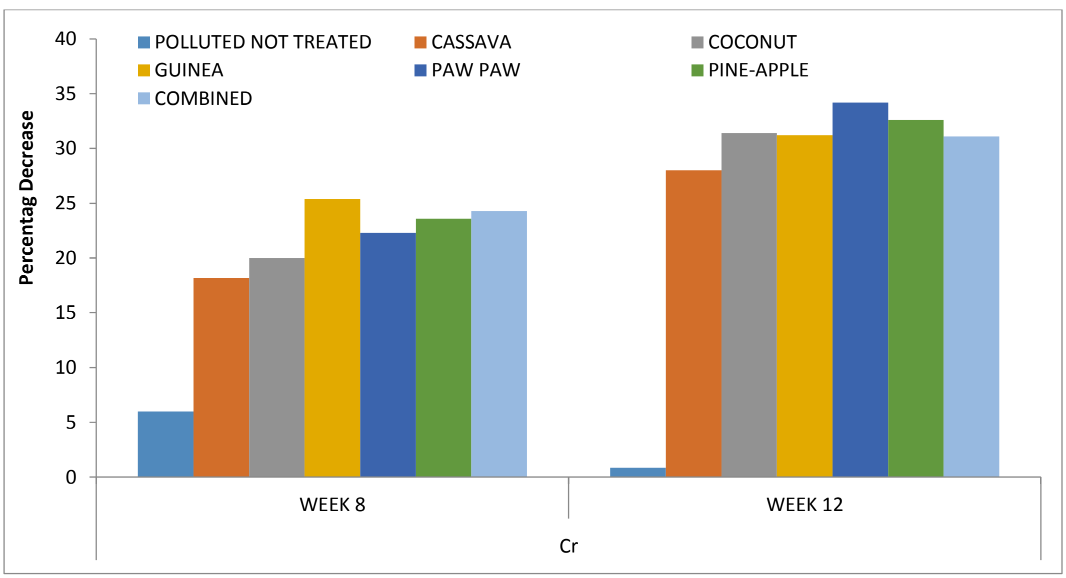

Fig 6. Percent Reduction in Chromium (Cr) - Treated and untreated crude oil polluted soil

A previous study by Makombe and Gwisai (2008) revealed that chicken droppings and tobacco compost performed better in remediating soil contaminated by TPHs, Pb, As, and Cd. Compost performed better as compared to *Brassica juncea* probably because compost contains many different species of microorganisms that are able to adapt and metabolize pollutants. There was limited remediation in the control experiment. Also, another study on Bacterial remediation of heavy metal polluted soil and effluent from paper mill industry by Nwaehiri *et. al*., (2020) showed the heavy metal remediation in soil samples across time with different treatments. Treatment 1 (treated with proteobacteria) reduced 74.5% of extractable (Pb) from the contaminated soil while Treatment 2 (treated with non-proteobacteria) reduced Pb concentration by 67.2%. Treatment 2 (53.8%) had a higher cadmium (Cd) removal from the contaminated soil than Treatment 1 (51.6%). Soil concentrations of Arsenic (As), Chromium (Cr), Zinc (Zn), Nickel (Ni) and Copper (Cu) were also reduced following the treatments administered. The Researchers reported significant decrease (P<0.05) in the concentrations of all the heavy metals from day 30–180 by Treatments 1 and 2 when compared to their respective concentrations at day 0 while Treatment 3 (Control group) was unchanged. Microbial identification in the same study revealed that *Pseudomonas*, *Staphylococcus*, *Erwnia*, *Enterobacter*, *Bacillus* and *Serratia* species were found in the polluted soil. In the present study, results obtained showed that the agro-residues under study can effectively enhance microbial removal of heavy metals in crude oil polluted soil. Specifically, bioaccumulation is a natural biological phenomenon where microorganisms use proteins to uptake and sequester metal ions in the intracellular space to utilize in cellular processes (e.g., enzyme catalysis, signaling, stabilizing charges on biomolecules) (Diep *et. al.*, 2018).

The significant decrease (P<0.05) in the concentrations of all the heavy metals from week 1 to 12 observed in this study might imply that the bacteria have an undiscovered and unexplored potential to remediate heavy metals in the soil. It was also inferred that the untreated group's performance in this study was poor as compared to other studies probably because the soil was heavily contaminated with TPHs which inhibited growth and development of crude oil biodegrading microorganisms.

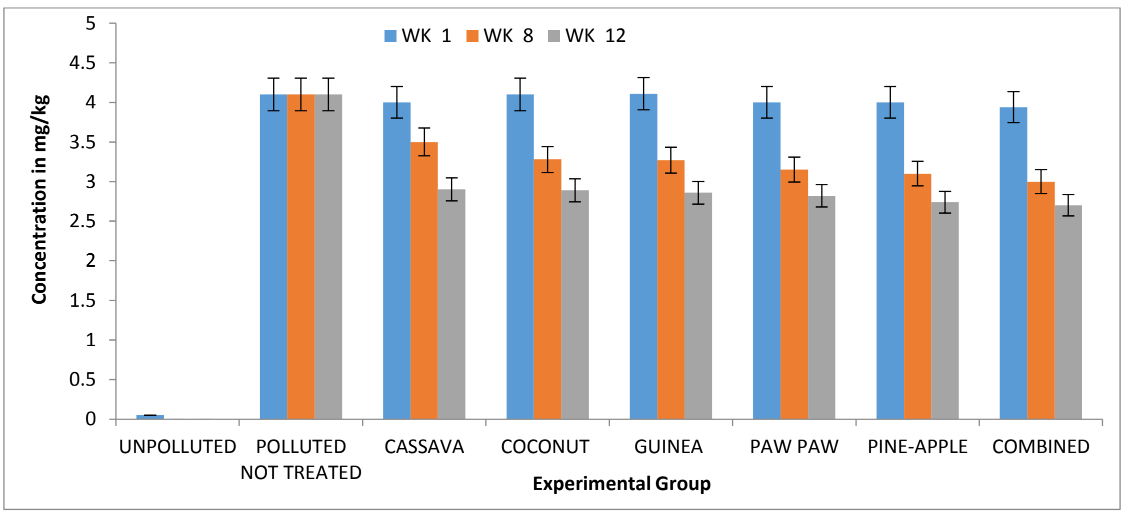

Fig 7. Standard Error Bar showing Cadmium (Cd) in treated and untreated crude oil polluted soil

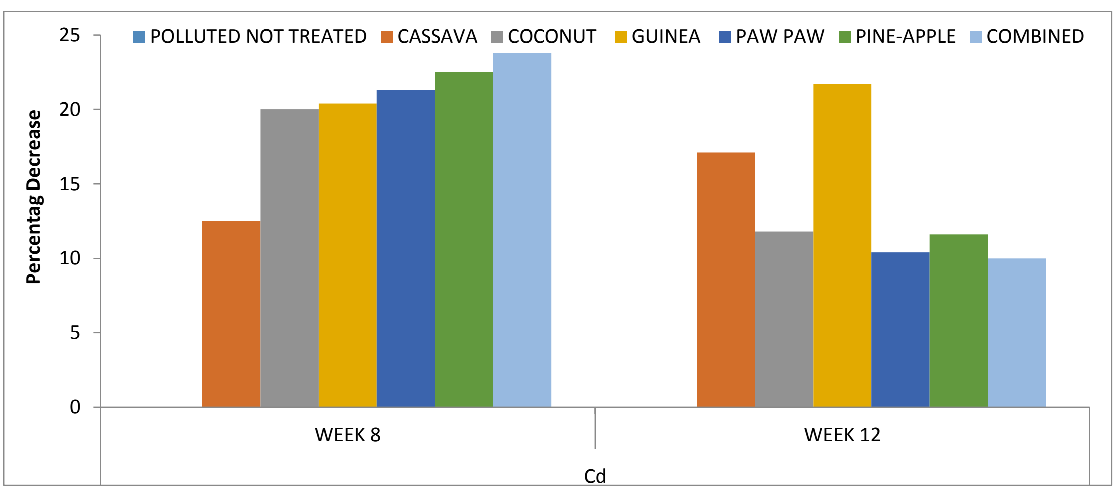

Fig 8. Percent Reduction in Cadmium (Cd) - Treated and untreated crude oil polluted soil

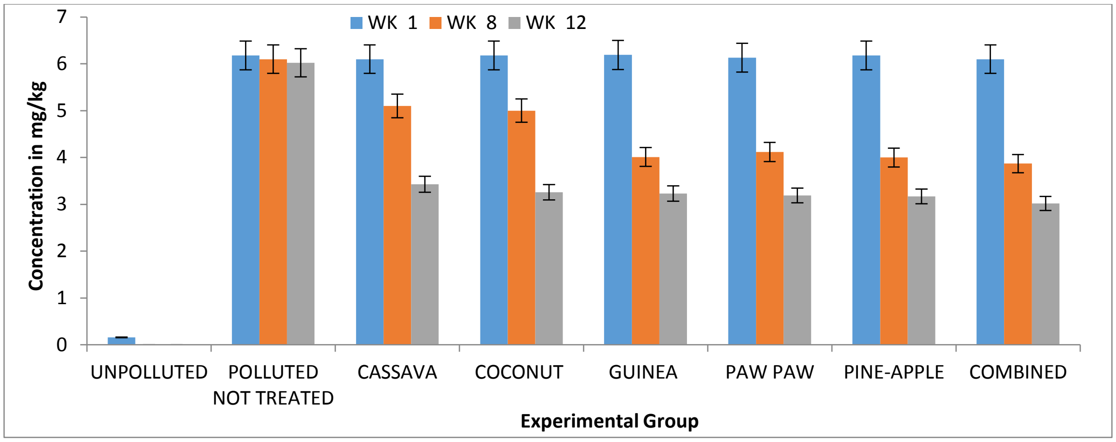

Fig 9. Standard Error Bar showing Arsenic (As) in treated and untreated crude oil polluted soil

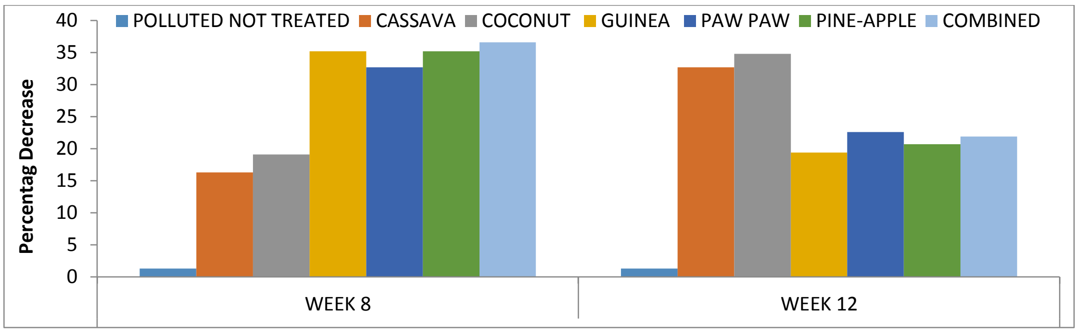

Fig 10. Percent Reduction in Arsenic (As) - Treated and untreated crude oil polluted soil

Conclusion: This study has shown that agro-residues used in this study have potentials to enhance microbial remediation of heavy metals in crude oil contaminated soil and transform heavy metals to be less toxic. Heavy metals, Cadmium (Cd), Chromium (Cr), Arsenic (As), Nickel (Ni) and Lead (Pb), in soil samples were successfully remediated, with a combination of the various agro-residues having a higher remediating potential than individual agro-residues. This may possibly be a suitable waste management process for agro-wastes.

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