Application of Caladium-Clay Composite as Oil Spill Treatment Agent in Soil from Bodo Oil Spill Site

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ABSTRACT

Soil sample from Bodo city oil spill site in Gokana, Rivers State was collected, air dried and sieved. The sample was mixed with varying concentrations (0.20 g, 0.40 g, 0.60 g, 0.80 g and 1.00 g) of caladium in a fixed mass (5.00 g) of calcined clay from Kono Boue, respectively. The samples were divided into two portions each. One part was kept in the dark for 21 days while others were exposed for 24 h, 7 days and 21 days respectively. The samples were analyzed using GC-FID for the determination of total petroleum hydrocarbon (TPH) content before and after treating with the caladium-calcined clay composite and the raw clay, respectively. The results obtained after 24 h of exposure to light, showed that the composite with the highest quantity (1.00 g) of caladium (organic matter) had the highest percentage degradation of 0.49 %. Upon further exposure to 7 days, % degradation increased to 6.02 % and finally to 18.36 % after 21 days of exposure. The unexposed had 4.90 % as the highest degradation after 21 days of the experiment. The result showed that, the greater the quantity of the organic matter in the composite, the higher the level of degradation of the contaminated soil. Also, exposure to light and oxygen was identified as co-factor that enhanced degradation of the TPH. Caladium-calcined clay composite can therefore be used as treatment agents for the remediation of crude oil polluted soils especially for durations longer than 21 days of exposure and higher concentrations of caladium.

INTRODUCTION

Pollution occurs when a change in environmental parameters negatively alters the quality of human life including effects on animals, micro-organisms and plants[1-5]. However of great concern to us is the one that occurred at Bodo city in Gokana Local Government Area of Rivers State of Nigeria in 2008. The volume of the oil spill was such that it attracted the sympathy of the international communities and the London Court that fined Shell international to compensate the inhabitants of that environment[6].

Notwithstanding, crude oil is the life-blood of our present day industrial society. Crude oil is a very complex mixture of different chemicals, therefore the effects of an oil spill on the environment is dependent on the exact nature and quantity of the oil spilt as well as other factors such as the prevailing weather conditions and the ecological nature of the affected region[7]. Constituents of dissolved oil such as BTEX (Benzene, Toluene, Ethylbezene & Xylene) are carcinogenic[8]. This was one of the major concerns of the UNEP report on Bodo (Ogoni) land which stated that the area's underground water was not good enough for drinking based on contamination with these carcinogenic components from crude oil[9,10].

Bioremediation is the application of biological techniques to return polluted environment to its natural state using natural materials. The materials of interest are those which are ecofriendly, cheap and locally available. On a general note, the application of bioremediation involves the use of enzymes, growth stimulants, bacteria, fungi or plants to degrade, transform, sequester, mobilize or control contaminants, organics, inorganics or metals in soil, water or air. This is in agreement with the "Doctrine of Infallibility" by Alexander which states that "there is no compound known to man that microorganisms cannot degrade". Ironically, the rate of biodegradation of some compounds is quite slow [11].

Techniques adopted in bioremediation depend on where they are applied. If on site, then it is said to be *in situ* remediation and if offsite, it is *Ex situ* remediation[12-14].

The *in situ* or *ex situ* could be bio-stimulation, that is natural remediation done by promoting conditions like aeration, addition of nutrients, pH and regulated temperature[15]. It also includes the use of selected wastes like cow dung and sewage, inorganic nutrients/fertilizers (N: P: K) or processes that leads to the production of CO_2 and water due to the depletion of organic matter by microbes[16-27]. Bio-augmentation on the other hand, is the addition of microorganisms (e.g. crude oil-degrading microbes) to supplement the native populations for the treatment of crude oil polluted environments[28-30]. The microorganisms could be bacteria or fungi[3,29,31].

The use of clay-organic matter (caladium) composites in remediation seemed not to have received attention by environmentalists. However, clay has been reported to be a better material for the removal of contaminants in its modified form taking advantage of its surface area and catalytic properties[32-34].

Caladium bicolour, on the other hand, is a non-edible plant with less economic value in this part of the world. The English trivial name is the heart of Jesus while the genus name is Araceae[35]. This study was designed to examine the possible use of raw clay (control experiment) and caladium-calcined clay (modified) composite in the treatment of oil spill polluted site.

MATERIALS AND METHODS

The caladium root (tuber) used was harvested locally while the raw clay sample was obtained from a clay mine at Kono-Boue in Khana Local Government Area of Rivers State, at a depth of 30 to 60 cm and stored in a clean black polyethene bag. Similarly, crude oil polluted soil samples were collected from Bodo city in Gokana, Rivers State at a depth range of 0 to 30 cm and stored in black polyethene bags. The Clay was sun dried for 72 h and sieved with a 2 mm mesh sieve. The caladium tubers were oven dried for 3 h, ground, soaked in water, filtered, decanted and the obtained caladium starch sun dried for three days. 5 ml of distilled water was added to 0.20 g, 0.40 g, 0.60 g, 0.80 g and 1.00 g of caladium respectively to form caladium gel. The sieved clay was calcined in a muffle furnace at 550 $^{\circ}$C for 8 h, cooled in a desiccator for 3 h to form the calcined clay. It was subsequently divided into10 groups of 5 g each. Furthermore, 0.20 g, 0.40 g, 0.60 g, 0.80 g and 1.00 g of caladium were added to each of the groups of the calcined clay and the resultant caladium-calcined clay composite used for the soil remediation in batches (**Plate 1**). The level of degradation of the contaminated soil was observed based on the reduction in the amount of total petroleum hydrocarbon (TPH) as monitored by the GC-FID. Data obtained from the studies were used to calculate the percentage reduction of the total petroleum hydrocarbon (TPH).

$$\%R = \frac{Co - Ce}{Co} x100 \qquad (1)$$

Where Co = initial amount of the TPH; Ce = Amount of the TPH at time, t and %R = the percentage of the degradation

Plate 1 Crude oil polluted soil + caladium-clay composite mixture

RESULTS AND DISCUSSION

Effect of a fixed weight of raw clay on the polluted soil (Control)

The % degradation of total petroleum hydrocarbons (TPHs) obtained for the raw clay (control experiment) in 24 h (1 day), 7 days and 21 days were 0.02, 0.62 and 3.75 respectively. The addition of the raw clay to the crude oil polluted soil resulted in a decrease in the TPHs concentration in the soil. This is shown in the graph of the effect of a fixed weight of raw clay on the polluted soil in **Figure 1**.

It was observed that the % degradation increased with time (days) though at a slower compared to when the modified clay was mixed with caladium before treatment. This agreed with the trend observed in literature where a mixture of contaminated soil with binding agents resulted in changes in the physical and physico-chemical properties[36-37]. Thus such possible changes in properties of the clay may be responsible for the observed decrease in the concentrations of the TPH.

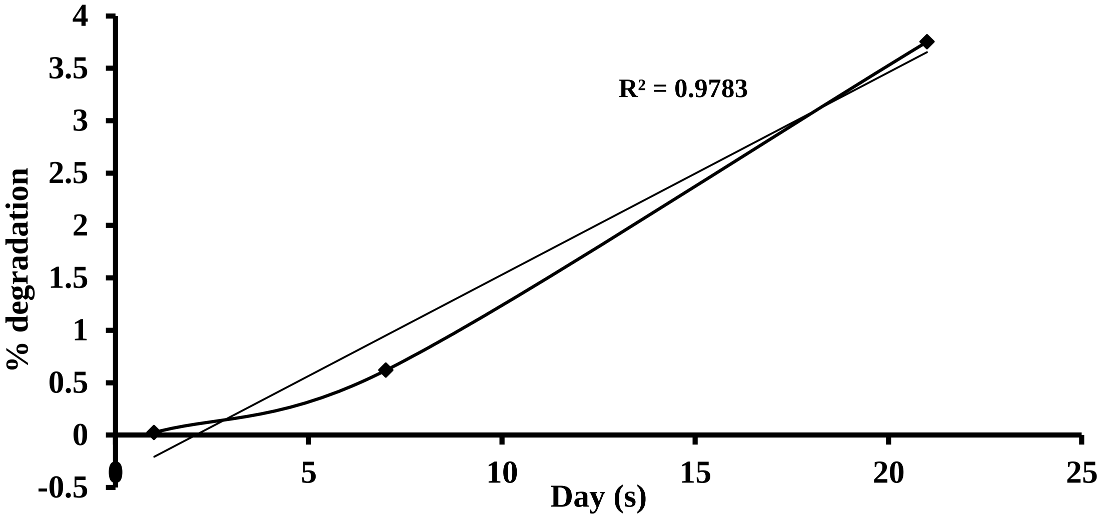

Figure 1: Variation of % degradation with days of a fixed weight of raw clay

Another report of higher biodegradation with time (days) when used lubricating oil was mixed with soil modified with organic wastes for 98 days against the control soil without organic matter also supported the observation[17,38]. The capacity of the raw clay to degrade TPH could also be linked to possible catalytic effect of the clay since the clay used have been shown to possess some catalytic properties[39]. It contains Fe^{2+} and Al^{3+} ions (Lewis acids) which could act as catalytic centres for heterogeneous catalysis. Increase in % degradation of contaminant with increase in time has also been observed when montmorillonite clay was applied to degrade diazinon (an organophosphate insecticide)[32,40]. The use of filtered raw clay and thorough mixing also helped to improve aeration in the soil and this could make the indigenous microorganisms to be more active with enhanced performance[15-23].

Effect of varying masses of caladium with a fixed mass of calcined clay on the polluted soil

The effect of varying the concentrations of caladium with a fixed mass of calcined clay (caladium-calcined clay composites) when mixed with a fixed mass of polluted soil after 1 day and 7 days are shown in **Figure 2**. It was observed that the % degradation increased with an increase in the organic content (nutrient). The highest % degradations obtained were 0.49 and 6.02 for days 1 and 7 respectively for 1 g of caladium in the caladium-calcined clay composites. The % degradation trend increased with increase in the concentration of organic nutrient except at 0.60 g where a slight deviation was observed on the 7th day. The reason for this deviation was unclear but the continual increase in the degradation may be attributed to the presence of more air, oxygen and nutrient which are useful in the bioremediation of crude oil polluted soils[41-42]. When the polluted sample was further treated for 7 days, it was observed that there was increase in the degradation of the crude oil polluted sample. This was attributed to the fact that in bioremediation, time is a factor for the remediation of a contaminated soil sample. The % degradation trend also increased with increase in the concentration of the caladium (nutrient) in the composite. The highest % degradation of 6.02 (after 7 days exposure) was obtained at 1.00 g of caladium in the composite.

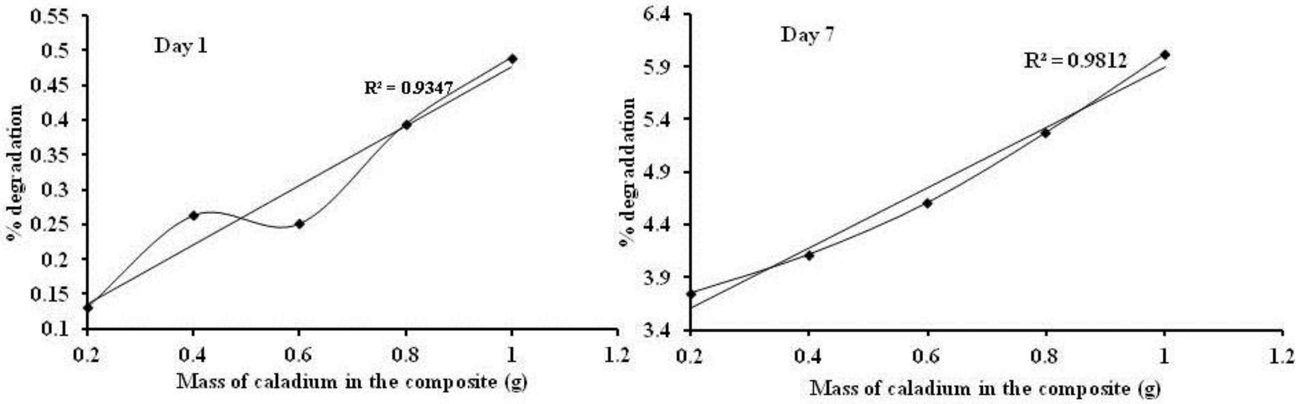

Figure 2: Variation of % degradation with varying concentrations of caladium in the composite

Comparison between the exposed and unexposed after 21 days of treatment

When varying concentrations of caladium in the composite with the polluted soil were kept after 21 days in the dark (unexposed), it was also observed that increase in % degradation increased with the nutrient such that the highest value of 4.9 % was obtained at 1.00 g. The results of the % degradation after 21 days of exposure and experiments in the dark respectively are presented in **Figure 3.** The results showed that the exposed samples' % degradations were greater than those kept in the dark.

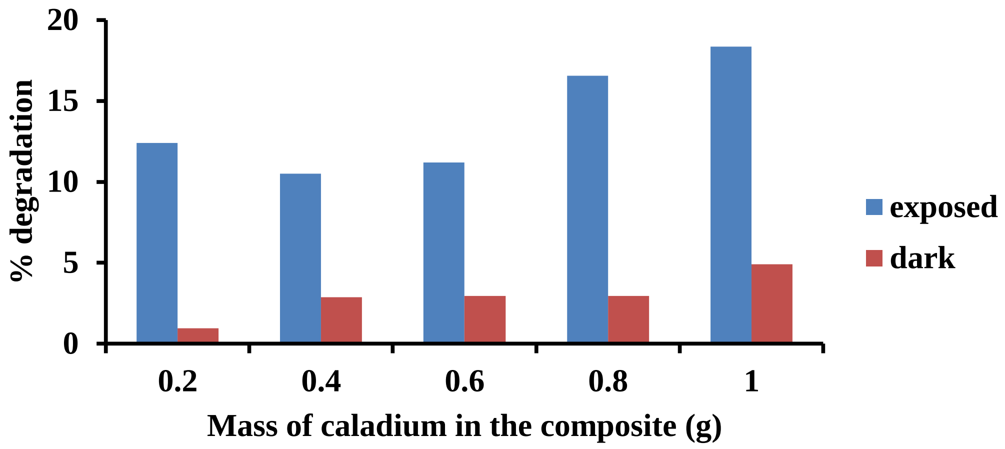

Figure 3: Comparison of % degradation between exposed and unexposed samples.

A bar chart of varying the concentrations of the nutrient in the composite in the polluted soil after 21days of exposure is shown in Figure 3.The maximum % degradation of 18.36 was obtained at 1.00 g of the nutrient in the composite. This could be due to enhancement of microbial growth with the added nutrient [17,43]. On the other hand, oxygen was also observed to have an effect on the % degradation of the polluted soil because some of the treatments were done in an enclosed black polythene bag and the % degradation were not as high as those that were exposed to air, using the same concentration of caladium and timing.

The % degradations of the unexposed treated samples were 0.94, 2.87, 2.94, 2.96 & 4.90 for 0.20 g, 0.40 g, 0.60 g, 0.80 g & 1.00 g of caladium respectively in the clay composite. The maximum % degradation of 4.90 was also obtained at 1.00 g of the nutrient in the composite. On comparison with the % degradation of TPHs after 21 days of exposure and those not exposed showed that the % degradation of TPHs in the light was almost four times higher than those in the dark. This observation may be attributed to possible photochemical reaction with oxygen (air) and light (hυ) [22].

The modified clay with the highest amount (1.00 g) of caladium recorded the highest % degradation of 18.36 after 21days of exposure in light compared to raw clay (control) which was 3.75. The reason for the results may be due to the differences in nutrients contents which stimulated the biodegradation particularly in the modified caladium clay and also an enabling environment like aeration amidst others[44]. Hydrocarbon utilizing bacteria require some nutrients to carry out effective and efficient biodegradation activities of xenobiotics in the soil environment. A related trend was also observed in hydrocarbon contaminated soil modified with poultry, pig manure composite, cow dung, lime and cement[25-27].

Biodegradation was enhanced with the use of the modified caladium clay composites giving a TPH removal ranging from 0.13 to 18.36%. This result could be due to combined factors of biostimulation and photochemical oxidation of the TPHs as reported in the literature[24,29,31].

Further analysis of the nutrient(phosphorus and nitrogen) contents of the raw clay and caladium calcined clay composites showed that the modified clay (caladium-calcined clay) had higher nutrient (nitrogen and phosphorus) values than the raw as shown in **Table 1**.

Table 1: P and K contents of the polluted soil after treating with raw and caladium calcined clays

Parameter	Control (raw clay)	0.20 g (caladium)	0. 40 g (caladium)	0.60 g (caladium)	0.80 g (caladium)	1.00 g (caladium)
Phosphorus (mg/kg)	17.71	19.18	20.94	21.12	21.47	22.59
Nitrogen (mg/kg)	3.16	3.88	6.92	7.34	8.03	10.67

CONCLUSIONS

Raw clay (control experiment) and caladium-calcined clay composites have been prepared and used as oil spill treatment agents in the remediation of Bodo crude oil polluted soil for the first time. The results showed increase in degradation of TPHs with increase in the concentration of the caladium-calcined clay composites when treated (mixed) with crude oil polluted soil within 21 days of the study.

However, the maximum rate of degradation recorded after the 21 days of exposure was 3.75 and 18.36 % for the raw and caladium-calcined clay composite respectively. The unexposed mixture of the caladium-calcined clay composite with the crude oil polluted soil was degraded by 4.90 % over the same period of study. Higher concentrations of caladium other than the range reported here and longer duration should be used in further studies since the results obtained showed that the rates of degradation of TPH in the polluted soil were functions of the concentration of caladium in the clay composite and time. The study also recommends that caladium-calcined clay composite should be used in remediating crude oil polluted sites based on its proven capacity to degrade TPH. The use of caladium alone should be investigated in further studies.

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