World Journal of Advanced Research and Reviews
eISSN: 2581-9615 CODEN (USA): WJARAI
Cross Ref DOI: 10.30574/wjarr
Journal homepage: https://wjarr.com/

(Research Article)

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Kinetics of bioremediation of crude oil polluted soil using potato peels as bio-stimulant

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World Journal of Advanced Research and Reviews, 2023, 19(01), 1553–1559

Publication history: Received on 14 June 2023; revised on 22 July 2023; accepted on 24 July 2023

Article DOI: https://doi.org/10.30574/wjarr.2023.19.1.1481

Abstract

This study investigated the utilization of bio-stimulant derived from agro-based resource (potato peels) in the remediation of crude-oil contaminated soil. At a constant proportion of crude oil contamination, varying concentration of the biostimulant (5ml, 10ml, 15ml and 20ml) were introduced for the treatment (bioremediation and degradation) of the contaminated sites and left for a degradation period in plastic vessels. Periodic sampling of soil from each vessel was carried out at 5 days interval for total petroleum hydrocarbon analysis. Results indicated that after 20 days of exposure to the organic biostimulants, biodegradation of crude oil contaminated soil samples was directly proportional to the potato peels dosage. The potato peels (PO) derived biostimulant recorded 94.43 percentage degradation at 20ml dosage and 20 days contact time. Oil contaminated soil samples amended potato peels biostimulant recorded half-life of 0.702day and biodegradation rate constants of 0.986day^{-1}. The zero order kinetic model best described the bioremediation kinetic behaviour of the bioremediation process. The findings of this research suggest that potato peels can be used as an effective organic amendment for the biodegradation of crude oil contaminated soil.

Keywords: Biostimulation; Crude oil pollution; Biodegradation kinetics; Organic nutrients; Bioremediation.

1. Introduction

The increase in the exploration and usage of petroleum products have resulted in widespread contamination of the environment. The pollution of the environment occurs when pollutants enter the natural environment, disrupts their balance and negatively affect the life of living organisms (Vidali, 2001). Indeed, the negative effects of pollutants in the environment and on human health are diverse and depend on the nature of the pollution. Between the soil, air and water media, soil contaminations have been reported to be the most threatening due to the fact that contaminants have the capacity to affect the indigenous organisms that dwell in the soil and destroy the food chain. (Floch*et al.*, 2011; Moreno *et al.,* 2009).

One of the major soil contaminations is caused by oil spillage due to the exploration and exploitation of crude oil. Frequent oil spill incidents have become a problem to ecological protection efforts. Increased use of petroleum and its products has led to severe contamination of the soil and ground water. These contaminants affect the chemical composition and physical matrix of soils culminating to the loss of soil fertility, changes in ecosystem and displacement of communities. (Adams *et al*., 2016). In order to prevent destruction to the terrestrial ecosystem of the polluted sites, these sites need to undergo a thorough treatment process. The estimated cost for the cleanup of terrestrial ecosystems with conventional techniques like solvent extraction, incineration and landfill have been reported to be enormous and insufficient. Thus, various strategies have been opted to investigate the most cost-effective solution to deal with contaminated sites. Also, inorganic soil remediation techniques have been reported to produce secondary pollution during treatment. (Johnsen *et al*., 2005).Therefore, there is an increasing demand for green, facile, ecofriendly, non-

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toxic, low-cost biodegradable methods for the treatment of oil spills. This has led to concerted efforts in studying the possibility of detoxifying oil contaminants using organic wastes (Romanus et al., 2015).

The biological method such as bioremediation offer reduced environmental risks as it is a natural process that depends on microorganisms to degrade the contaminants in soil and water sources. Bioremediation is recognized as a cost-effective treatment technology for oil-contaminated soils (Cerqueira*et al*., 2014).Bioremediation is the treatment of contaminated environment by using biological mechanisms. It's an environmentally friendly treatment technique. When hydrocarbon-containing contaminants spill on land, degradation by indigenous microorganisms progresses slowly due to inadequate nutrients and microorganism populations (Abed *et al*., 2014). The term biostimulation is used to describe the additionof essential electron acceptors such as nutrients to enhance the microbial growth (Yu *et al*., 2005; Sayara*et al*., 2011).

This study was conducted to find a quick solution to soil contamination due to the leakages of crude oil from transmission pipelines, oil refineries, and underground storage tanks. Even a small crack on pipe along the oil transmission pipelines causes leakages to natural soil and nearby surface waters. It is very common that several incidences of oil leakages occur every year.When these incidences occur, a remediation team reacts to the incident very fast before it spreads,and recovers the contaminated soil and treats them ex situ before final disposal. Generally, these contaminated soils are either incinerated or landfilled at hazardous waste landfills. However, the bioremediation and recovery of these contaminated soils should be preferred to prevent the loss of fertile soils. Therefore, rapid ex situ or in situ disposal of these soils is very crucial. In this study, addition of a nitrogen, phosphorous, and potassium (NPK) nutrients (biostimulation) were performed in simulated crude oil contaminated soil samples to treat the contaminated soil.

The overall aim of this study is to assess the efficiency of biostimulation with addition of nutrients; nitrogen and phosphorus, and potassium for Total Petroleum Hydrocarbon (TPH) degradation. In achieving this aim the crude oil biodegradation rate in a freshly contaminated soil using the biostimulation process, treatment time needed for each process and half-life for the treatment processes were investigated.

2. Materials and Methods

2.1. Materials

The composite soil sample used in this study was collected from Nnamdi Azikiwe University, Main Campus, Awka South Local Government Area, Anambra State, aseptically with a sterile hand trowel into clean plastic buckets (Eziuzor and Okpokwasili, 2009). The soil was collected at depths of 0 –15 cm and the Co-ordinates of the soil sampled point was determined using handheld Global Positioning System (GPS) (6.2459° N, 7.1199° E). The crude oil was obtained from mile 1 market in Port-Harcourt, Rivers state, Nigeria. Plant waste, potato peels (PT), were obtained from Eke-Awka market in Awka South Local Government Area, Anambra State, Nigeria. Potato peels (200g) were air-dried for 7 days and size reduced into semi-fine particles using a sterile mortar and pestle. Physicochemical analyses were carried out and recorded before the bioremediation study.

2.2. Methods

2.2.1. Baseline Study

1,000 g of soil in a mixer was contaminated with 100 ml of crude oil and homogenously mixed. The unpolluted soils were analyzed for physicochemical and petroleum hydrocarbon compositions to serve as the baseline (control) thus, establishing a standard (Ezekoye et al., 2015).

2.2.2. Physicochemical Composition

The pH, moisture content, nitrogen content, phosphate content, potassium and iron were determined.

2.2.3. Bioremediation Kinetic Study

5g of polluted soil sample solutions was transferred into a 25ml flask and 20ml of n-hexane was added. The mixture was shaken vigorously using a mechanical shaker for 25min and allowed to stand for 10min until total extraction of crude oil from the soil sample solution. The solution was then filtered using a Whitman filter paper and the liquid filtrate was diluted by taking 1ml of the extract into 50ml of hexane. The absorbance of this solution was measured spectrophotometrically at a wavelength of 460nm using n-hexane as blank. The absorbance obtained was converted to concentration by comparing it with standard calibration curve of hydrocarbon in hexane chart. The TPH was determined at 5days interval of 25days. The actual TPH was calculated using equation (1).

$$TPH = \frac{Instrumental\ reading\ (Concentration\ obtained\ from\ Curve) \times Volume\ of\ extract\ (ml)}{Weight\ of\ sample\ (kg)} \quad (1)$$

The Biodegradation percentage was determined using eqn. (2) (Latinwo& Agarry,2015).

$$\%\ \text{Biodegradation} = \frac{\text{TPH(o)} - \text{TPH(i)}}{\text{TPH(o)}} \text{X } 100\% \quad (2)$$

2.2.4. Kinetics model and half-life of crude oil biodegradation

The TPH data obtained in this study were substituted into the zero-order equation (3), first order equation (4) and second order equation (5) (Agarry *et al.,* 2013; Mohajeri, 2010).

$$\text{TPH}_t = \text{TPH}_o - \text{kt} \quad (3)$$

$$\text{In}\frac{TPH_i}{TPH_o} = -\text{Kt} \quad (4)$$

$$\frac{1}{TPHo - TPH_i} = k_2 t + \frac{1}{\beta} \quad (5)$$

Where TPH_0 is the initial TPH content in the soil (mg/kg), TPH_t is the residual TPH content in the soil (mg/kg) at time t, K is the biodegradation rate constant (day^{-1}) and t is time (day). The model estimated the biological half-life ($t_{1/2}$) as the time taken for half of its original amount to be converted. Half-life was evaluated using the model in equation (6) (Agarry, 2013; Agarry *et al.,* 2013).

$$\text{Half-life } (t_{1/2}) = \frac{\ln 2}{K} \quad (6)$$

Where K is the biodegradation rate constant (day^{-1}).

3. Results and Discussion

3.1. Physicochemical Characteristics

The result of the physicochemical characteristics of the soil sample before crude oil contamination is presented in Table 1. The study revealed that the soil is acidic in pH, low in nitrate and phosphate, high in potassium and iron content, low in moisture content.

Table 1 Physicochemical characteristics of soil sample before crude oil contamination

Parameter	**Soil**
pH	5.85
Nitrogen (mg/kg)	0.602
Phosphorus (mg/kg)	7.89
Potassium (mg/kg)	71.40
Moisture (%)	2.80
Iron (mg/kg)	25.7

From the results in table 1, the pH, moisture content, nitrate, phosphate, potassium and Iron were 5.85,2.80%, 0.602 mg/kg, 7.89 mg/kg and 25.7 mg/kg respectively.

3.2. Total Petroleum Hydrocarbon (TPH) Degradation Analysis

In this study, the percentage biodegradation of TPH in crude oil contaminated soil as mediated by organicnutrients were evaluated at different biostimulant dosages and contact time. Several authors have examined nitrogen and phosphorus content of these wastes in accelerating the bioremediation of oil contaminated soil ecosystem (Orji *et al*., 2012; Ezekoye *et al*.,2015). It was observed from figure 1 that the %biodegradation continued to increase with increase in the biostimulants dosages and the contact time required for remediation. This implies that addition of more nutrients to the indigenous bacteria through the biostimulants for the breaking down of hydrocarbon leads to increased and faster degradation of crude oil within the study period. The peak %biodegradation shown by the biostimulant, PO, is 94.43% (Figure 1).

It is remarkable to note that increased amount of organic nutrients was active in biostimulating the petroleum hydrocarbon degraders which eventually led to a decrease in petroleum hydrocarbon in the soil polluted with crude oil. Previous studies by Abioye et al. (2009) examined the effects of these nutrients on oil contaminated soil had similar findings to the ones in this study.

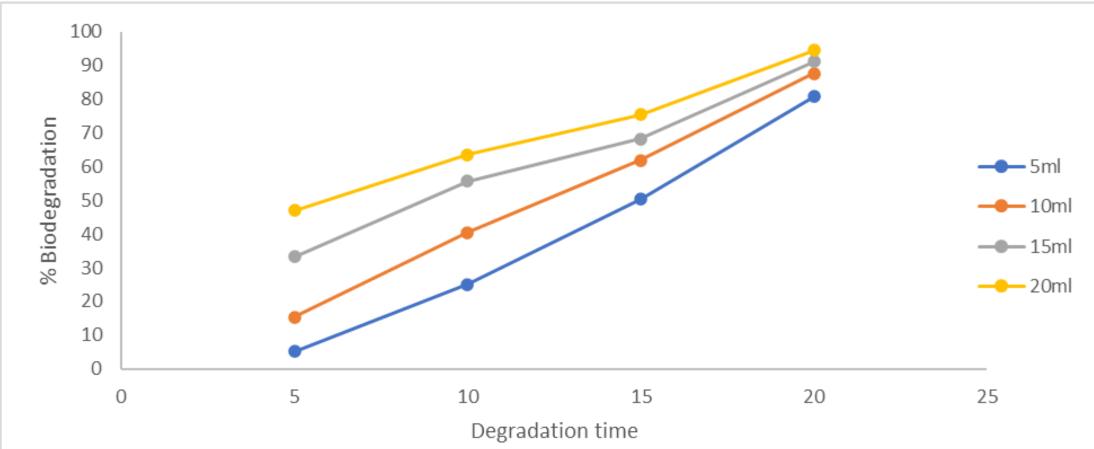

Figure 1 Percentage biodegradation of petroleum hydrocarbon in potato peel biostimulant amended soil contaminated medium

3.3. Biodegradation kinetics

The experimental data were fitted into zero order, first order and second order kinetic models. The plots of the linearized form of the zero order, first order and second order models are shown in figures 2-4. Table 2 contains the zero order, first order and second order kinetic rate constant obtained from the slope of the linear plots of TPH against time, InTPH against time, and $1/TPH_0 - TPH_i$ against time respectively.

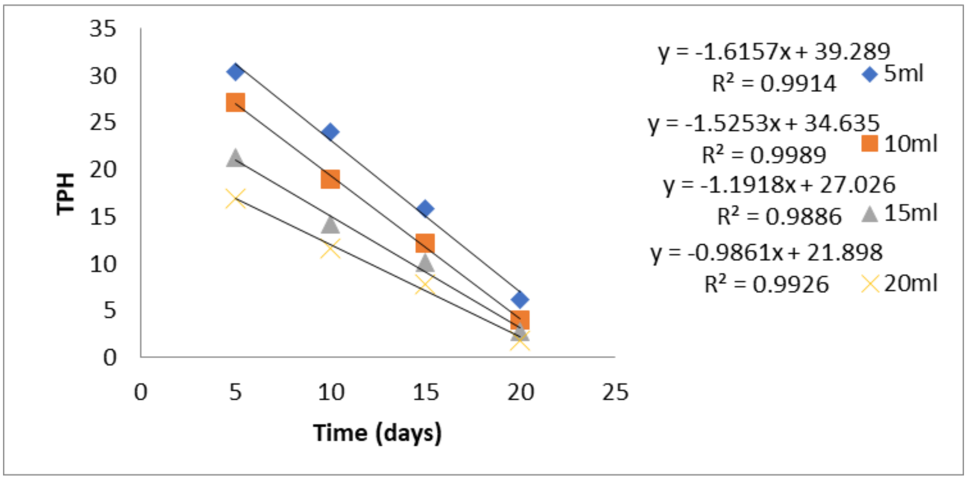

Figure 2 Zero Order Kinetic Plot

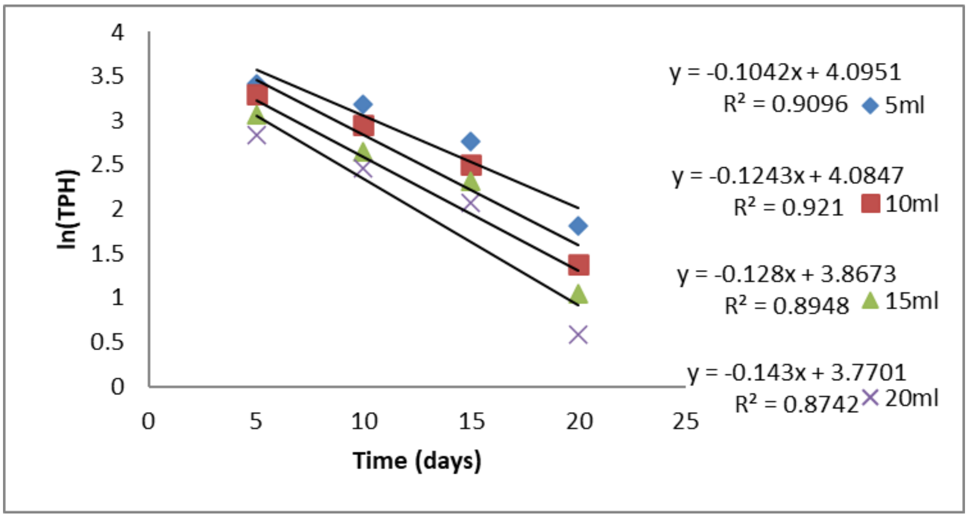

Figure 3 First Order Kinetic Plot

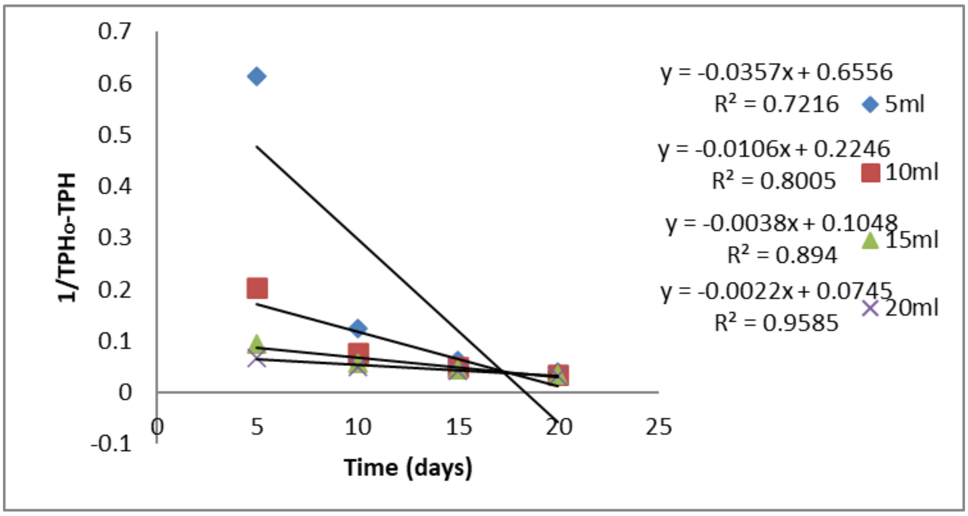

Figure 4 Second order kinetic plot

The coefficient of determination obtained as recorded in table 2 reveal that zero-order kinetic model presented coefficient of determination values closest to unity. Thus, the zero-order kinetic model best described the experimental data.

Table 2 Kinetic Data

Dosage (ml)	**Zero Order**			**First Order**			**Second Order**		
	K_o	TPH_o	R^2	K	TPH_o	R^2	K_2	B	R^2
5	1.615	39.28	0.991	-0.104	1.410	0.909	-0.035	1.527	0.721
10	1.525	34.63	0.998	-0.124	1.407	0.921	-0.010	4.464	0.800
15	1.191	27.02	0.988	-0.128	1.352	0.894	-0.003	9.615	0.894
20	0.986	21.89	0.992	-0.143	1.327	0.874	-0.002	13.514	0.958

The result of the biodegradation rate constant(k) and half-life ($t_{1/2}$) of TPHs in amended polluted soil samples during the study period is presented in Table 3. From the results presented in Table 3, 15ml potato peel biostimulant dosage had the highest biodegradation constant of 1.911 day^{-1} and the lowest half-life 0.363 days. The increasing rate of degradation with low half-life observed in contaminated soil treated with potato peel biostimulant may be as result of its high content of nitrogenous, phosphorus and potassium source which were made available to the native microbial flora in the oil contaminated soil. (Adesodun and Mbagwu, 2008; Agamuthu et al., 2013; Omoni et al., 2015).

Table 3 Rate constant and its corresponding half-life for various treatment levels using biostimulant from potato peels.

Dosage	K (day^{-1})	Half-life (Day)
5ml	1.615	0.429
10ml	1.525	0.455
15ml	1.911	0.363
20ml	0.986	0.702

4. Conclusion

The findings from this study revealed that bioremediation of crude oil contaminated soil with the use of different dosage of organicnutrients (potato peels) as biostimulating agents led to faster elimination of petroleum hydrocarbon. Therefore, the addition of organic nutrients efficiently and significantly boosted the degradation and loss of petroleum hydrocarbon in crude oil contaminated soil with higher biodegradation constant and lower half-life. The technology used in this study offers a promising, better, cheaper and more eco-friendly system that if adequately applied in crude oil polluted soil will lead to a harmless and non-toxic environment for plant, animal and general public.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to disclosed.

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