Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **9(4),** 39-45, October **(2019)** *Res. J. Chem. Sci.*

Impact of remediation on the physicochemical characteristics and heavy metal concentration of crude oil contaminated water samples

Chikwe T.N. and Mac-Arthur O.O.
Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323, Choba, Port Harcourt, Nigeria
templechikwe@yahoo.co.uk

Available online at: www.isca.in, www.isca.me
Received 12th July 2019, revised 3rd October 2019, accepted 16th October 2019

Abstract

The adsorption characteristics of three terrestrial plants; Bitter Leaf (Vernonia Amygdalina), Water Leaf (Talinum Triangulare), and Vetiver Grass (Vetiveria Zizanioides) were used in the remediation of crude oil contaminated water samples. The phytoremediation characteristics of these plants where determined through their ability to clean up crude oil contaminated water samples and bring their physicochemical parameters and heavy metal concentrations within World Health Organization (WHO) acceptable limits. The leaves of these plants were dried at a temperature of 65 ^{0}C, ground and sieved to a mesh size of 30 µm. Physicochemical characteristics and Heavy metal concentration of the oil contaminated water samples were determined before and after phytoremediation using American Standard for testing and Materials (ASTM) and Atomic Absorption Spectrometer (AAS) respectively. Results obtained showed that apart from the pH, the other physicochemical parameters such as temperature, electrical conductivity, dissolved oxygen and salinity were within WHO acceptable limits (before and after remediation). Apart from Lead (Pb), the concentration of the other heavy metals (Zinc (Zn), iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni) and copper (Cu)) were within acceptable WHO limit after the simulated spill on water, though consistent exposure to crude oil contamination through spillage may result in the accumulation of these heavy metals within the environment. The concentration of Lead (Pb) was above WHO acceptable limit even after remediation with bitter leaf, water leaf and vetiver grass hence the plants lack the ability to clean up Lead (Pb) from the water body. High concentration of Lead (Pb) has a lot of catastrophic effect on the ecosystem such as retardation of growth in animals, negative impact on photosynthesis, destruction of microbial activity in the soil etc. The total percentage reduction of heavy metal concentration after remediation with bitter leaf, water leaf and vetiver grass were 55.00 %, 45.00 % and 30.80 % indicating that bitter leaf is the best amongst the other plants in the cleanup of heavy metal from the water samples.

Keywords: Heavy metal, physicochemical, absorption, remediation, oil spillage, toxic, contamination.

Introduction

Over the years, heavy metal concentration in the environment have been largely due to mining operations, crude oil exploration, refining of petroleum and oil spillage[1]. Since 1960, an estimate of more than four thousand cases of crude oil spillage have occurred in the Niger Delta region of Nigeria and several million barrels of crude oil which sometimes contain heavy metals have been released into the soil, water or air of the surrounding areas. These metals vary in their individual toxicity, they can lead to the inhibition of different cellular processes and their impacts are mostly concentration dependent[2]. Crude oil spillage is the deposition of petroleum hydrocarbons into the ecosystem due to human activities, it is predominant within the marine ecosystem however spills may also occur on lands[3]. There is an offset in the entire physicochemical properties of an area once it is contaminated with petroleum owing to the availability of some toxins in the crude. Heavy metal contamination of soil and water are also associated with oil spills [4]. A heavy metal can be defined as a metal with a relatively high density (>7g/cm^3) or atomic weight (>20) and is often assumed to be toxic. Heavy metals predominant after oil spillage includes Aluminum (Al), Cadmium (Cd), Chromium (Cr^{3+} and Cr^{6+}), Vanadium (V), Copper (Cu), Mercury (Hg), Cobalt (Co) Nickel (Ni), Lead (Pb) and Zinc (Zn)[5]. Oil spillage on land negatively affects certain characteristics of the soil such as temperature, structure, nutrient status, cation exchange capacity, mineral / organic matter content, redox properties and pH value. Oil spillage in water can lead to reduction in dissolved oxygen concentration owing to transformation from organic components into inorganic compounds, it can also lead to biodiversity reduction through a decrease in amphipod population which is crucial in the marine ecosystem food chain and eutrophication[6]. When Crude oil spills at sea, it forms noticeable bands on the sea surface which go through several pathways into other zones of water bodies, some may flow into the mass of seawater and researchers suggest they may be retained within the water body for a long time before their degradation by aquatic microorganisms[7]. The immiscibility of the surface bands formed from the spill forms a water-in-oil emulsion due to its viscosity. Stagnant water bodies make the oil to be retained in the environment for long, resulting in long-time exposure of the plants and animals which exposes the plant, animals and humans to lots of health issues and diseases. Oil spillage on water may also lead to various damages to marsh vegetation by reducing the density of plant, rate of photosynthetic growth and height of plant stem[1]. There are various remediation techniques for crude oil spills in both water and land however the most suitable remediation is determined by physicochemical properties of oil and the location of the Spill[8]. Remediation has come out to be one of the best environment friendly and successful remediation techniques for crude oil spills. Remediation is a plant –based cost-effective approach of remediation which is based on plants ability to concentrate environmental elements and compounds as well as metabolizing various contaminants in their tissues. Remediation is basically targeted towards toxic heavy metals and organic pollutants[9]. In recent years characteristic functions and molecular mechanisms of remediation has developed in addition to biological and engineering strategies designed to optimize and improve remediation. Also, several field trials have confirmed the effectiveness of using plants for environmental remediation[10]. The ability of various plants to facilitate the remediation of oil contaminated sites thereby bringing the physicochemical characteristics and heavy metal concentration of such sites to acceptable limits have been identified. For plants to be suitable for remediation they must possess some specific characteristics which includes extensive fibrous root systems for effective absorption of hydrocarbons and heavy metals, ability to accumulate and tolerate crude oil in their stems and leaves, ability to fix nitrogen and not compete for limited supplies of available soil nitrogen at oil contaminated sites with microorganisms and other plants. Some of the plants used for remediation are leguminous plants like alfafa, clover, beans etc, grasses such as wheat grass, ryegrass, vetiver grass and vegetables such as water leaf and bitter leaf[2]. The aim of this study is to determine the physicochemical characteristics and heavy metal concentration of crude oil contaminated water samples (simulating oil spillage in an aquatic environment) after remediation with water leaf (*Talinum Triangulare*), bitter leaf (*Vernonia Amygdalina*) and vetiver grass (*Vetiveria Zizanioides*). remediation is basically restricted to living plants however this study is aimed at considering the remediation characteristics of plants in their nonliving synthetic state. The essence of the study is to ascertain the remediation ability of each of these plants in the reduction of heavy metal concentration in oil contaminated water samples as well as their ability to restore the physicochemical parameters of the oil contaminated water samples to acceptable standards with basic emphasis on the leafs of the plants. Waterleaf (*Talinum triangulare*) is a perennial herbaceous plant widely grown in Nigerian and other warm regions as a leaf vegetable, it belongs to the *Portulacea* family. The seed germinates as a slim, aqua-coloured plant before growing into a more pronounced plant with larger leaves, this herbaceous plant is referred to as waterleaf due to its high moisture contents of approximately 91.0gm per 100.0 gm[11]. Figure 1 shows the picture of Water leaf.

Bitter leaf *(Vernonia amygdalina*) is a leafy small woody plant that occurs untamed in most countries of tropical Africa, It occurs naturally along rivers and lakes, in forest margins, woodland and grassland and it is the largest genus of the tribe *Vernonieae.* Bitter Leaf *(Vernonia amygdalina)* can grow into a tree, but in cultivation it is mostly pruned to a shrub or hedge. The picture of bitter leaf is shown in Figure-2.

Vetiver grass (*Vetiveria zizanioides*) is an important plant used for its flavor and aroma, it belongs to the Poaceae family. Though it originates in India, it is widely cultivated in India, Burma, Ceylon, and from Southeast Asia to tropical Africa and it can be found in most parts of Nigeria. The root system of vetiver is finely structured and very strong. It can grow 3m (10 ft) to 4m (13 ft) deep within the first year[2]. Figure-3 shows the picture of vetiver grass.

Materials and methods

Sample collection and preparation: Water leaf, bitter leaf and vertiver grass were freshly obtained, properly washed with distilled water and oven dried at 65 ^{0}C with the laboratory temperature maintained and controlled at standard temperature and pressure for 96 hours (4 days). The dried leaves were thereafter crushed using electrical grinder machine and subjected to shaking using magnetic shaker into fine particles of 30 µm.

Sample simulation: Oil spillage in an aquatic environment was simulated using four (4) thermoplastic containers of 60 liter capacity each labelled A, B, C and D with A, B, and C representing oil contaminated sites to be remediated with bitter leaf, water leaf and vertiver grass and D representing the oil contaminated site not remediated by the plants. Measured amount of forty (40) liters of tap water was added to each of these containers respectively and 2 liters of bonny light crude oil were thereafter added to each container. The choice of experimental containers for the remediation purpose was made to make sure the crude oil contaminated water exceeds 250 mm depth/height. The water-oil mixture were allowed to equilibrate for 24 hours to allow for contact time and then 10g of each of the powdered plant samples were sprinkled differently into containers A, B and C. No plant sample was added to container D.

Remediation processes: The remediation process was practically carried out using solid – phase technique of extraction (SPTE). The Environmental protection agency (EPA) remediation method (EPA – 33535) was adopted for contaminated sample remediation. Samples from containers A, B and C were set up in a laboratory cartridge, the set up was uninterruptedly allowed to stand for duration of 10 days as the remediation time, thereafter, the liquid was allowed to elute from the laboratory cartridge. Physicochemical parameters and Heavy metal concentrations of the eluted samples were measured. Analyses were also carried out on the tap water as a control for the experiment.

Figure-1: Water Leaf ((*Talinum triangulare*)[11].

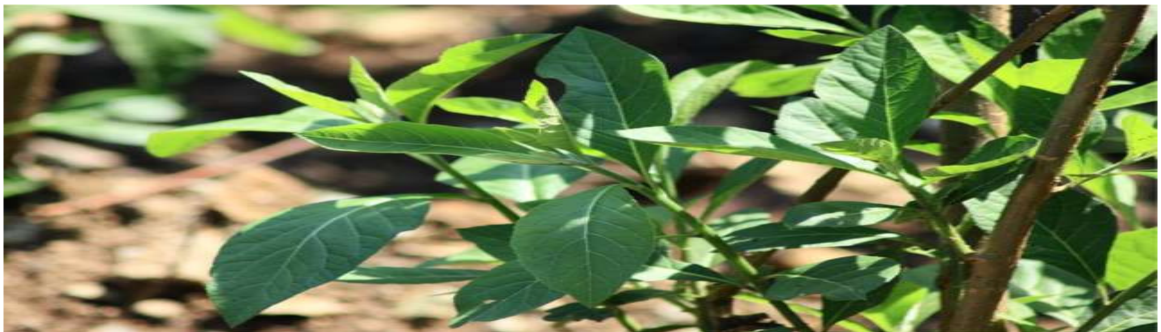

Figure-2: Bitter Leaf (*Vernonia Amygdalina*)[11].

Figure-3: Vertiver Grass (*Vetiveria Zizanioides*)[11].

Experimental work: Physicochemical parameters and heavy metal concentration of samples were determined using the following methods: pH by Glass electrode method[12], Temperature[13], Electrical Conductivity using Conductivity Meter[14], Salinity using Mohr's method (APHA 4500-Cl), Dissolved Oxygen using modified Winkler's method[15] and Heavy Metal concentration (Iron Fe, Copper Cu, Lead Pb, Cobalt Co, Zinc Zn, Manganese Mn, and Nickel Ni) using Unicam 929 Atomic Absorption Spectrometer[16].

Results and discussion

One of the factors that affect the remediation characteristics of an adsorbent are the physicochemical parameters of the environment (adsorbate). The physicochemical parameters of Tap water which was used as a control was compared with the physical and chemical parameters of oil spilled water samples after remediation with bitter leaf, water leaf and vetiver grass as shown in Table-1. Physicochemical parameters considered were pH, temperature, conductivity, dissolved oxygen and salinity of the water samples. The pH is an important parameter used in determining water quality, it indicates the degree of acidity or alkalinity of a liquid, affects the biochemical processes within the aquatic system and can be used to determine the level of effluent discharges within the environment[17]. Water temperature is also an important parameter because it plays an important role in determining chemical reaction rates within the water body. Reactions such as evaporation volatilization and are affected by temperature. Moderately high temperature supports degradation and remediation process by plants. A study showed that remediation by plants rises with a rise in temperature up to 30^{o}C but reduces again at 35^{o}C, results proved that remediation process is greater at higher temperatures than lower temperatures[18]. It has been observed that biodegraded oil accumulations occur at temperatures less than 30^{o}C, however, not all oil accumulations at temperatures less than 30^{o}C are biodegraded[19]. Electrical conductivity gives the measure of the dissolved ionic compounds in the water hence its electrical characteristics. It is also a good indication of the value of total dissolved substances in water. Salinity of a water body is a very important parameter that determines the survival of aquatic plants and animals and it is a measure of the amount of salts dissolved in water[17]. Dissolved oxygen (DO) is another important parameter that affects the survival of aquatic lives. The less than 100% air saturation in salt water reduces the dissolved oxygen in it as compared to what is obtainable in freshwater. DO concentration recommended for humans and aquatic organisms must not be less than 5 mg/L[20]. Results from Table 1 shows that the pH and dissolved oxygen (DO) concentration of the oil contaminated water increased after remediation by each of the plants. The increase in pH after remediation indicates that the crude oil used in contaminating the water sample is slightly acidic. Reduction of DO is expected after crude oil spillage considering the fact that crude oil on water prevents atmospheric oxygen (which is a major constituent of DO in water) from getting in contact with the water surface, there is therefore an increase in DO after cleanup of oil by the plants[18]. The conductivity and salinity of the crude oil contaminated water samples reduced after remediation indicating that the increased conductivity and salinity is related to the crude however Results from Table-1 show that apart from the pH all the physicochemical parameters of the oil contaminated water samples before / after remediation with bitter leaf, water leaf and vetiver grass as well as those of the tap water were within World Health Organization (WHO) specification for portable water[21].

$$\%\ Reduction\ of\ Heavy\ metal\ Concentration = \frac{U-T}{U} \times 100 \qquad (1)$$

Where: U = Heavy Metal Concentration before Remediation, T = Heavy Metal Concentration after Remediation.

$$R = \frac{\sum(X-Mx)(Y-My)}{\sqrt{\sum(X-Mx)^2 \sum(Y-My)^2}} \qquad (2)$$

Where: X = Heavy Metal Concentration after Remediation with Bitter Leaf, Y = Upper limit of WHO Spec. for Heavy metal Conc. For Portable Water, Mean of X (M_x) = 0.026, Mean of Y (M_y) = 7.961, $\sum(X - M_x)(Y - M_y) = 0.232$, $\sum(X - M_x)^2 = 0.002$, $\sum(Y-M_y)^2 = 2069.600$.

Pearson correlation coefficient (R) = 0.1203, Coefficient of determination (R^2) = 0.0145.

Table-1: Physicochemical Parameters / Heavy metal concentration of oil contaminated water samples before and after Remediation.

Parameters	A	B	C	D	Tap Water	WHO Spec.
pH	6.400	6.100	6.960	5.800	6.530	6.5-8.5
Temperature, °C	26.800	25.900	25.600	25.700	26.300	No Spec
Conductivity (µS/cm)	171.000	181.000	92.100	194.200	107.000	<1000
Dissolved Oxygen, (mg/L)	3.300	2.900	3.700	2.200	3.950	No Spec
Salinity (mg/L)	90.000	90.000	60.000	95.000	80.000	<500
Pb	0.060	0.064	0.070	0.096	0.005	0.01
Zn	0.023	0.032	0.045	0.053	0.007	3.00
Fe	0.031	0.116	0.098	0.128	0.049	0.5 - 50
Mn	0.028	0.027	0.047	0.033	0.037	0.500
Co	0.018	0.016	0.021	0.027	0.008	0.200
Ni	0.006	0.008	0.005	0.016	0.013	0.020
Cu	0.014	0.009	0.027	0.032	0.003	2.000

Heavy metals are measured in mg/L. A = Parameters after remediation with Bitter leaf, B = Parameters after remediation with Water leaf, C = Parameters after remediation with Vetiver grass, D = Parameters after oil spill (before remediation).

Table-2: Percentage Reduction In Heavy Metal Concentration Of Oil Contaminated Water Samples After Remediation By Bitter Leaf, Water Leaf And Vetiver Grass.

Heavy metals (mg/L)	A (%)	B (%)	C (%)
Pb	37.5	33.3	27.1
Zn	56.6	43.4	15.1
Fe	75.8	9.4	23.4
Mn	66.3	67.5	43.4
Co	33.3	40.7	22.2
Ni	62.5	50	68.8
Cu	56.3	71.9	15.6
Average % reduction	55.5	45.2	30.8

Table-3: Correlation of Heavy Metal Concentration after Remediation with Bitter Leaf.

Parameter (mg/L)	X	Y	$X – M_x$	$Y - M_y$	$(X - M_x)^2$	$(Y– M_y)^2$	$(X – M_x)(Y-M_y)$
Pb	0.06	0.010	0.034	-7.951	0.001	63.225	-0.273
Zn	0.023	3.000	-0.003	-4.961	0.000	24.616	0.013
Fe	0.031	50.000	0.005	42.039	0.000	1767.241	0.222
Mn	0.028	0.500	0.002	-7.461	0.000	55.673	-0.017
Co	0.018	0.200	-0.008	-7.761	0.000	60.24	0.06
Ni	0.006	0.020	-0.020	-7.941	0.000	63.066	0.157
Cu	0.014	2.000	-0.012	-5.961	0.000	35.539	0.070

Table-1 also shows the heavy metal concentration of the crude oil spilled water before and after remediation. Results obtained show that the concentration of Lead (Pb) before remediation was above WHO specification for portable water. Pb is one of the most important toxic heavy metal within the environment, the higher values of Pb above the permissible limits for portable water calls for serious attention because Pb at elevated level affects intellectual performance in children, increase in blood pressure as well as impairment of cognitive development in adults[22]. Pb can cause a lot of negative symptoms in plants such as growth reduction, negative impacts on the green coloring of plants, root decoloration as well as inhibition of seed germination. High concentration of Pb also negatively affects microbial activities in the soil[23]. The concentration of the other heavy metals in samples A, B, C, D and Tap water are within WHO specification as shown in Table 1 however consitent spill of crude oil could lead to the accumulation of these heavy metals above acceptable limits. Table 2 shows the percentage reduction of each of the heavy metals after remediation with bitter leaf, water leaf and vetiver grass. Results from the average percentage reduction of all the heavy metals show that bitter leaf has the best remediation ability with the highest average percentage reduction while vetiver grass has the least remediation ability with the least average percentage reduction.

Pearson's correlation analsis was adopted to correlate the relationship between the heavy metal concetration of the crude oil contaminated water sample after remediation with bitter leaf (best remediation agent) with the upper limit of the WHO specification for heavy metal concentration as shown in Table 3. Results obtained showd a positive correlation (R) which implies that an X variable with high value is proportional to a Y variable with high value and an X variable with low value will be proportional to a Y variable with low value. On the other hand, a negative correlation means that an X variable with low value will go with a Y variable with low value (vice versa). However with a coefficient of determination of < 0.1 it implies that the correlation between X and Y cannot be fully determined by the Pearson's correlation model[24].

Conclusion

One of the basic factors that determines the cleanliness and environmentally friendliness of a crude oil contaminated site after remediation is the heavy metal concentration. Heavy metals are metals with relatively high density (>7g/cm^3) or atomic weight (>20) and are toxic to humans, animals plants and the environment even in small concentration. Apart from Lead (Pb), the concentration of the other heavy metal after the simulated spill on water were within acceptable WHO limit though consistent exposure to crude oil contamination through spillage may result in the accumulation of these heavy metals within the ecosystem. The concentration of Lead (Pb) was above WHO acceptable limit even after remediation with bitter leaf, water leaf and vetiver grass. High concentration of Lead (Pb) within the environment can result to various negative impacts ranging from high blood pressure, impairment of cognitive development in humans to growth reduction, negative impacts on photosynthesis, decoloration of roots and inhibition of seed germination in plants. Bitter leaf has the best remediation ability with the highest percentage reduction of heavy metals while vetiver grass has the least remediation ability with the least percentage reduction of heavy metals. Apart from the pH, all the physicochemical parameters of the oil spilled water samples before and after remediation with bitter leaf, water leaf and vetiver grass as well as those of tap water (control) were within (WHO) specification.

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