

A Water Purification System using Locally Sourced Materials and Removal of Total Petroleum Hydrocarbon in Contaminated Water

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Abstract: The contamination of surface and groundwater through oil spillage resulting from the production and exploration of crude oil is a critical problem in the world today. This study is focused on constructing a simple and cheap technology using natural and readily available materials as filter beds for the remediation of water polluted by crude oil. Filter bed materials used were clay, corn cobs, activated carbon, fine sand, sand, egg shells, cotton wool, and pebbles. Four glass filters were blown from glass columns of lengths 32cm and inner diameters of 3.3cm each. The filter performance was assessed by analyzing the physical and chemical water quality determinants such as Turbidity level, pH TSS, Hardness, Nitrate, TDS COD, BOD, DO, and EC_w. The total petroleum hydrocarbon (TPH) level was determined using gas chromatography and electron capture (GC-ECD). The result shows that the total petroleum hydrocarbon contaminants in water at an initial concentration of 77.09mg/L were adjusted to 5.07mg/L in the treated sample after 20 days. The results in this study suggest that the filter made of locally sourced materials purified crude oil contaminated water and can be used as an efficient water remediation tool for areas faced with oil spillage issues.

Keywords: Adsorption, Crude Oil, Filter Beds, Total Petroleum Hydrocarbon, Water Pollution,

1. Introduction

Water is considered a critical resource to all living organisms and environmental systems and processes. However, the availability of water continues to dwindle with increasing exploitation, changing climate, and pollution of sources, all of which have collectively compromised the quality of water for various uses including ecosystem services function, and domestic and commercial usage [1] Water pollution through the spillage of crude oil and its fractions is now an existing problem over the years in various parts of the world and has consequently drawn universal attention in recent years [5]. Surface and groundwater resources contamination via crude oil and related products is now commonplace in the oil-bearing regions of the world [2]

A mean value of about 83 million barrels of crude-oil spillage took place yearly between 1994 and 1996 in the United States according to research records; every of this spill contributed about 50,000 barrels of crude oil [3]. According to research, about 9 to 13 million barrels of crude oil were spilled in 2010, and yet during the clean-up exercise, how about 70% of it was not recovered [4]. The Sustainable Development Goal (SDG) number 6 seeks to ensure the sustainable management and availability of water and sanitation for all by the year 2030. Specifically, Goal 6.1 aims to ensure universal and fair access to safe and affordable drinking water for all while Goal 6.3 focuses on improving water quality by decreasing emissions [28], preventing contamination and minimizing the release of toxic chemicals and materials, halving the proportion of untreated wastewater, and increasing recycling and safe reuse of water by a considerable percentage, globally UN[39]. To attain this goal, massive water purification must be adopted at the local levels in low-income nations including Nigeria. Effective water purification requires a good understanding of the type, nature, and sources of pollutants which invariably inform the development of and adoption of appropriate water purification techniques [1].

In Nigeria, the Niger Delta region is one of the areas acquainted with this problem and it has resulted in the distortion of the aquatic life and has denied the indigenes access to clean water and ecosystem services.[13][26][27] due to the extensive level of pollution and contamination since oil exploitation began in commercial quantities over 5 decades ago. It has been reported that such contaminations are often a

result of industrial effluents from oil wells and refineries, ships, pipeline vandalization, and illegal oil bunkering [6][7].

Currently, multiple methods of purification have been developed for the treatment of wastewater from crude oil contamination [29]. These methods include photocatalytic reduction, Reverse Osmosis, Advanced oxidation processes, Distillation, adsorption/absorption, and Electro dialysis amongst others. [8]. However, research has shown however that the application of these methods of water treatment is quite expensive for a low-income economy such as Nigeria and many times ineffective in the removal of pollutants [9] [10].

It has become imperative to develop affordable, environmentally congenial, and technologically appropriate methods of water treatment using locally sourced and modified adsorbents. This study used biological and non-biological but readily available and easily affordable locally-sourced materials such as corn cobs, sand, clay, egg shells, activated carbon, and cotton wool to develop a water purification technique for water contaminated with crude oil and total petroleum hydrocarbons.

The main aim of this study is to focus to construct a simple and inexpensive technology by exploiting natural and readily available materials as filter beds for the remediation of water polluted by crude oil.

2. Materials and Methods

2.1 Study Area

The crude oil contaminated water was obtained from the Kpean community, Khana Local government area of River state Nigeria. Khanalocal government has its headquarters in a small town called Bori, with an area of 560 km² and a population of 294,217 as of the 2006 census. The local dialect among the indigenes Khanna [9][10]. The indigenous members of the community are mainly peasant farmers mostly cultivating farm produce such as tubers and vegetables. Crude oil exploration and development is the major industrial operation in kpean region of Rivers State, Nigeria.

2.2 Collection of Water Sample

Crude oil-contaminated water (10 liters) was collected in two polyethylene gallons. The temperature was determined on-site using a mobile thermometer and an average temperature of 26.40°C was recorded. 10ml of 0.2M H₂SO₄ was added to the sample obtained and it was stored at a temperature of about 4 °C as recommended by [11] [12]

2.3 Collection of Materials

Coconut shells, Corn cobs, Eggshells, Pebbles, gravel, fine sand, and clay (earthenware) were collected from Jos north metropolis and their sizes were reduced using pestles, mortars, and sieves to a range of 0.2mm- 2.0mm and stored in a cool and dry cupboard for further application.

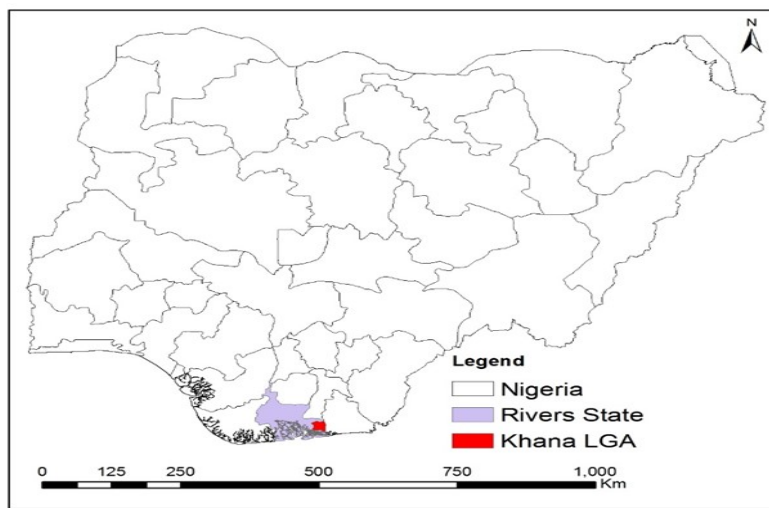


Fig.1. Map of Nigeria, Showing Study Area (Khana LGA)

2.4 Filter Design

A glass column of about 32cm in length with an inner diameter of 3.3cm was blown into a filter column and clamped using a retort stand, Fig 1. There were major things to consider in building the filter beds which affected the filter performance. That was the filter's length or width, the diameter and thickness of its individual constituents. These were the length or depth of the filter, the diameter, and the thickness of its individual constituents [1] [13] [15]. The disposition was based essentially on the function of the single ingredient present in the filter column. From the top down there is clay, corn cobs, egg shells, activated carbon, fine sand, sand, activated carbon, cotton wool, and pebbles, as shown in Fig. 2a and Fig. 2b

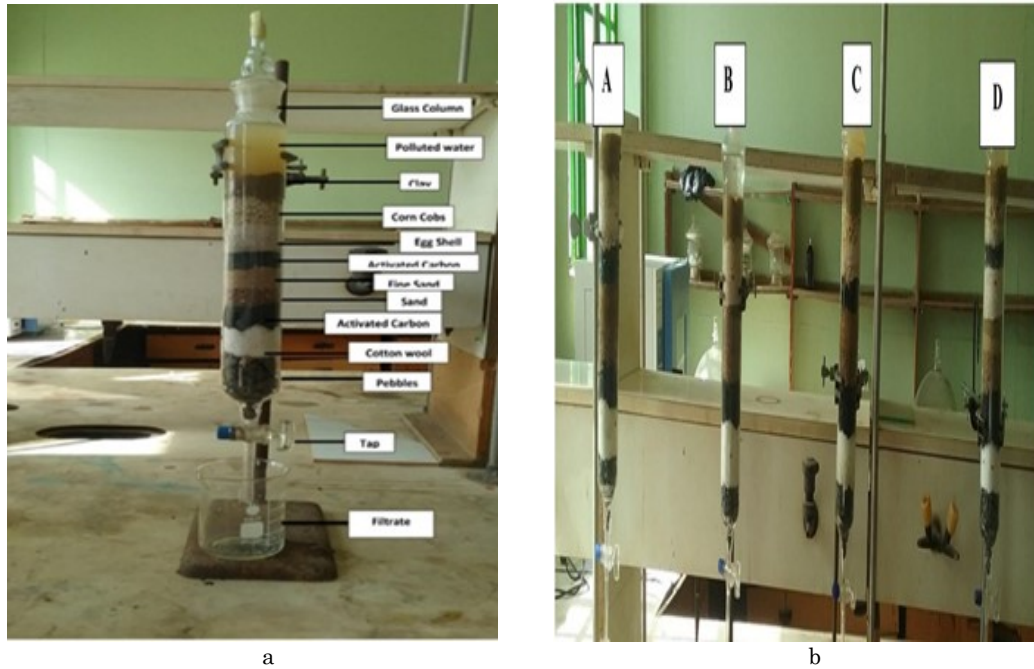


Fig.2. Systematic models of filters (a) Filter profile, and (b) Filter sand

3. Results and Discussion

Flow rate studies (Graphical representation of flow rates as a function of time). Figs 3, 4, 5, and 6 represent the flow rates during the period of the experiment. The filter flow rate was determined by monitoring the elution time of the filtrate through the filter beds using a stopped clock at different time intervals of 5, 10, 15, and 20 days for A, B, C & D respectively. The filters containing the sample were permitted to stand for one hour to ensure full interaction with the filter beds, after which the highest, lowest and average flow rates were determined as described by [1] [2][14] [15] [16].

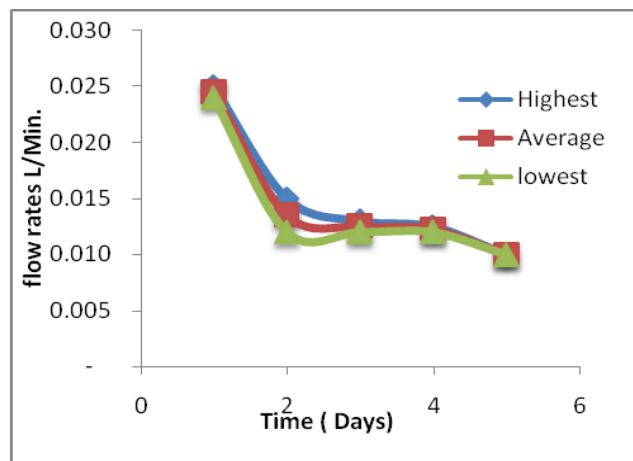


Fig.3. Flow rate Curve for Filter a after 5 Days

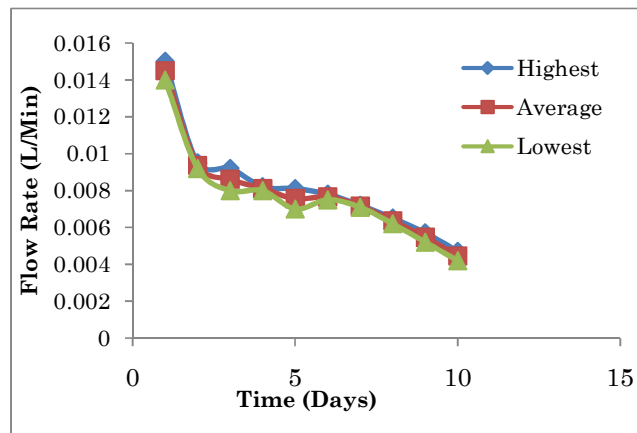


Fig.4. Flow rate Curve for Filter B after 10 Days

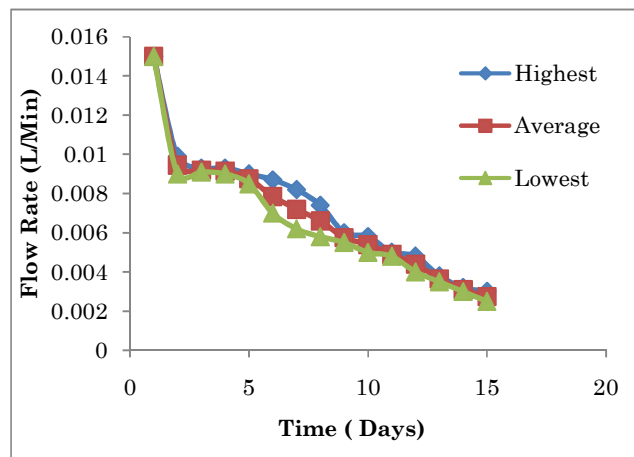


Fig.5. Flow rate Curve for Filter C for 15 Days

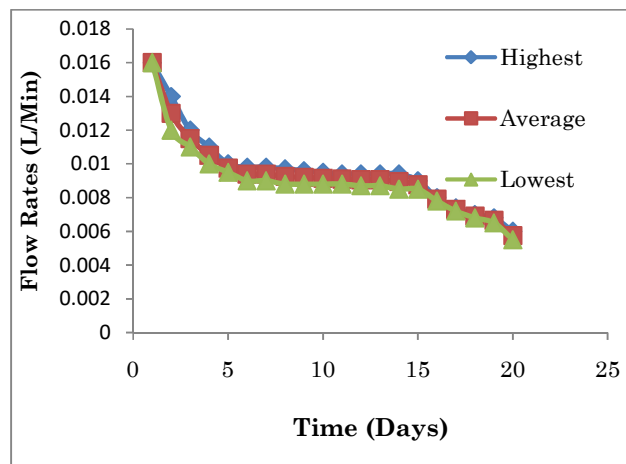


Fig.6. Flow Rate Curve for Filter D for 20 Days

From the graphical representations (Figures. 3, 4, 5 & 6) the flow rate for each of the filters was observed to reduce as filtration time increased. The longer it took for the contaminated water to flow through the filter beds the better the filtration was observed. The graphs showed a quick decline in flow rate as time passed. In the beginning, the sharp decline through the filter was larger than it was after some time and the difference in the maximum, minimum, and average values were seen until around the 5th, 6th, 13th, and 16th days. The graph shows that the ability for water to flow through the filter beds

was greater at the beginning, and as time passed by the permeability of the filter decreased as a result of clogging particles present hence decreasing the flow rate. [1] [2][15].

Water quality is characterized by three basic parameters which the chemical, physical and its rheological parameters based on its conviviality for specific uses such as portable, agricultural, and household uses. [2][17] indicators of water quality are divided into three groups which are physical, chemical, and biological. Temperature, conductivity, turbidity, total dissolved solids, color, odor, and water taste are known as physical indicators. While pH, total hardness, dissolved oxygen, and chemical oxygen demand is referred to as chemical indicators include [2].

The measure of acidity is defined as pH, this is an important water quality indicator as small changes in its value can adversely affect life. From Table 1 the pH value of untreated was slightly acidic (5.96) and as the purification process went on, it was observed that there was a gradual adjustment from (5.96-7.27). This was significantly close to the control and also within the prescribed guidelines of FEPA [37] and NIS[36] in collaboration with the SON governing council guidelines for drinking water.

When the concentration of suspended particles in water increases there is a tendency that the amount of sunlight penetrating the water surface to decrease hence turbidity increases [14]. Water can be considered to be dangerous to aquatic life if it is highly turbid [20] [25] however, it will not be correct to think that clear water is healthy always [19]. Slightly turbid water can be very healthy, while microscopic toxins or impermissible levels of nutrients could be present in clear water [21] [22]. From Table 1 it is observed that the turbidity of the untreated water was 670 NTU and decreased as the number of days of treatment passed by for each of the filters, Indication that the dissolved and suspended matter constituting the water contamination was gradually adsorbed as the contact time was increased. The results also indicated that the turbidity value was relatively high and slightly above the control value (18mg/L) for filter D and significantly above the prescribed guidelines. This could be attributed to the granular and particulate nature of the adsorbents used in the filters [2].

TDS comprises ionic particles dissolved in organic matter as well as sand particles. In determining the quality of water the analysis of TDS is critical as it gives useful information about the purity of water [20]. Impure water may have high values of TDS indicating that the water may be harmful to aquatic life such as fish and consequently affect fish eggs depending on the ionic properties of water [21]. From Table 1, the TDS value of the untreated sample of water was analyzed to be 405 mg/L. The results revealed that as the contact time increased, the TDS level was adjusted from 405 (Untreated) to 360.0, 251.0, 140.0, and 121.0mg/L for filters A, B, C, and D respectively as a result of adsorption of dissolved solids on the surface of the adsorbents over time.

Table 1. shows that the untreated water detected a nitrate content of 350mg/L, and after treatment, the nitrate content was reduced to 41.3, 18.0, 4.1, and 1.5mg/L for filters A, B, C, and D respectively, indicating that the adsorbents used were capable of adsorbing nitrate contaminants on to their surface hence removing them from water by 88.20%, 94.85%, 98.82%, 99.57% for filters A, B, C, and D respectively [2]. The results also showed that although filtrate from filter D still had some nitrate content (1.5mg/L), it had no adverse health effects on humans, plants, and aquatic animals as it was still within the permissible limits for water use when compared with standard guidelines (10-50mg/L).

The total suspended solid (TSS) is a measure of the undissolved solids in a solution which indicates the concentration of Total solids (TS) and (TDS) in water [14]. Table 1 shows the initial concentration of TSS as 4500mg/L and after treatment, the TSS was observed to have decreased for filters A, B, C, and D as 3832, 2100, 1500 and 1300 mg/l respectively, while the control sample was found to be 1000mg/L. The ability of the oil to attract particulate matter to itself causing a thick layer to be formed on the surface of the water may be responsible for the increases in TSS and TS [23]

The susceptibility levels of oxidation of organic and inorganic substances present in water bodies, sewage, and industrial effluents are often analyzed using chemical oxygen demand (COD) [14] [22]. From Table 2, the COD for untreated water samples appeared to be higher (205.0mg/L) but it was observed to reduce gradually by significant amounts as the filtration process went on for filters A, B, C, D, and the control. The recorded values of 150.0, 122.0, 79.0, 37.0, and 15.0 mg/L were shown for filters A, B, C, and D and the control sample respectively, which were within the guidelines of the World Health Organization [34].

The biological oxygen demand (BOD) is used to determine the level of carbon loading in the water as well as a biochemically degraded organic matter [14] [22]. From Table 2, the BOD for the untreated water sample was analyzed to be 2.01mg/L and after treatment, it was observed that the BOD was found to increase for filters A, B, C, and D as 2.33, 2.40, 2.66, and 2.85 respectively, with the control sample as 4.10mg/L.

The quantity of gaseous oxygen dissolved in water which is considered a very important factor for all forms of aquatic life is known as dissolved oxygen (DO). Almost all forms of chemical and biological activity within water bodies are influenced by the amount of oxygen dissolved in water [14][24]. When

there is no less than 2mg/L of oxygen in a particular water sample it means life cannot exist in it and also it indicates the presence of microorganisms or particles in it therefore the amount of oxygen dissolved in a sample must not be less than 2mg/L. From Table 2, the dissolved oxygen for untreated water was determined to be 1.5mg/L. It was observed that there was a significant increment in the concentration of the dissolved oxygen for all of the filters (A, B, C, and D) with values of 3.0, 5.0, 4.0, and 6.5mg/L, respectively.

Table 1. Obtained water quality results for treated and untreated water

Filter	pH	Turbidity(NTU)	TDS(mg/L)	Nitrates(mg/L)	Viscosity(cp)	Ash content %
Untreated	5.96	670.0	405.0	350.0	3.32	0.38
A	6.06	78.8	360.0	413.0	3.08	0.35
B	6.86	51.1	251.0	18.0	3.07	0.02
C	6.95	38.9	140.0	4.1	3.07	0.02
D	7.72	21.0	121.0	1.5	3.07	0.02
Control	7.40	18.8	117.0	0.0	3.07	0.02
WHO[34]	8.2-8.8	1.5	-	50	-	-
USEPA[35]	-	-	-	10	-	-
FEPA[37]	6.5-8.5	-	500	50	-	-
NIS[36]	6.5-8.5	5.0	500	50	-	-

Table 2. Obtained Water Quality results for Treated and Untreated water

Parameters	TSS(mg/L)	COD(mg/L)	BOD(mg/L)	DO(mg/L)	E/C (μs/cm)	T°C
Untreated	4500.0	205.0	2.10	1.5	280.0	29.6
A	3832.0	150.0	2.33	3.0	290.0	27.3
B	2100.0	122.0	2.40	5.0	300.0	27.1
C	1500.0	79.0	2.66	4.0	190.0	27.3
D	1300.0	37.0	2.85	6.5	190.0	27.5
Control	1000.0	15.0	4.10	8.0	180.0	27.5
WHO[33]	1000.0	12.5	0.8-5.0	7.14	1000.0	Ambient
USEPA[35]	1000.0	-	-	-	1000.0	Ambient
FEPA[37]	1000.0	-	-	-	1000.0	Ambient
NIS[36]	1000.0	-	-	-	1000.0	Ambient

The measure of the salinity and the extent to which water can conduct an electric current is referred to as electrical conductivity in water (EC_w) and it is measured in micro Siemens per centimeter (us/cm). EC_w gives information about the concentrations of (TDS) or the level of salt in a particular water body [14] [25]. Table 2 shows the electrical conductivity of untreated water, which was determined to be 280μs/cm for the untreated water and increased to 290 and 300μs/cm for filters A and B, respectively. The increase in the magnitude of the electrical conductivity was a result of the nature of the adsorbents such as the egg shells used as they produced more dissolved solids and CO_3^{2-} ions in the treated water, hence giving rise to the high electrical conductivity of water.

From Table 2, filters C and D were observed to have a lower and constant electrical conductivity value of 190μs/cm as a result of the saturation of the filter beds in filters C and D, respectively. This value was also observed to be very close to that of the control sample. When compared to standard guidelines for water quality, it was found that the electrical conductivity was within the set guidelines (1000μs/cm) for both treated and untreated water samples.

The amount of petroleum-based hydrocarbons in the environment that can be measured is generally referred to as TPH. The results of TPH simply indicate that petroleum hydrocarbons are present in a sampled media.

To extract polar organic substances from the non-polar hydrocarbons present in the solvent, the crude oil-contaminated water extracts were pretreated with silica gel. TPH was determined using gravimetric analysis. Gas chromatography (GC) was used to determine the total petroleum hydrocarbon (TPH) from the analysis of petroleum hydrocarbon (PH). Using gas chromatography (Perkin model 5890) with an electron capture detector (Ni 63) and a low polar HP-5 column of 30m length, 0.32mm i.d, and thickness of 0.25μm film was used. The carrier gas was nitrogen-flowing at a rate of 50ml/s. An HP 3396 integrator was used for the data processing. For this research, the temperatures of 240 and 310 °C were set for the injector while the oven temperature for the detector was programmed at 150 °C at the beginning (5-

minute hold) and was finally increased to 310 °C at the rate of 5 °C/min for a total duration of 35 minutes analysis [12].

Table 3. GC-ECD Results for Untreated and Treated water samples

Compounds	Retention Time[min]	Untreated Sample Conc.	Treated Sample Conc. [Filter D= 20 days]	% Removal
n-8	9.524	ND	ND	-
n-9	10.502	ND	ND	-
n-10	11.716	ND	ND	-
n-11	12.357	ND	ND	-
n-12	13.864	ND	ND	-
n-13	14.876	ND	ND	-
n-14	15.782	ND	ND	-
n-15	16.685	3.54463	0.04431	98.74%
n-15	17.521	2.85761	0.25149	91.19%
n-16	18.448	6.89344	0.49754	92.78%
n-17	18.928	0.85433	0.33613	60.66%
n-18	20.026	8.56542	0.01598	99.80%
n-19	20.665	6.12383	1.07583	82.43%
n-20	21.436	4.34065	0.04064	99.06%
n-21	22.161	0.65454	0.04047	93.8%
n-22	22.819	7.64534	0.22532	97.05%
n-23	23.464	7.81154	0.31852	95.92%
n-24	24.058	7.35455	0.32506	95.92%
n-25	24.827	7.35455	ND	-
n-26	25.501	7.55465	0.49964	93.38%
n-27	26.355	3.67546	0.48853	86.70%
n-28	27.262	3.44454	0.49754	85.56%
n-29	28.382	3.78964	0.02664	99.30%
n-30	29.701	1.00116	0.34656	65.38%
n-31	31.206	0.97650	0.03550	96.36%
n-32	33.187	ND	ND	-
n-33	33.530	ND	ND	-
Total		Σ 77.08783	Σ 5.0657	93.42

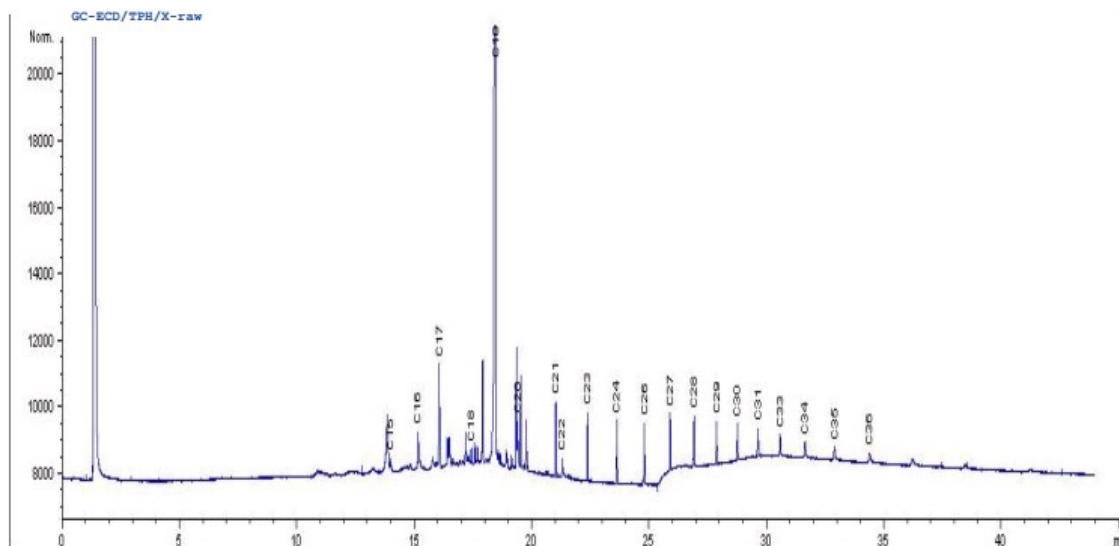


Fig.7. GC-ECD Chromatograph for Untreated Water Sample

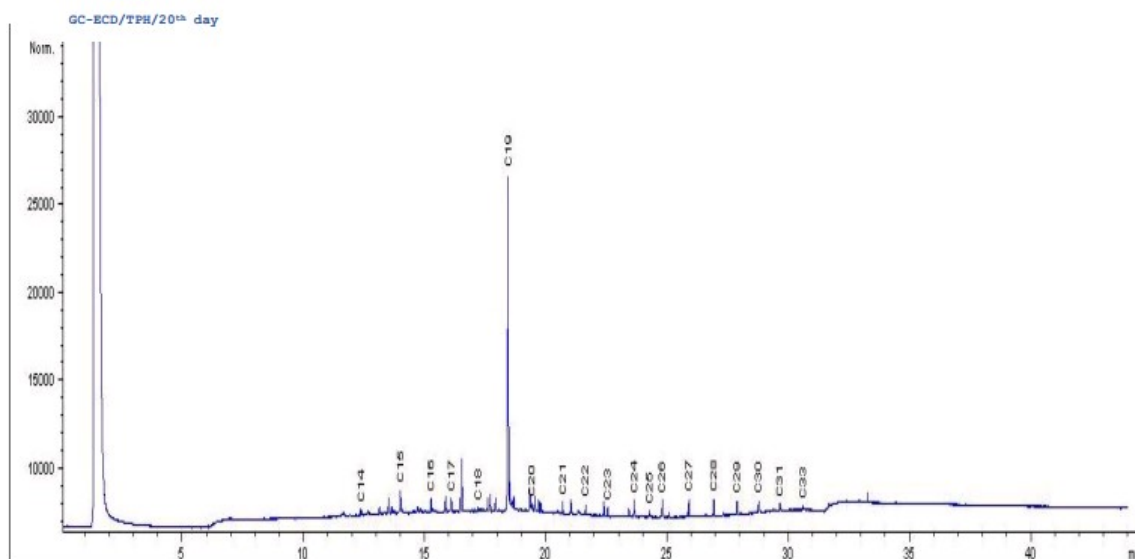


Fig.8. GC-ECD Chromatograph for Treated Water Sample

Fig. 7 and Fig.8 show the TPH concentration for treated and untreated water samples. The GC-ECD analysis showed that the organic contaminants were of the alkane homologues series and were detected from C₁₄ to C₃₀ with an initial TPH concentration of 77.01mg/L for the untreated water sample (Fig. 7). After treatment the organic compounds were removed individually in significant amounts from a range of 60.66% to 99.80% with the complete removal of pentacosane (C₂₅) from the treated water [2]. The TPH concentration after treatment with filter D (20 days) was analyzed and found to have reduced to 5.07mg/L (Fig. 8) as shown in Table 3 with total removal of 93.42%. When compared with the standard guidelines set by (DPR [38]) and (FEPA [37]), the result obtained for the treated water was within their permissible limits of 10mg/L.

While several studies [30][31][32] have been conducted to show levels of water pollution in parts of Nigeria, the novelty of this study is in the fact that it seeks to develop a local solution to water treatment, a much-needed effort towards achieving the SDG 6 in a country like Nigeria where resources are scarce in the face of extensive water pollution caused by decades of neglect and poor management of crude oil activities. The combination of locally sourced materials as adsorbents used in the purification of crude oil contaminated water is capable of removing organic compounds such as pentacosane (C₂₅) completely from water while reducing other polluting agents by very significant amounts in the range of 60.66% to 99.80%, resulting to a TPH Removal of 93.42%. An adjustment in water pH, turbidity, TDS, TSS, COD, BOD, Nitrates, Ash Content, and viscosity was observed for the four filters A(5 Days), B(10 Days), C(15 Days), and D(20 Days) as the number of days for the experiment increased. The filters generally showed an adjustment in the water quality parameters of the treated water samples when analyzed. It also was seen that the water quality parameters were adjusted to a level significantly close to the guidelines set by WHO, USEPA, FEPA, NIS, and DPR. Filter D (20 days) was observed to give the best filter performances in terms of water quality obtained when compared to filters A (5 Days), B (10 Days), and C (15 Days).

4. Conclusion

This study was mainly focused on constructing a simple and cheap technology by employing natural and readily available materials as filter beds for the remediation of water polluted by crude oil. From the outcome of this study, it is suggested that further work should be carried out to determine the effect of the filters on biological parameters such as E-coli form and viruses from organic, inorganic, and feces produced by humans and animals. Also, the effect of a longer contact time and filter saturation point should be investigated to maximize the purity and safety of the treated water. The results obtained have shown that better quality and purity of water are obtained from the filter when the water takes a long time to flow through the filter beds. However, the safety and lifetime of the filter should be ascertained in order to know the biological and health implications of the treated water at any given time.

Compliance with Ethical Standards

Conflicts of interest: Authors declared that they have no conflict of interest.

Human participants: The conducted research follows the ethical standards and the authors ensured that they have not conducted any studies with human participants or animals.

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