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DEVELOPMENT OF BIOSORBENT MATERIALS FOR THE REMOVAL OF TOXIC ELEMENTS SOLUBLE PETROLEUM FRACTIONS FROM OIL SPILLED CONTAMINATED WATER BODY

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Abstract
Advance materials are new materials with enhanced properties that are internationally designed for superior performance. This study was centered on the uses of Comonsus Ananas and Blighia sapida plant extracts synthesized as a biosorbent materials for removing petroleum fractions from oil spilled water body. Ananas comosus leaves, Blighia sapida seeds and raw oil spilled water are the combined materials used for this work. Adsorbent preparation and characterization for sorption studies was carried out. Simulation of oil spilled water and adsorbent raw samples, chemical treatment with thiol groups and modification of adsorbents for sorption studies were carried out and application of the adsorbent to raw oil spilled water was determined. Adsorption Isotherms test was carried out alongside with Batch adsorption experiment. Identification of Metal ions and Binding Functional Groups were all characterized Using Fourier Transform infra-red spectroscopy (FTIR) and the heavy metal removal from the oil spill were determined. The result obtained confirmed that biosorbent material synthesized (Pinesorb) was capable of removing toxic petroleum fraction from oil spilled water body.

Keywords: *Comonsus ananas, blighia sapida; biosorbent; potentially toxic elements*

Introduction

Long time ago, oil spillage in the area where oil and gas operations had taking place has been a disturbing issue, hence with increasing environmental awareness and legal constraints imposed on oil spillage, there is need to develop cost–effective alternative technologies for the removal of potentially toxic elements (Ifeoma et al., 2019). Considerable attention has been devoted to the development of novel and cost elevating and environmentally friendly materials for the remediation of oil spillage. It is known that water being a vital resource for life is increasingly being polluted by anthropogenic activities such as oil spillage, urbanization, population growth, poor land use, and agricultural activities had led to rapid degradation of surface and ground water quality. This oil spillage remains a serious concern especially in oil producing regions of the world. Lots have been done to address oil contamination of water by regulating bodies such as Environmental Protection Agency (EPA, 2018). Oil spills occurred as a result of inadequate servicing and maintenance of the oil and gas facilities such as preventer blowout, wellhead, flow lines or pipelines, sabotage, accidental and equipment failures by the oil companies. Moreover, the implementation of wise use concept of wetlands ecosystem as an approach, within the context of sustainable development goals as a centerpiece of modern efforts to manage wetlands will help the policy makers to integrate wetlands ecosystem to environmental planning to ensure availability and sustainable management of water and sanitation for all (Hycienth et al., 2009).

However, on yearly basis, both the government and various multi-national private oil companies contended with hazards of crude oil spillage which affected both aquatic and terrestrial ecosystems. Most of these oil spills occur due to underground oil well blowouts, tanker accidents, storage tank failures, production platform blowouts, intensified petroleum exploration on the continental shelf, transfer operations between ships and shores, economic sabotage and youth restiveness like the Niger Delta militias in South-South, Nigeria as reported by Egwaikhide et al. (2017). It can be recast that Oil spillage has been a global issue that has been occurring since the discovery of crude oil, which was part of the industrial revolution. The total spillage of petroleum into the oceans, seas and rivers through human activities is estimated between 0.7 - 1.7 million tons per year (Adati, 2012). Oil spills have posed a major threat to the environment of the oil producing areas, which if not effectively checked can lead to the total destruction of ecosystems (Muhammed, 2021), as presented in Plate 1 and Plate 2.

Moreover, Niger Delta is among the ten most important wetlands and marine ecosystems in the world. The oil industry located within this region has contributed immensely to the growth and development of the country. Oil exploration activities has rendered the Niger Delta region one of the five most severely damaged ecosystems in the world (Jacqueline, 2016).

This research is centered on the development of a biosorbent material from agricultural waste product for removal of Potentially Toxic Element (PTE) and soluble petroleum fractions in the oil spilled affected area. This is justified as the conversion of these agricultural waste into adsorbent that can remove potentially toxic metals and soluble petroleum fractions from oil spill affected water body would constitute a significant contribution in the search for cheaper adsorbent material with the added elegance of using one environmental problem to help solve another.

government to enforce the law catalyzed by corruption which are the major reasons for this problem. The analysis of Variance Approach on the Causes and Terrain of oil spillage in Niger Delta Region of Nigeria, using two-way Anova model was carried out and result of the two-way ANOVA shows that sabotage is majorly the cause of oil spillage in the Niger Delta irrespective of the terrain or incident site (Ifeoma et al. 2019). Ascertaining the changes in the physicochemical properties and heavy metals level of crude oil polluted soil, using the randomized block design. It was discovered that crude oil affects soil properties irrespective of seasons as reported in the work of Ohanmu et al., 2018). Also, Muhammed et al. (2021) carried out a research on description of techniques for combating main oil spills on the chemical dispersants, the mechanical recovery and in situ burning and looked at their possible application in the Arctic, the Arctic according to them were described as part I and in their part II, the description of the techniques used in ascertaining the environmental effects was investigated and in Part III, they monitored the effect of the spills and its responses and so on. They concluded by saying that wildlife shouldn't be exposed to these oil spillages likewise humans. Olusola et al. (2018) investigated the application of an enduring model that could aid in natural environmental conservation by the use of descriptive legal analysis and secondary data sources to ensured prudent management, sustainable development strategies and environment conservation were imperative and necessities for the Nigerian economy. The result of the studies shows that oil spills in Nigeria should be addressed and, that positive attitude should be put in place by the oil operators and the government alike so as to reduce the health hazard caused by these spillages.

Okonkwo (2014), examine the socio-economic impacts of oil spills which includes the damage of

Plate 1: Oil Impacted Site in Ogoni land oil field

Plate 2: Spilled oil in Ogoni land Oil field

farmlands, prostitution and rape, impacts of traditional institutions of authority on cultural values, conflicts, destruction of cultural areas and spirituality, destruction of communities as well as forced displacement, migration, and environmental refugees. The socio-economic impacts of the oil spill

Muhammed, (2021) carried out a research work on Environmental Public Health and Socio-Economic Issues of Oil Spillage in Niger Delta, Nigeria and find out that Oil spillage is indeed a global issue, but obviously, it is on its high side in the Niger Delta which was due to the failure and weakness of the are really multi-dimensional and contribute a lot to most of the insurgencies in the Niger Delta and Nigeria at large. Nieva et al. (2020) Investigated the potential of powdered pineapple crown leaves (PCL) as an effective adsorbent for the removal of crystal violet (CV) from aqueous solution using batch and column studies. The study shows that FTIR analysis of PCL surface before and after adsorption revealed that hydroxyl and carboxyl functional groups are among the groups responsible for surface bonding with CV. In addition, SEM photographs of the adsorbent before and after revealed clumping on the surface of PCL, possibly indicating the sites where CV had been adsorbed. Elemental analyses through XRF revealed that K^+ ion is a major part of PCL, and this could explain the affinity of CV for PCL through cation-π interactions (Ahmad et al., 2009).

Materials and Methods

Materials and Equipment

The materials used for this research work are "Ananas comosus" stems, "Blighia sapida" seeds and raw oil spill water as shown in Plates 3 (a-d) and 4 (a-c). Ananas comosus leaves were collected as remnant from a local market (Oja-Oba) in Kabba, Kogi State, Nigeria. The oil spilled water body sample was collected from Nembe oil field in Bayelsa State, Nigeria. Analytical grade chemicals and reagents used, were purchased from Debos Scientific, Ibadan, Oyo State, while Blighia sapida seeds were procured from Niger Republic central market. The pH values were adjusted as desired with the aids of NaOH pellets and HCl acid. Contaminants in the peels of the mixture of Ananas Comonsus leaves and Blighia sapida seeds was handpicked and then soaked in water to free the sample completely from impurities. The sample, was first sun dried for 7 days before being oven dried for 24 h at 130oc to obtaine fine particles of < 0.5 mm were obtained via simultaneous milling and sieving. The sample was calcination in a crucible at 681.10oC for 2.60 h (Popoola et al., 2018) using a muffle furnace (Carbolite, ELF11/6B, S/N 21–403,009), at National Research Institute for Chemical Technology, Zaria (NARIT). The following equipment were used for the research work: Fourier Transform infra-red spectroscopy (FTIR), Flame Atomic Absorption Spectrometer (FAAS), Inductive Couple Plasma-Optical Emission Spectroscopy (ICP-OES), Inductive Couple Plasma-Mass Spectroscopy (ICP-MS), Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD).

Ananas Comonsus is in the bromeliad family. It has about 45 general and 2000 species. Some of the species are consumable while others are not edible. They are mostly found in savanna and guinea savanna region. Blighia sapida belong to the family of Sapindaceae, it is soapy in nature and the fruiting period is between March and September. The English name is Akee, in Igbo it is called Okpu and called Isin in Yoruba language.

Methods

Adsorbent preparation and characterization for sorption studies were carried out. Simulation of oil spilled water and adsorbent raw samples, chemical treatment with thiol groups and modification of adsorbents for sorption studies were equally carried out and application of the adsorbent to raw oil spilled water. In addition, Adsorption Isotherms test was carried out and Batch adsorption experiment. Determination of the contact time, pH value, particle sizes, biosorbent dosage, background ions, temperature, kinetics, adsorption isotherm model's characterization of the adsorbents were all

Plate 3: (a) Red Spanish (b) Queen (c) Smooth (d) Abacaxi: (Representation of different species of Ananas Comonsus, (https://www.Sciencedirect.com)

Plate 4: (a) Akee black seed (b) Akee Apple (c) Sauverry Akee brown seed

(Different species seed of Blighia Sapida, (https://www.Sciencedirect.com) determined including moisture content, ash content, bulk density, and surface area of the substrates and Identification of Metal ions Binding Functional Groups Using FTIR.

3.3. Experimental Design

Taguchi 2 X 3 experimental design was applied to optimize the adsorption of heavy metals (Pb2+, Zn2+, Fe2+ and Cu2+) mixture with the aids of activated carbon prepared from Ananas comosus leaves and Blighia sapida seeds. The effects of four factors namely: adsorbent dosage (2, 4 and 6 g), reaction time (1, 2 and 3 hrs), temperature (30, 40 and 50 ◦C) and pH (2, 6 and 8) on the adsorption of each heavy metal from produced mixture using the local activated carbon were studied. An L9 orthogonal approach with a set of 9 experiments was applied at three levels designated as 1, 2 and 3 as shown in Table 1.

The responses were expressed as the percent removal of (Pb2+, Zn2+, Fe2+ and Cu2+) from produced mixture. Stirring rate of the temperature-controlled equipment was kept constant at 140 rpm. Batch Adsorption experiments Table 2 shows orthogonal Taguchi parameters variation for the experimental design of batch removal of heavy metals from produced water via a heater (Stuart heat-stirrer SB162) designed with stirring and temperature adjustable features. Four process parameters were varied within three levels. A specified dosage of the activated carbon from Ananas comosus" leaves, "Blighia sapida" seeds was used for 60 mL of produced mature or water in 300mL flask. Solution pH was adjusted by adding NaOH pellets or HCl solution and placed in a beaker at a constant rotation speed of 170 rpm. The temperature was adjusted while reaction was stopped after the reaction time was attained as

Table 1: Description of examined process variables at different level

S/No	Variable	Description	Unit	Type	Level		
1	D	Dosage	g	factor	2	4	6
2	t	Time	hr	factor	1	2	3
3	T	Temperature	°C	factor	40	50	60
4	p	pH	_	factor	2	6	4
5	L	Pb^{2+}	96	response	_	_	_
6	Z	Zn^{2+}	96	response	_	_	_
7	f	Fe^{2+}	96	response	_	_	_
8	C	Cu^{2+}	96	response	_	_	_

Table 2: Experimental Design for Removal of Toxic Metals from Produced Mixture / Water

Run	Dosage (g)	Time (hrs)	Temperature (◦C)	pH
1	2	2	30	4
2	4	4	40	6
3	4	3	40	6
4	4	2	50	2
5	6	1	50	6
6	6	1	40	0
7	2	2	30	2
8	4	4	40	4
9	6	6	50	0

specified, Table 2. The filtrate and residue were separated using Whatman filter paper. The filtrates were stored in separate sample bottles while spent adsorbents (residues) were separately wrapped with aluminum foil and placed in a desiccator for further laboratory analysis. The concentrations of heavy metals in each filtrate were determined using Atomic Adsorption Spectrophotometer (Buck scientific model 210 VGP). The percentage of each heavy metal removed from produced mixture/water using activated carbon from Ananas comosus leaves Blighia sapida seeds was calculated using Equation 2.

FTIR, SEM and XRD characterization

The prepared activated carbon from Ananas comosus stems and Blighia sapida seeds was characterized before and after heavy metals removal from produced mixture / water using (FTIR, SEM and /EDX) to ascertains the mineral contents, physical properties and mechanical viability, following the procedure of the research carried out by Popoola, (2019).

Method of Data Analysis

Primary sources of data were generated with the use of test-tube, absorbent, adsorbates and raw oil spilled water. Also, Langmuir Isortherms Equation was considered base on the following assumptions:

i. Adsorption is always monolayer.
ii. The adsorbed layer is homogeneous across the adsorbent
iii. No interaction between the molecules that are adsorbed next to one another
iv. Each adsorbent has different energy sites, but the adsorption energy (heat of adsorption) is the same for all of them.
v. Adsorption is a reversible process. The rate of adsorption depends on the fraction uncovered and pressure.

The Derivative of the Langmuir Adsorption Isotherm

Langmuir proposed that gas molecules collide with a solid surface and get adsorbed. Some of these molecules then quickly evaporate or are desorbed. Between the two opposing processes in an irreversible process, adsorption, and desorption, a dynamic equilibrium is eventually established as preented in Equations 1-2 (Lekan et al., 2022).

$$qe = (C_i - C_e)v/m \qquad (1)$$

$$\%\ \text{removal} = (C_i - C_e)/C_i\ x\ 100\% \qquad (2)$$

Where Ci is the initial dye concentration (mg/L), Ce is the equilibrium dye concentration in solution (mg/L), V is the volume of the solution (L), and m is the mass of the biosorbent (g). Moreover, the percent removal of the dye from the solution was calculated using Equation (2).

3.7. The Biosorption Isotherms

The equilibrium data were fitted to Langmuir and Freundlich isotherm models, which are expressed as Equations (3) and (4), respectively (Chakraborty et al., 2012).

$$C_e/qe = C_e/qm + 1/(K_L qm) \qquad (3)$$

$$Log\ qx = Log\ K_f + 1/nLogC_e \quad (4)$$

where qe and Ce are solid and liquid phase concentration of adsorbate at equilibrium (mg/L), respectively, qm is the maximum adsorption capacity (mg/g), KL is the Langmuir adsorption equilibrium constant (L/mg), KF is the Freundlich constant related to sorption capacity (mg/g) (L/g)1/n where n is the heterogeneity factor which gives the measure of biosorption favorability.

Results and Discussion

The result of the experiment carried out are presented and discussed as illustrated in Figures 1-4.

As shown in Figure 1, the produced pinesorb adsorbent contained OH^- group found in the cellulose part of the mixture of comonsus ananas and Bliphia Sapida whose transmission frequency was identified at 3405.06 cm^{-1} before the adsorption and 3415.67 cm^{-1} after the adsorption process. Also, the carboxylic group -COOH was identified at the peak value of 2923.15 cm^{-1} and 2922.02 cm^{-1} before and after adsorption respectively. While the aldehyde and ketone components of the adsorbent were identified at peak values of 1733.82 cm^{-1} and 1734.42 cm^{-1} before and after adsorption process was carried out. Therefore, the functional groups proved that the adsorbent was produced from Comonsus ananas and Bliphia Sapida Seeds.

Figure 2, shows the effect of dye concentration and colour removal using the adsorbent produced. As shown in Figure 2a, as the bio-sorbent capacity is increased, the dye (the dye is the violent colour pigment released into the water by the contaminant from the petroleum fuel in contact with the water body) concentration also increased to 150 mg/L. However, as the amount of adsorbent incorporated is enhanced, the rate of dye removal was also enhanced as shown in Figure 2b, where it was evidence that, the dye concentration was reduced from 98 % down to 88 %.

The efficiency of the produced adsorbent was further justified by the linearized Langmuir and Freundlich adsorption isotherm as depicted in Figure 3. As shown in both Figure 3 a and b, the isotherms were fitted in first order linear adsorption isotherm, which proved that both Langmuir and Freundlich isotherm suggested earlier were enough to predict the order.

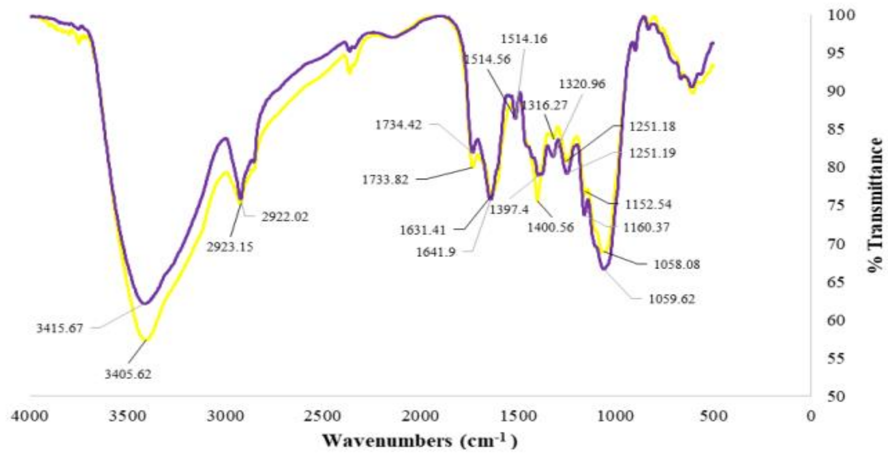


Figure 1: FTIR spectra of powdered Adsorbent before (●) and after adsorption (●)

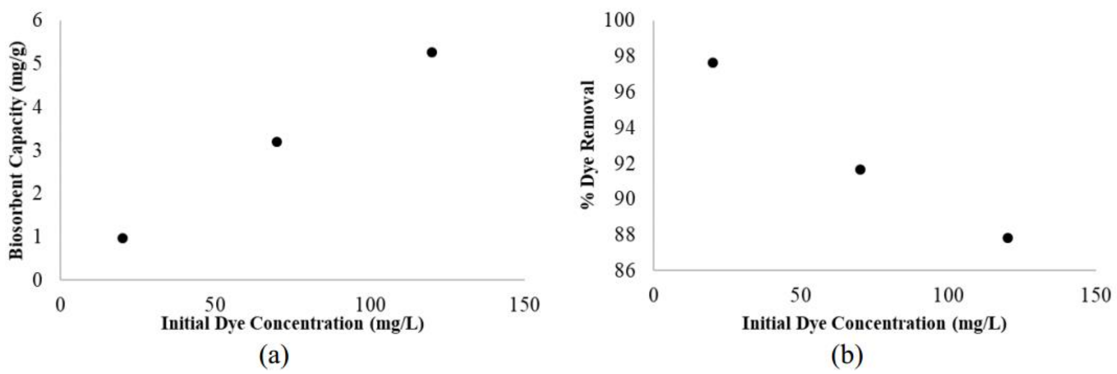


Figure 2: Effect of initial dye concentration on (a) bio-sorbent capacity and (b) %removal of CV on powdered PCL

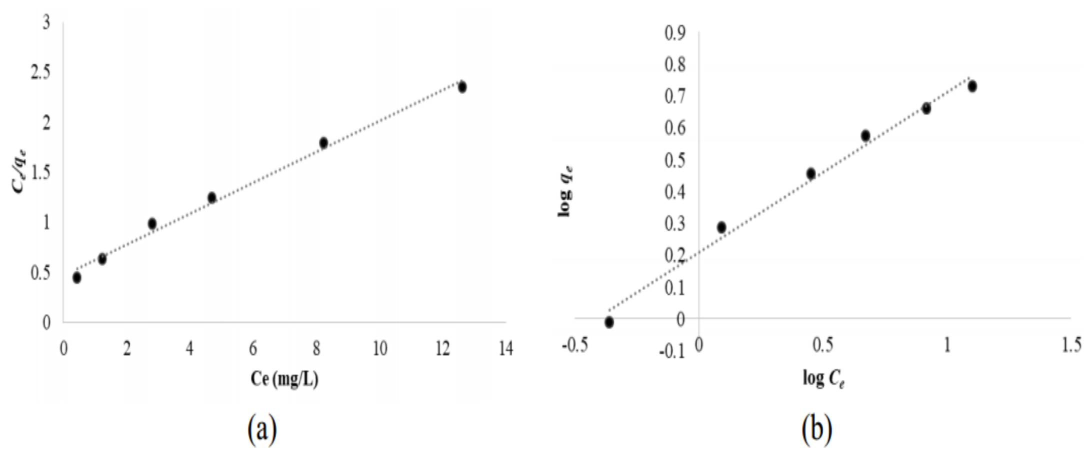
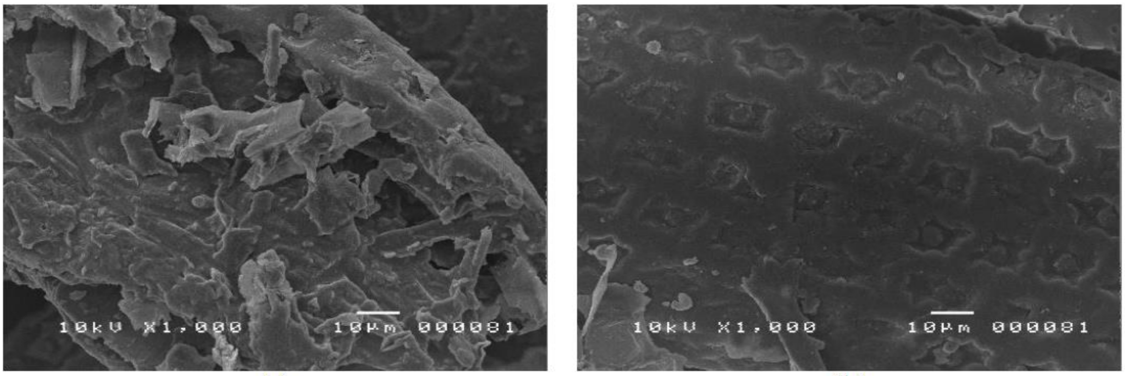


Figure 3: Linearized (a) Langmuir and (b) Freundlich adsorption isotherms



(a) (b)

Figure 4: SEM micrograph of powdered adsorbent presented the SEM image of the morphology of the adsorbent before and after adsorption.

The morphology of the adsorbent is more compacted before adsorption process as shown in Figure 4a, when compared to Figure 4b that shows clearly more dispersed morphology, indicating that, reaction has taken place, adsorbing the spilled oil and incorporated it within its body. This proved that, the adsorbent produced was able to adsorbed the oil efficiently and remove the heavy metal or contaminants injected / released into the water in coming contact with the oil spillage.

Conclusion

This research work has established the method of developing a biosorbent material from agricultural waste product for removal of heavy metal or petroleum contaminant from oil spilled water body. The pinesorb adsorbent produced contained OH^- group whose transmission frequency was identified at 3405.06 cm^{-1} before the adsorption and 3415.67 cm^{-1} after the adsorption process. In addition, the carboxylic group -COOH that was identified at the peak value of 2923.15 cm^{-1} and 2922.02 cm^{-1} before and after adsorption respectively enhances its performance to donate proton and accept electron to neutralizes the violent colour pigment contain in the oil spilled water body from the petroleum contaminant. While the aldehyde and ketone components of the adsorbent were identified at peak values of 1733.82 cm^{-1} and 1734.42 cm^{-1} before and after the absorption processes were efficient in adsorbing the violent colour pigment in the oil spilled that caused water contamination. This is the evidence from the FTIR, the colour degradation and SEM micrograph analysis carried out to justify the adsorbent viability.

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