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Research Article

THE ADSORPTION POTENTIALS OF PLANTAIN PEEL FOR OIL SPILL CLEAN UP

[1,*]Alozie, A. C., [2]Madu, P. C., [3]Audu, S. S., [4]Anifowose, O. and [5]Ayim, P. B.

[1]Department of Chemistry, Faculty of Natural and Applied Sciences, Nasarawa state University, Keffi, Nigeria
[5]National Research Institute for Chemical Technology, Basawa Zaria, Kaduna State, Nigeria

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Abstract

The production and transportation of crude oil has resulted in serious environmental pollution via oil spillage, generating a great burden to humanity. This spillage has induced different kinds of pollution that have serious adverse effects on man, animals and plants. These adverse impacts to the ecosystems and the long-term environmental pollution necessitated an urgent need to develop a wide range of material for clean-up of oil from affected areas. The oil producing companies and state government have not done enough to effect immediate oil spill remediation after an oil spillage has occurred, and it may be due to technology, economic cost or outright negligence. The methods and developed sorbents have not been inadequate in meeting up with the required efficacy of oil spill removal. Hence, the deployment of certain agro wastes that is biodegradable and eco-friendly (green adsorbent) becomes a `good option in oil spill remedy. The important contribution of this research to existing knowledge includes modifying the undervalued and neglected agricultural waste residues to valuable sorbents for oil spill clean-up that have the potential of providing economic incentives. Similarly, it substantiated the fact that plantain plantain peel has well documented capacity for oil sorption and the lack of dimensional stability due to associated hydroxyl functionality was corrected by modification. The adsorbent was subjected to sample preparation by washing, sun dried and crushed to a specific size. It was then oven dried at 350 ° C and allowed to cool and subjected to FTIR analysis. It was subjected to modification by a reaction with acetic anhydride with sulpuric acid as catalyst. The modified adsorbent was subjected to crude oil recovery efficiency test. Sample characterization results showed moisture content of 1.370%, ash content of 14.260% and hausner ratio of 1.209. IR result indicated absence of spectra bands at 1740 -1745 $cm^{-1}$and 1020 -1040 cm^{-1}. The result of the oil removal efficiency was subjected to kinetic models (pseudo-first order, PFO, pseudo-second order, PSO, intraparticle diffusion, IPD, and film diffusion, FD). Correlation value, R^2 obtained for PSO and FD were close to unity, an indication that the plantain peel as an adsorbent was inclined to PSO kinetics with adsorption outlook to film diffusion than the IPD. The high value of R^2 (0.9851 for the pseudo second order, PSO and 0.9556 for the film diffusion, FD) obtained in the adsorption kinetics justifies the potency of plantain peel as a sorbent in oil spill remediation. A recommendation for further research on more efficient methods to enhance the oil adsorption capacity of the modified material should be explored and encouraged. This work is also an indispensable reference and an essential reading for everyone concerned with oil spill cleanup in mangroves and wetlands, providing strategies for the conversion of agricultural wastes to effective oil spill sorbents.

Keywords: Adsorbent, adsorbate, plantain peel, sorbent, sample etc.

INTRODUCTION

The importance of crude oil as a very decisive element in defining the politics, rhetoric and diplomacy of states cannot be denied. Yet behind this great value of crude oil, not much have been said or done about oil spill impact to the environment (Sharma *et al.,* 2024; Yergin, 2008). However, its exploration has resulted in serious environmental pollution ranging from air, water and soil pollutions. Crude oil is a known teratogen and the benzene component is also a known carcinogen (Krishnan *et al.,* 2022). An oil spill is known to be the accidental or unintentional discharge of petroleum hydrocarbons into the environment, especially the marine ecosystem. An oil spill on water can be transported by wind and current, and the distributed oil evaporates or forms a surface slick, disperses in water, or submerges and accumulates in the sediments (Liu *et al.,* 2012). Oil spill can severely impact on all living organisms by limiting the amount of oxygen reached from the surface and the presence of highly toxic components (Ukhurebor etal., 2021). Oil spill can be released during production, distribution, and usage. The account of global oil spills has been summarized by Idris *et al.,* (2013) with the oceans becoming more polluted every day from oil spills due to routine shipping, draining, and dumping activities (Akpan, 2022), with about 400,000 (metric tonnes) of oil spillage taking place per year around the world through various avenues. In disaster management, oil spill remediation has been reported to be expensive, at about $ 4230 to $ 5283 per m^3 in the U.S.A., thus having substantial economic consequences (Singh *et al.,* 2020). Many researchers have reviewed the aspects and impacts of these spills on the ecosystem over time (Omer *et al.,* 2024) and developed various methods and chemicals for oil spill response.These include the use of booms, skimmers, dispersants, in-situ burnings, bioremediation, sorbents, membranes, and magnetic nanocomposites (Hoang *et al.,* 2021) but they have not been able to resolve oil spill cleanup problem. Noticeably, oil producing companies and state governments have not done enough to effect immediate oil spill remediation after an oil spillage has occurred, and it may be due to technology, economic cost or outright negligence.The methods and developed sorbents have not been inadequate in meeting up with the required efficacy of oil spill removal. These adverse impacts of oil spill to the ecosystems and the long-term environmental pollution necessitated an urgent need to develop a wide range of material for clean-up of oil from affected areas. Invariably, the deployment of a certain agro waste, plantain peel that is biodegradable and eco-friendly (green chemistry) as a sorbent becomes a `good option in oil spill

Corresponding Author:** ***Alozie, A. C.,
Department of Chemistry, Faculty of Natural and Applied Sciences, Nasarawa state University, Keffi, Nigeria.

remedy. Plantain peel isthe major by -product of plantain fruit, constituting about 40% of the bulk of the fruit found in plantain and banana (FAO, 2023). The approach on clean-up processes employed by the oil companies have not met up expectations and at sometimes dangerous to the aquatic life and affect the food chain (Igbani *et al.,* 2023). Therefore, there is an urgent need to develop a wide range of sorbent materials for oil cleanup for the oil impacted areas. The important contribution of this research to existing knowledge is, to modify the undervalued and neglected agricultural waste residue, plantain peel, to valuable sorbent for oil spill clean-up that have the potential of providing economic incentives, thus turning waste to wealth. The study was aimed at exploring the adsorption potential of plantain peel as a sorbent for oil spill cleanup in the affected areas of Niger Delta and beyond. The work investigates the use of agricultural waste in environmental remediation of petroleum spill in water bodies of south-south geopolitical zone of Nigeria. It involved the use of analytical instruments like XRF, SEM/EDS and FTIR, and statistical tools like ANOVA and adsorption/kinetic theories to determine the cleanup efficiency of the modified sorbents, using variables of time; carry out the adsorption kinetics on the adsorption efficiency of the modified sorbent and determine the oil recovery efficiency of the used and modified sorbent.

MATERIALS AND METHODS

Sample Collection

Corn husk sample (25 kg) was collected from karu market in Abuja metropolis. Crude oil sample (3.5 L) was collected from Nigerian National Petroleum Corporation (NNPC) Port-Harcourt, Nigeria.

Sample Preparation

The method adopted is as described in this article. The plantain peel sample was thoroughly washed with distilled water. The washed sample was then sun-dried for 15 hours (5 hours per day for 3 days). The sun-dried sample was placed in the oven at 110 ^{0}C and heated for 90 minutes. The sample was allowed to cool and crushed in grinding machine and sieved through a 75 mm British Standard Sieve (BSS Sieves). The dried and crushed sample was stored in an air tight container and kept for further use.

Characterization of the Sample

Proximate characteristics of the sample were determined for the following parameters; Bulk and tapped density, true density, moisture content and ash content.

Bulk and tapped density: A portion (15 g) of the sample was measured accurately into a 100 ml graduated cylinder. The cylinder stoppered and the bulk volume v_o recorded. For the tapped density, the cylinder was tapped on a hard surface to a constant volume (until no more settling of the material occurred). The final constant volume (v_1) noted to be the tapped volume. The bulk and tapped densities D_{bulk} and D_{tap} are determined using equations 1 and 2.

$$D_{bulk} = \frac{w}{v} \qquad (1)$$

$$D_{tap} = \frac{w}{v_1} \qquad (2)$$

Where,
w =weight of the sample,
$v_o =$ bulk volume,
$v_1 =$ tapped volume
2.3.2 True density

A portion (15 g) of the sample was weighed accurately and poured into a 100 ml graduated cylinder, and distilled water carefully measured into the cylinder to the level of the material. The true density is calculated using equation 3.

$$\text{True density} = \frac{w}{v_o} \qquad (3)$$

Where,
w = weight of the sample and water and
v_o = volume of the sample.
2.3.3 Moisture content

A portion (5 g) each of the sample was measured into a wash glass. The sample was placed in the oven for 24 hours at 105 ^{o}C. After 24 hours, the oven dried sample was reweighed and the moisture content determined as in the equation below (ASTM, 2023).

$$Mc = \frac{(w_o - w_1)}{w_o} \times 100 \qquad (4)$$

Where,
Mc = moisture content
w_1 = new weight after drying
w_o = initial weight of the dry sample.
2.3.4 Ash content

Ash content was determined using a modified method employed by (Liu, 2019). Dry sample (5 g) was placed in a pre-weighed porcelain crucible and transferred into a pre-heated muffle furnace set at 350 ^{o}C for 2 hours after which the crucible and its content were transferred to a desiccator and allowed to cool. The crucible and its content were reweighed and the new weight noted. The percentage ash content is as in equation 5.

$$Ac\,(\%) = \frac{w_a}{w_o} \times 100 \qquad (5)$$

Where,
Ac = ash content in percentage
w_a = weight of ash after cooling and
w_o = original weight of dry sorbent

Characterization of Crude Oil

The characterization index of the crude oil was done in correlation to the viscosity, density, specific gravity and the API value.

Viscosity: The viscosity of the oil sample was obtained using an NDJ-85 Digital rotary viscometer at 27 ^{o}C. The sample (15 ml) was pre-warmed and placed in the sample chamber of the apparatus. The sample was brought to room temperature within 30 minutes and the motor started. The viscosity was automatically measured at 1 minute interval. The mean of the viscosity was calculated and recorded.

Density: The density of the oil sample was obtained using the method of (Hassan *et al.,* 2018) with a specific gravity bottle. The bottle was filled with the oil (15 g) and weighed at 30 °C in a thermo-started water bath. The density of the oil was calculated using equation 6.

$$\rho = \frac{ms - m_b}{v_b} \tag{6}$$

Where,
$ms\text{-}m_b$ = mass of the oil used
v_b = volume of water used
ms = mass of oil and bottle and
m_b = mass of bottle.

Specific gravity: The specific gravity of the oil sample was calculated using the result obtained for density. The specific gravity being a more standard measurement is obtained by multiplying the density obtained with the density of water (0.998 g/dm^3).

The American petroleum institute (API) – Gravity: This is obtained by using the formula API gravity given by (Nwankwere *et al.,* 2010) and expressed as in equation 7.

$$API = \frac{141.5}{s.\,g} - 131.5 \tag{7}$$

Where,
s.g = specific gravity of the oil used.

If API gravity is less than 10, it will sink in the water; higher than 10, it will float. This is because the API of water is 10.

Carbonization and Modification of Sample

The dried sample was carbonized in a muffle furnace at 350 °C for 2 hours. The carbonized sample was left to cool and stored in an air tight container for further use. Sample was subjected to acetylation process using acetic anhydride. The acetylation of each of the sample was under a slight modification of (Onwuka *et al.,* 2016) method, in the presence of sulphuric acid as catalyst, using acetic anhydride. In the method, the amount of substrate and reactant were combined in a ratio of 1:20 (g dried sorbent/ml acetic anhydride) with a reaction temperature of 30 °C, time of 1 hour and the catalyst concentration of 0.2 g. The mixture of raw sorbents, acetic anhydride and catalyst were placed in a round bottom flask fitted to a condenser and refluxed for 1 hour. The flask was placed in an oil bath on top of a thermostatic heating device. Thereafter, the flask was removed from the bath and the hot reagent was decanted off to produce modified sample. The acetylated (modified) sorbent was thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid formed by-products. The modified product was dried in an oven at 105 °C for 2 hours prior to further analysis. The modified sorbent was stored in air tight containers for further use. The modified adsorbent was characterized with the Fourier Transform Infrared (FT-IR Shimadzu 8400s) spectrophotometer in the range of 4000-400 cm-^{1}.

Crude oil adsorption efficiency of the modified sorbent

The adsorption technique of removal oil from water was carried out using a slight modification of the method of (Mohammad *et al.,* 2021). To simulate the situation of oil spill and minimize experimental variation, the crude oil sample was held in a beaker for one day in open air to release volatile hydrocarbon contents.

The modified sample was then subjected to crude oil sorption test. 100 ml of distilled water in a 250 ml beaker, 5 g of crude oil was added and stirred for 2 minutes. A portion (5 g) of the sorbent was added into the mixture in the beaker. The mixture was allowed to stand for 5 minutes with good agitation. The sorbent was then removed from the beaker using sieve net and left to drain by hanging the net over the beaker in an oven for 30 minutes at 60 °C and reweighed. The same procedure was repeated thrice. The oil sorption capacity was calculated by taking into account the weight of sorbent, weight of sorbent and oil and weight of the sieve net as in equation 8.

$$\text{Oil sorption capacity (g/g)} = \frac{S_{st} - S_o}{S_o} \tag{8}$$

Where,
S_o = initial mass of the dry sorbent
S_{st} = mass of the sorbent with oil at the end of the sorption test and
$(S_{st} - S_o)$ = net oil sorbed (all of the masses in g).

The amount of crude oil adsorbed at equilibrium (q_e) in milligrams per gram was determined using the following mass balance in equation 9.

$$q_e = \frac{(Co - Ce)\, v}{m} \tag{9}$$

Where,
Co = initial oil concentration in mg/l
Ce = the equilibrium oil concentration in mg/l
v = the volume of the solution in liters and
m = the mass of the adsorbent in g

Oil Recovery Efficiency

The distillation technique used for oil recovery efficiency in this work was carried out using a slight modification of the method of (Yang *et al.,* 2021; Doshi *et al.,* 2018). In the method the wetted adsorbent was removed from the beaker; oil and water were filtered through a 0.45-micron porous membrane filter and weighed. The water content in the adsorbent was measured using the dean and Stack distillation technique described in ASTM D4006-11. The wetted adsorbent was refluxed with hexane. Organic solvents condense into a trap. The water settled in the graduated section of the trap and the solvent was returned to its content for storage. This procedure was repeated for the sorbent under the same operating conditions. Yields of 81.50 – 85.60 % were obtained.

Regeneration (Reusability) of the Agro-waste Sorbents

The ability of the agro-waste adsorbent to be regenerated for further use was carried out with a slight modification to the method described by (Chen *et al.,* 2022; Xu *et al.,* 2018). The used modified agro-waste adsorbent weighed into separate crucibles and introduced into the furnace with the temperature pegged at 300 °C for 2 hours as to burn off the adsorbed crude oil. They used sorbent was allowed to cool. Features of the adsorbent after heat treatment were ascertained by proximate analysis. Thereafter, further studies were carried out with the regenerated agro-waste sorbent as to compare their viability with the unused modified sorbent.

RESULTS AND DISCUSSION

Results

Table 1. Results of the Characterization of Plantain peel

Properties	Plantain Peel
Moisture Content (%)	1.960 ± 0.015
Bulk Density (g/cm^3)	0.330 ± 0.005
Tapped Density (g/cm3)	0.405 ± 0.006
Hausner ratio	1.227 ± 0.015
Ash Content (%)	13.370 ± 0.305
Volatile Matter (%)	52.990 ± 1.470
Fixed Carbon (%)	18.780 ± 0.930
Caloric Value (mJ/Kg)	24.310 ± 1.030

Values are mean ± standard deviations, n = 3.

Table 2. Mineral Composition of plantain peel (mg/g)

Minerals	Plantain Peel
K_2O	63.13 ± 3.05
MgO	8.40 ± 0.39
CaO	10.15 ± 0.75
SO_3	1.82 ± 0.10
P_2O_5	2.25 ± 0.10
ZnO	0.01 ± 0.01
Fe_2O_3	0.81 ± 0.01
CuO	0.09 ± 0.00
PbO	0.01 ± 0.00
Zno	0.01 ± 0.00

Values are mean ± standard deviations, n = 3.

Table 3. Physical Parameters of the Crude Oil

Property	Crude Oil
Density (g/cm^3)	0.8592
Viscosity at 25^{o}C (Pa.s)	66.8500
Specific gravity at 25^{o}C	0.8504
API gravity (o)	34.8923

Values are mean ± standard deviations, n = 3.

Table 4. Crude Oil Recovery Efficiency (%) for Plantain peel (C_o =5.00 g)

Time(t)	Conc. at time t (C_t)	Quantity adsorbed at time t (q_t)	Oil recovery
2.00	2.21 ± 0.025	2.79 ± 0.224	55.80 ± 1.50
3.00	2.14 ± 0.025	2.86 ± 0.025	57.20 ± 1.52
4.00	2.10 ± 0.022	2.90 ± 0.023	59.00 ± 1.53
5.00	1.87 ± 0.020	3.13 ± 0.023	62.60 ± 1.55
6.00	1.76 ± 0.020	3.245 ± 0.022	64.90 ± 1.54
7.00	1.62 ± 0.019	3.385 ± 0.022	67.70 ± 1.53
8.00	1.48 ± 0.018	3.525 ± 0.024	70.50 ± 1.53
9.00	1.30 ± 0.015	3.70 ± 0.024	74.00 ± 1.54
10.00	1.13 ± 0.012	3.875 ± 0.025	77.50 ± 1.55
11.00	0.96 ± 0.010	4.045 ± 0.025	80.90 ± 1.56
12.00	0.78 ± 0.010	4.225 ± 0.025	84.50 ± 1.56
13.00	0.69 ± 0.008	4.315 ± 0.026	86.30 ± 1.57
14.00	0.65 ± 0.007	4.35 ± 0.026	87.00 ± 1.57
15.00	0.63 ± 0.007	4.37 ± 0.026	87.40 ± 1.58
16.00	0.62 ± 0.007	4.38 ± 0.026	87.60 ± 1.58

Values are mean ± standard deviations, n = 3.

Table 5. Summary of Kinetics from the Plots of Modified Plantain peel

Kinetic models	Values
Pseudo-First Order, PFO	
Q(mg/g)	0.4838
R^2	0.7949
K_1	37.316
Pseudo-Second Order, PSO	
Q(mg/g)	4.9877
R^2	0.9851
K_2	0..0986
Intraparticle Diffusion, IPD	
K_d	0.9342
R^2	0.8742
C	1.0806
Film Diffusion, FD	
K_{fd}	0.1060
R^2	0.9556
C	2.4110

Table 6. Results of the Proximate Analysis of the Regenerated Sorbent

Properties	Plantain Peel
Moisture Content (%)	2.060 ± 0.02
Ash Content (%)	14.308 ± 0.31
Volatile Matter	45.845 ± 1.47
Fixed Carbon	18.780 ± 0.93
Caloric Value (MJ/Kg)	24.310 ± 1.03
Percentage of Oil Recovered	64.407 ± 1.65

Values are mean ± standard deviations, n = 3.

Discussion

The characterization of plantain peel: Moisture content of 1.960 ± 0.015 reported in this study is within the acceptable limit of 5%, similar to results reported by Farmer and Kennepohl, (2022) who investigated on the chemistry of acid anhydrides. Bulk and tapped densities measure the flowability of a material. A higher density indicates a better potential for a material to flow and re-arrange itself under compression. The results derived from this study are moderate and are consistent with findings elsewhere by Alfa Test Laboratory (2023) who worked on materials and methods -wait a minute, there is more than one density. Hausner index is estimated as the ratio of the difference between tapped and bulk density and estimates cohesion between particles. A value of 1.227 ± 0.015 reported in this study is within the acceptable limit of 1.25% as reported by Deepak (2024) in understanding Hausner ratio and compressibility index. The ash content reports the percentage of inorganic constituents in the agro waste and the value of 13.37 ± 0.305 is within the acceptable limit of 15.75 as reported by Puri (2024) in their study, critical review of the role of ash content and composition in biomass pyrolysis. Mineral analysis was done by X-ray fluorescence and the result showed that corn husk contained some essential minerals in high proportion and others in trace values as in Table 2. Mineral analysis was done by X-ray fluorescence (XRF) and the results showed that corn husk contained essential minerals like potassium and calcium in high proportion as in Table 2. Calcium plays a significant role in photosynthesis, carbohydrate metabolism, nucleic acids and binding agents of cell wall. It also assists in teeth development as reported by Moody (2024). Copper is a trace mineral and was found present in all the samples in trace amounts. It helps the body make red blood cells and keeps nerve cells and your immune system healthy. To the plant species, copper activates some enzymes which are involved in lignin synthesis and it is essential in several enzyme systems. It is also required in the process of photosynthesis, is essential in plant respiration and assists in plant metabolism of carbohydrates and proteins as reported by Xu (2024). Iron was found present in all the samples as a micro nutrient and it is involved in the manufacturing process of chlorophyll, and it is required for certain enzyme functions. Characterization of the physical parameters of crude oil was carried out in respect of the density, viscosity, Specific gravity and API gravity**.** The specific gravity of the crude oil at 0.8592 shows that the crude oil is less dense than water, within the standard limit of 0.79 – 0.86 and therefore can float on it. API value was 34.89. Viscosity is a measure of an oils' resistance to flow. The crude oil gave a high viscosity value of 66.85 which is within the standard limit of less than 100 Pa.s for crude oil of API greater than 22.

Kinetics of adsorption efficiency of the modified sorbent: Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. It is the capability of all solid substances to attract to their surfaces, molecules of gases or solutions with which they are in contact with (Xing *et al.,* 2022). This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption kinetics is thus a curve or line that describes the rate of retention or release of a solute from an aqueous environment to a solid-phase interface at a given adsorbents dose, temperature, flowrate and pH (Wang and Guo, 2022). In essence, adsorption kinetics is the study of the amount of adsorbate adsorbed by the adsorbent as a function of time variation. Note that adsorption efficiency can only be verified by subjecting the results to the various adsorption kinetics. The results of the adsorption efficiency of the modified sorbent are presented in Tables 4 and values indicated in Table 4 were reappraised to fit to the adsorption kinetics models of Pseudo first Order (PFO), Pseudo Second Order (PSO), Intraparticle Diffusion (IPD) and Film Diffusion (FD).

Pseudo first order (PFO): The reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substances (Wang and Guo, 2022)

The PFO model is expressed by the equation 10.

$$\ln (q_e-q_t) = \ln q_e - k_1 t, \qquad (10)$$

Where,

q_e=amt of adsorbate adsorbed at equilibrium, mg/g;

t = time. min^{-1} or h^{-1}

q_t = amt of adsorbate adsorbed at time, t, mg/g;

k_1 =pseudo-first orderrate constant, min^{-1} or h^{-1},

A plot of **ln (q_e-q_t)** vs **t,** gives a linear graph with qe as intercept and k1 as the gradient.

Pseudo second order (PSO): It is assumed that the adsorption rate is influenced by the interaction sites on the adsorbent surface with the adsorbent throughout the adsorption process (Xu, 2024). PSO adsorption kinetics is used to accommodate some adsorption processes that require longer time to fill the adsorption sites**.**

The PSO model is expressed by the equation 11.

$$t/q_t = t/q_e + 1/k_2 q_e^2 \qquad (11)$$

Where,

k_2 = pseudo-order second rate constant, min^{-1} or h^{-1}.

A plot of **t/q_t**vs **t,** gives a linear graph with 1/qe as intercept and 1/k2qe as the gradient

Intraparticle diffusion (IPD): It was proposed by Weber and Morris (Chu *et al.,* 2025). It is used to elucidate the adsorption mechanism which proceeds in three stages i) external surface adsorption or instantaneous adsorption occurs at the first step/stage ii) gradual adsorption step where IPD is the rate controlling stage. iii) the final equilibrium step where the solute moves slowly from larger pores to the micropores, causing a slow adsorption rate (Wang and Guo, 2022).

The IPD model is expressed by the equation 12:

$$q_t = k_d t^{1/2} + I \qquad (12)$$

Where,

I = the intercept, which is thickness of the boundary layer

k_{dt} = the intraparticle diffusion rate constant.

A plot of **q_t vs $t^{1/2}$** gives a linear that as to pass the origin.

Film diffusion (FD):It describes diffusion as a two-stage process of solute dissolving from the solid to form a saturated film and then diffuse out of the film.Simply, diffusion is the movement of molecules across a membrane by a concentration gradient. Film diffusion involves transport from the bulk of one phase to the phase boundary or interface, then movement from the interface into the bulk of the second phase (Chu *et al.,* 2024). In this model, three steps are involved – a) diffusion of the adsorbate across the liquid film surrounding the adsorbent particle (external film diffusion); b) diffusion within the adsorbent particle (intraparticle diffusion) which may be due to pore diffusion or surface diffusion or a combination of both: c) adsorption on the pore surface (surface reaction).

The FD model is expressed by the equation 13.

$$\ln (1-F) = k_{fd} t \qquad (13)$$

Where, F = q_t/q_e.

The model shows a straight line passing through the origin in a plot similar to Boyd and the slope of the line is related to the film mass transfer coefficient (Chu *et al.,* 2024).

Kinetics of the modified plantain peel: The kinetics of the modified plantain peel was studied by fitting obtained data in rate curves presented earlier in Table 4. The predicted kinetics from the linear plots of pseudo- first order, pseudo-second-order, intra-particle diffusion and liquid film diffusion models were all considered. However, the plot of only the pseudo-second order kinetics gave the best fit as presented in figure 4. In Table 5 showed the summary of the kinetics derived from the plots of modified plantain peel. From the table, the pseudo second order gave a higher R^2 value of 0.9851, which is better than the pseudo first order value 0.7947. The very high R^2 therefore suggests that it is the optimum expression to represent the adsorption process of modified plantain peel. The plot of q_t versus $t^{1/2}$ and the high value of R^2 value of 0.8742 were obtained for intra- particle diffusion model and the plot did not pass through the origin. It indicates that a rapid adsorption occurred within a short period of time. Hence, an indication that the rate determining step may not be intra particle diffusion and could be due to other mechanisms. A plot of ln (1-F) versus t with a zero intercept would suggest that the kinetics of modification was controlled by diffusion through the liquid film surface surrounding the solid sorbent. However, the liquid film mechanism produced a high R^2 value of 0.9556. The linearity of the plot for the liquid film diffusion model indicated the high applicability of this model, and similar to Nwadiogbu et al. (2014), though this did not pass through the origin. This could be due to adsorption on the pore surface (surface reaction) as a result of particle size and stirring speed. The adsorption process of modified plantain peel indicated that surface sorption was more predominant than penetration into the pores of the material. Therefore, from the results it can be concluded that the liquid film diffusion model is more applicable to the adsorption process of modified plantain peel.

Spectra and Micrograph Analysis:

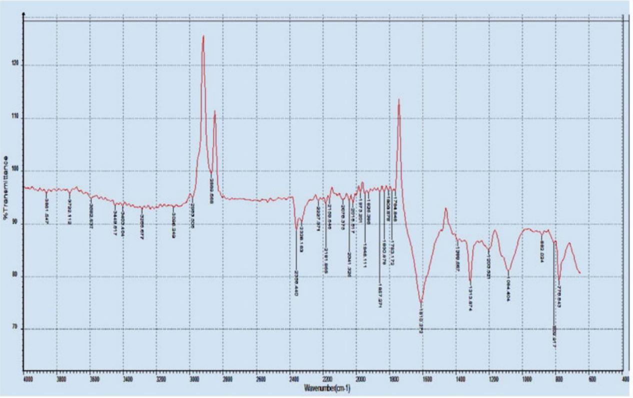

Figure 1. FTIR spectrum of modified plantain peel

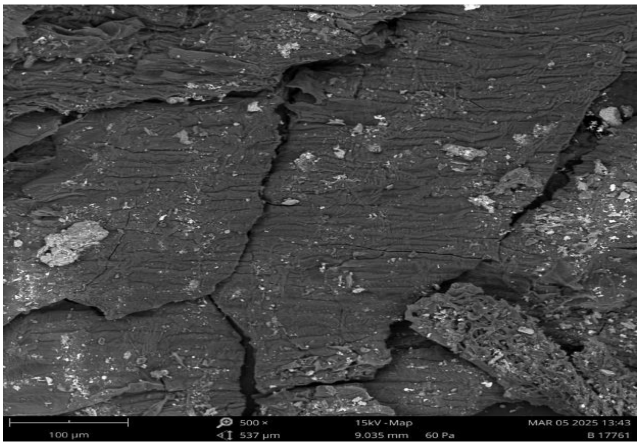

Figure 2. SEM micrograph of raw plantain peel

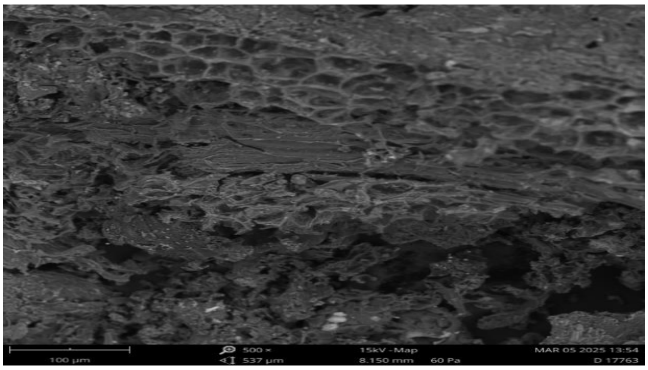

Figure 3. SEM micrograph of modified Plantain Peel

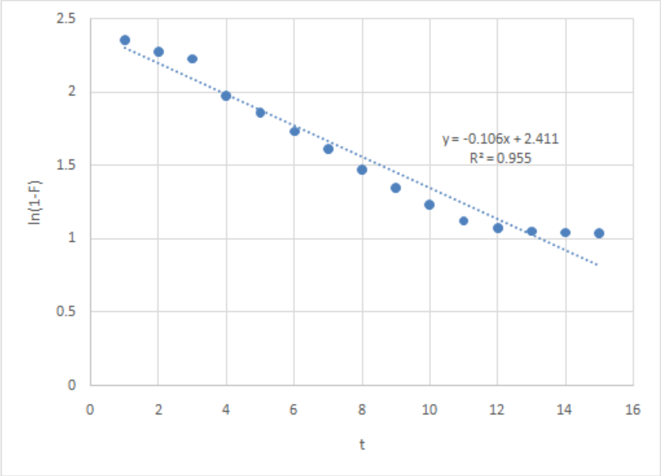

Figure 4. Graph of PSO kinetics for Plantain Peel

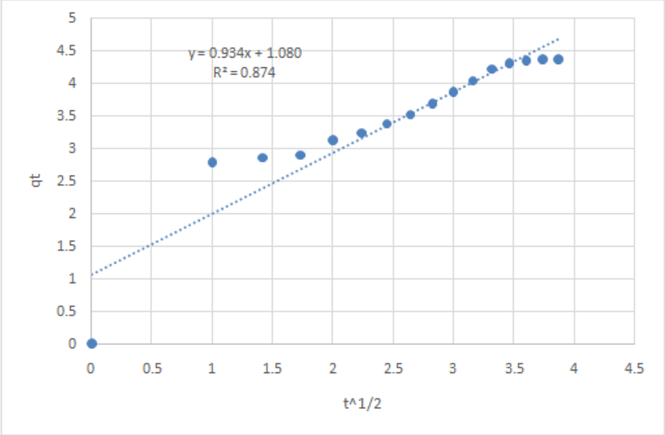

Figure 5. Graph of IPD kinetics for plantain peel

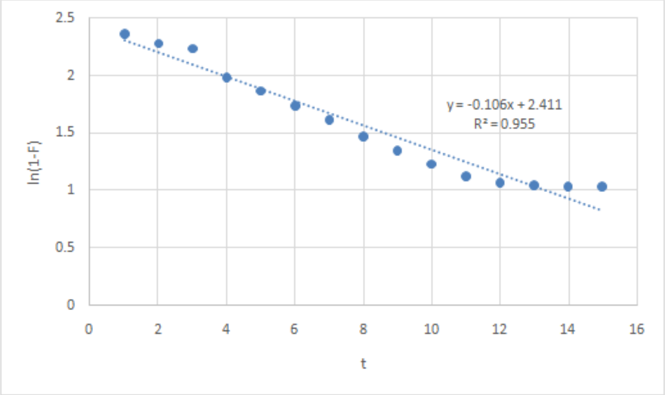

Figure 6. Graph of FD kinetics for Plantain Peel

Spectra and micrograph analysis

The absence of the band at 1740-1745 cm^{-1} in the modified sample showed that the acetylated sample was free of unreacted acetic anhydride while the absence of the peak at 1020-1040 cm^{-1} also indicated that the acetylated product was free of acetic acid by- product. This result is similar as investigation reported by Farmer et al. (2025) who investigated on the chemistry of acid anhydrides. See attached spectrum in figure 1. SEM analysis showed the surface morphologies and cross section of raw and treated plantain peel. The surface and cross section of raw corn husk exhibits a smooth surface without any ripple due to the coverage of plant wax. The amount and rate at which oil is adsorbed into the sorbent is closely related to the physical configuration of the sorbent such as surface roughness, hollow lumen, porosity and twist. The surface of the modified sorbent was more ruptured along with different degrees of wrinkles and grooves which increased the surface area and noticeable increase in the number of pores in the sorbent. These pores make oil entrance into the internal parts of the material easier and helpful in the adsorption process. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism, similar to Wang et al. (2023) as in their study, responses on aquatic vegetables to biochar amended soil and water environment.

Conclusion

This study aimed at utilizing the adsorption potential of plantain peel as an option in oil spill cleanup. It substantiated the fact that agro-waste has well documented capacity with oil sorption and the lack of dimensional stability due to associated hydroxyl functionality can be corrected by modification. This was achieved by modifying the agro-waste sorbent by acetylation which increased the adsorption potentials of plantain peel thus making it a viable option as sorbent for oil spill remediation. It also enhanced the possibility of converting waste into wealth and turn interest into the deployment of agro-waste as sorbents, which will increase our local content in the downstream sector and generate employment. The low values of hausner ratio, moisture and ash contents obtained in proximate analyses which are within the acceptable limits are pointers that a modified plantain peel is a good adsorbent. Also, the absence of spectra bands at 1740-1745 cm^{-1} due to unreacted acetic anhydride and at 1020-1040 cm^{-1}due to acetic acid by- product indicated that the modification of the sorbent by acetylation was a success. Micrograph of the SEM analysis showed surface of the modified sorbent more ruptured along with different degrees of wrinkles and grooves which increased the surface area and number of pores in the sorbent, helpful in the adsorption process. The high value of R^2 0.9851 for the pseudo second order, PSO and 0.9556 for the film diffusion, FD) obtained in the adsorption kinetics justifies the potency of plantain peel as a sorbent in oil spill remediation. A recommendation for further research on more efficient methods to enhance the oil adsorption capacity of the modified material should be explored and encouraged. This work is also an indispensable reference and an essential reading for everyone concerned with oil spill cleanup in mangroves and wetlands, providing strategies for the conversion of agricultural wastes to effective oil spill sorbents.

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Data Availability: The data supporting the conclusion of this research are presented in this article.

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