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Orange Peel and Pine bark Waste as Media for Metal Removal from Crude Oil

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ABSTRACT

Crude oil contains trace metal species that hinders performance during refining, poison catalysts, and results to environmental contamination. Conventional metal-removal processes, such as hydrotreating and solvent extraction, are energy-intensive and costly. In this study, organic wastes such as orange peel and pine bark were evaluated as alternative media for extracting metal-containing complexes from crude oil. Model experiments using iron, nickel and metal free phthalocyanines dissolved in toluene showed that all complexes were transferred intact into the adsorbent. Hydroxylated species and free ions coupled with the pH of the adsorbent were suspected as the major factors responsible for extraction. Across the formulations tested, more acidic organic waste systems consistently delivered higher extraction efficiencies. The methodology was then applied to a Nigerian crude oil sample to assess performance under realistic conditions. Organic waste effectively extracted metalloporphyrin and other metal species while maintaining good phase separation. A simple filtration-based workflow enabled recovery of the organic waste with minimal energy input, demonstrating the potential for operationally straightforward and metal-removal processes. Overall, this work establishes orange peel and pine bark as efficient, mechanistically understood, and potentially low-energy media for the extraction of metal species from crude oil, offering a promising basis

for next-generation upgrading technologies.

INTRODUCTION

Crude oil is a yellowish-black almost incompressible mixture of hydrocarbons. This fluid is separated into different products by a process called fractional distillation which separates the components based on their boiling point range which is related in part to their molecular weights, volatility, viscosity, and colour.[1] It is called the mother of all commodities as it manufactures various products such as pharmaceuticals, plastics, gasoline, synthetic fabrics, etc. Petroleum or crude oil has been the world-leading source of energy since the 1950s. Petroleum is composed of various hydrocarbons in liquid, solid and gaseous forms. The lighter hydrocarbons methane, ethane, propane and butane exist as gases, while the others, like pentane and heavier ones, are found as liquids or solids. [2]

Crude oil also contains a diverse array of more polar constituents incorporating sulfur, nitrogen, and oxygen heteroatoms, together with trace metals such as nickel, vanadium and iron, and small quantities of ionic species (Na^+, Ca^{2+}, Cl^-).[3,4] The compounds found are a hybrid of the crude oil constituent, bitumen and coal. They are problematic in crude oil processing as they increase viscosity and lead to smokey or sooty flames during combustion. They can also lead to blockages and deposits in fuel systems and so strenuous efforts are made to remove them from fuels before combustion. Once present, metal complexes can deactivate cracking catalysts, promote inorganic deposition that compromises heat transfer, and accelerate the degradation of lubricants. [5,6]

Metals become incorporated into crude oil either from the animals or plants which decomposed to make the oil e.g., iron from hemoglobin or from the oil contacting a mineral containing ore. The high concentration of N- and S-containing heterocyclic compounds enables metal solubilization. Principally cyclic ligands such a phthalocyanines are the primary ligands encountered. Again, many of these are present from the plants and creatures that produced the oil. [7] All indigenous crude oil is made up of inorganic substances. Analysis of crude oil from different oil fields shows they contain different trace metals. These metals include but not limited to: Al, Fe, Ti, Mn, Mg, Na, K, Ag, As, B, Ba, Ce, Co, Cr, Ca, Cu, Ga, La, Mo, Nd, Ni, Pb, Sn, Sr, V, Zn, Zr, U. [8]

The most abundant of all is vanadium and nickel. Nickel ranges from 0.001 to 500μg/g while vanadium ranges from 0.01 to 1500μg/g in crude oil. Others are present in much lower concentration.

Trace metals which are joined in the organic matrix of crude oil may have been formed in four different ways.

1. From the rock minerals in the oil reservoir or the formation water.
2. During primary or secondary migration, it can be taken up from an aqueous or mineral phase
3. It can be through the incorporation and chemical, physical, and biological changes (diagenesis) of the metal complexes of the original biological materials
4. Also, through incorporation into the organic matrix during diagenesis of the biological materials in the source rock.

The main compound of importance here is the porphyrin. Porphyrin which was derived from the Greek word “purple” is made up of a 16- atom rings which contains four nitrogen atoms as shown in **Figure 1** below;

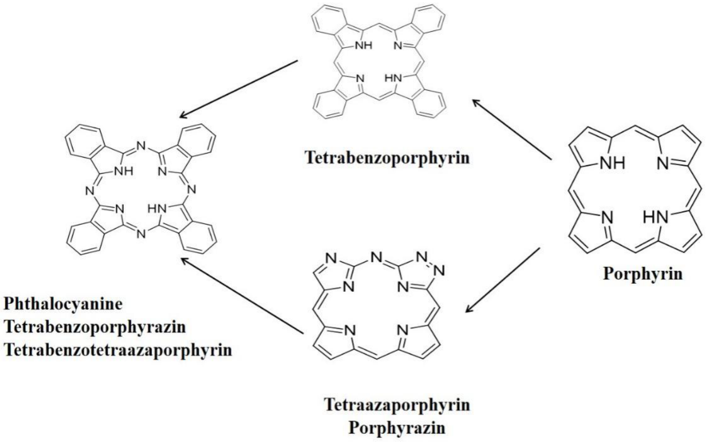


***Figure 1** Different forms of porphyrins*

Porphyrin can bind almost all metals. Porphyrin is of biotic and abiotic origin. In the biotic origin, the structures are present in the remains of animals and plants through the hemoglobin in the animals and the chlorophyll in the plants. Generally, porphyrin occurs in the protoplasm, and act as a metal – binding cofactor in the hemoglobin, the chlorophyll and some particular enzymes. Metals bonded to the center of porphyrin is known as metalloporphyrin with a metal ion charge of 3+ or 2+ which is found in the N4 central cavity usually formed as a result of the loss of two protons as shown in **Figure 2** below.[9]

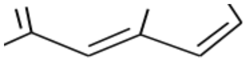


Figure 2 *A metal porphyrin complex*[9]

The whole process is known as pheophytinization. This is where during the period of deposition; the chlorophyll molecule loses its magnesium. The metals replace magnesium and form complexes with the porphyrin. An equation of the reaction process is shown below:[10]

$PH_2 + M^{2+}$ ′n $MP + 2H^+$

PH_2 = Free base porphyrin

M^{2+} = Metal ions

MP = Metalloporphyrin

H^+ = Hydrogen ions

These metals have effects on the petroleum. Some of the notable effects of these metals are.

1. They may bring out false readings on certain crude oil well. Crude oil well readings include data collected from well tests, caliper logs, directional surveys. The data is used to monitor the oil reservoirs, evaluate well performance, and make decisions about crude oil production.

2. They can bring about serious refining problems because they are poisonous to cracking catalysts and if they are not removed, they may limit the life span of the catalysts.

3. The products from inorganic deposition can result to problems in heat transfer, cause equipment deterioration and also premature failure.

4. Trace metals can accelerate chemical reactions in petroleum compounds and their derivatives. They can cause breakdown of lubricants and wear and tear of engine.

Organometallic compounds are substances added as additives to lubricating oil. This is to enhance the properties of the lubricating oil in its composition. A good example is the compounds of lead and copper which makes lubricating oil corrosion resistance. Some of them possesses properties as high-pressure, anti-wear, and even reduce friction (Organoboron). Others like Organozinc also reduces wear and tear. It should be worthy of note that whether these compounds can reduce wear and tear cannot be predicted with certainty with their chemical structure alone[11]

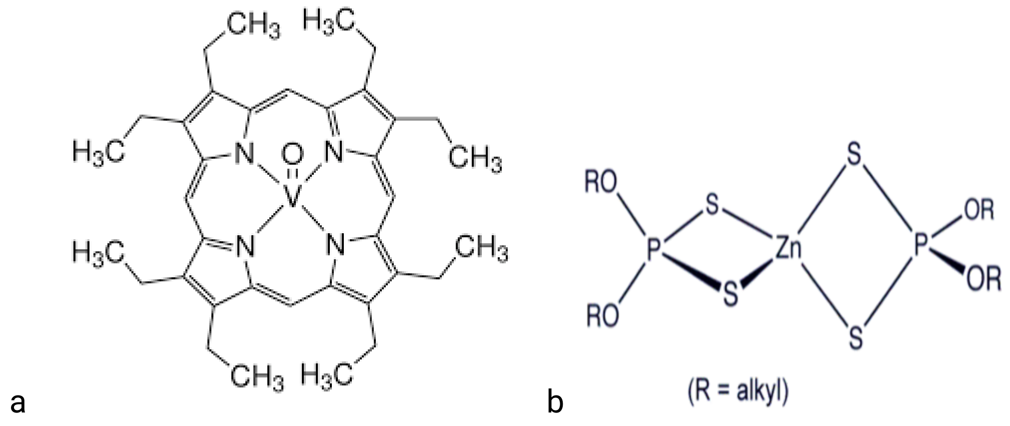


Figure 3 (a) *Vanadium containing porphyrin,* ***(b)*** *zinc dialkyldithiophosphate. A* *typical anti-wear additive in engine oil.*

At present, the most widely applied method for removing sulfur-, nitrogen-, oxygen- and metal-containing species is catalytic hydrotreating.[11-13]

Solid-liquid extraction remains one of the best non-hydrotreating approaches to metal extraction among other methods.

The support of the World's >8bn population requires an industrialized food and resource production system.[14,15] Some of the estimated amount of food produced globally are: 124.73 million metric tons (MMT) of citrus, 114.08 MMT of bananas, 84.63 MMT of apples, 74.49 MMT of grapes, 45.22 MMT of mangoes, mangos teens, and guavas and 25.43 MMT of pineapples.[16-18] All of these, while efficient, produce a large amount of waste much of which is mildly acidic from naturally occurring carboxylic and polyphenolic compounds.

Two types of wastes are generated from processing fruits.

1. The solid wastes of the peel/skin, seeds, stones etc.
2. The liquid wastes from the juice and the wash water.[19]

Improper handling methods and infrastructural deficiency has led to a waste of a very big portion of these food items, their residue and their by-products.[19] It is estimated by the United Nation Food and Agricultural Organization (FAO) that, one third of the food we produce in the world is lost as waste which is estimated at 1.3 MMT p.a.[20-23] It was reported in 1994 by the Washington State Department of Ecology that a reduction of waste will lead to increase in profit, it will bring down liability, reduce use of water and waste, and it will also bring about good public relation. [23]

Food and vegetable wastes could be used for the extraction and isolation of useful and harmful compounds in the oil, food, cosmetics, pharmaceutical, and textile industries. Even though some of the wastes are considered unavoidable, proper planning and use of these wastes for metal extraction can help to reduce the price of refining crude oil and also solve some environmental problems associated with trace metals in crude oil. Most plants produce a range of acidic compounds which protect them from being eaten due to their bitter taste. These compounds tend to be concentrated in parts of the plant which are most important to survival i.e., bark, leaves and fruit. Polyphenolic compounds are found in bark and have been used for tanning leather for thousands of years. Pine bark has also been used to extract heavy metals from the environment.[24]

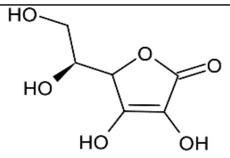
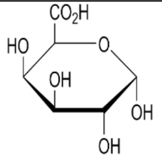
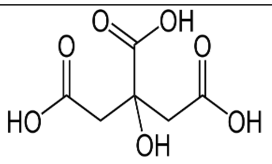
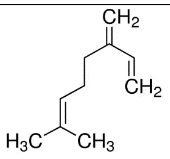
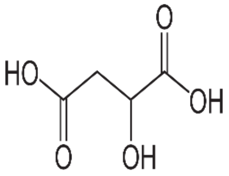
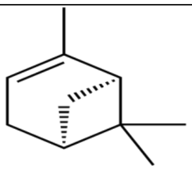
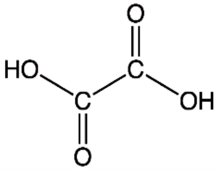
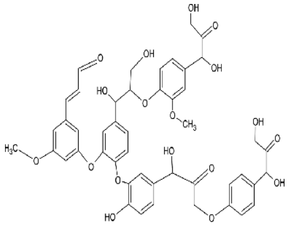
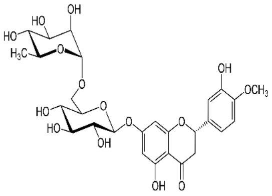
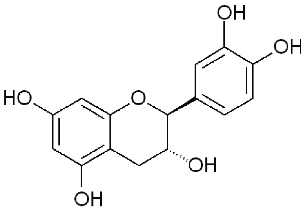
A lot of work has been done on the removal of heavy metals from waste water using chemically modified plant wastes but there seems to be little or no work on the removal of metals from crude oil using fruit waste. Metal ions like Cd, Ni, Cu, Pb and Zn have been extracted from waste water using chemically treated plant wastes and a good percentage of extraction efficiency was achieved.[25-28] A recent study used fruit peels to extract and reuse precious metals from end-of-life lithium-ion batteries. They successfully recovered 90% of Co, Li, Mn and Ni using orange peel and citric acid from citrus fruits.[29] Citric acid is a good multidentate ligand for complexing transition metals.

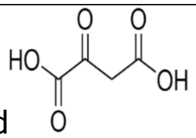
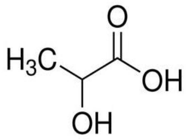
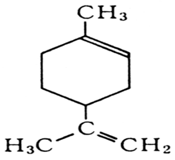
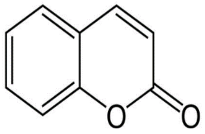
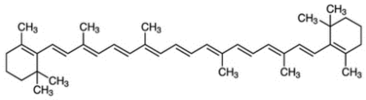
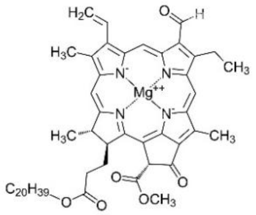
Heavy metals can be removed from solution using a variety of methods including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation and floatation. Nevertheless, these processes generate a significant amount of metallic residue which needs further disposal thus making metal recovery difficult. These processes are also very costly and needs high level of expertise. Adsorption methods can in some cases be reversible but they can have lower costs, they tend to be easier to apply and are generally more robust. Biosorption has previously been used to remove heavy metals from solutions.[30] Biosorption can be defined as the removal of substances from solution by using biological material. These substances can be inorganic or organic. They can be in the soluble or insoluble forms. Major components of agricultural residues are lignin and cellulose including other polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids and ethers which can speed up the process of metal complexation which result in biosorption of metal ions from wastewater.[31] There are so many active components in plants and animals that can chelate and form complexes with metal ions.

This research studies the extraction of Fe (II)Pc, NiPc and Pc using lemon peel and lime peel, as sorbents. They contain active compounds.[32] These components can also chelate with metal ions.[32] The ability of fruit peel to act as an absorbent also depends on its form and water content.

Table 1 shows some of the active materials in addition to starch and cellulose which make up the structural components of fruit peels.

Table 1 General chemical components of fruit peel .[27]

Compound and structure	Compound and structure
Ascorbic acid 	Pectin 
Citric acid 	Myrcene 
Malic acid 	α – Pinene 
Oxalic acid 	Lignin 
Hesperidin 	Tannin 

Oxaloacetic acid 	Lactic acid 
Limonene 	Coumarin 
β-carotene 	Chlorophyll-b, 

The aim of the present study is to establish whether lemon and lime peel can be used to extract metals directly from crude oil *via* solid–liquid extraction. Our working hypothesis is that protonation of the macrocyclic ligand framework—specifically porphyrinato metal complexes—facilitates efficient metal transfer by rendering the coordinated species more compatible with the solid phase. To develop and test this mechanistic model, we first employ metallophthalocyanines dissolved in toluene as a tractable molecular system that mimics the behavior of porphyrinic metal complexes in a simplified hydrocarbon environment. We then extend the optimized extraction conditions to Nigerian crude oil, a well-characterized petroleum system whose trace metal composition is representative of many terrestrially derived crude oils.[33]

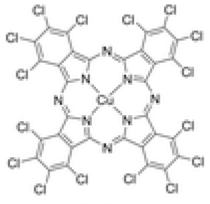
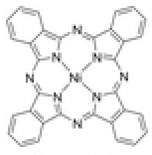
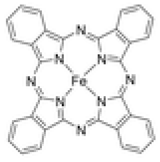
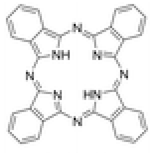
EXPERIMENTAL SECTION

Materials

All reagents and solvents used in this study are listed in **Table 2** together with their suppliers and stated purities. The materials were used as received without further purification. The crude oil sample was gotten from the Samabiri/Biseni flow station in

Bayelsa State, Nigeria.

Table 2 List of reagents used in this study

Materials and solvents	**Origin**	**Formula and structure**	**Purity**
Copper (II) phthalocyanine green ([Cu (Pc^{Cl16})])	Chem Cruz	 $C_{32}Cl_{16}CuN_8$	98%
Toluene	Fisher	$C_6H_5CH_3$	99%
Nickel (II) phthalocyanine ([Ni (Pc)])	Thermo Scientific	 $C_{32}H_{16}N_8Ni$	95%
Iron (II) phthalocyanine ([Fe (Pc)])	Thermo Scientific	 $C_{32}H_{16}FeN_8$	95%
Phthalocyanine (H_2Pc)	Thermo Scientific	 $C_{32}H_{18}N_8$	95%
Triton X-114	Sigma-Aldrich	$C_{14}H_{22}O[C_2H_4O]_8$	

Preparation of Organic Samples

Primary samples of each fruit (orange peel and pine bark) were taken from three different packages from one supplier. Three fruits were taken randomly from each package. To prepare laboratory samples, each fruit was peeled in whole and was homogenized, treating the sample as a whole (peel and bark). These steps were performed immediately after purchase. Prior to homogenization, each fruit was washed separately with distilled water (about 60–70°C) and dried with a paper towel to remove impurities that could affect the assay result. The samples were homogenized using the BUCHI mixer B-400 with ceramic blades. The homogenized samples were placed in plastic flasks and kept deepfrozen at -80°C until analysis. Part of the homogenates were oven-dried for the determination of extraction efficiency of the dried peel.[34]

Extraction experiments with metallophthalocyanines

Iron (II) phthalocyanine ([Fe (Pc)]), nickel (II) phthalocyanine ([Ni (Pc)]) and free-base phthalocyanine (H_2Pc) were dissolved individually in toluene at 25 °C to give stock solutions. Solid–liquid extraction was performed by contacting the metallophthalocyanines solution with the lemon and lime waste peel under controlled mixing conditions.

The concentration of metallophthalocyanines remaining in the toluene phase after extraction was determined using a Shimadzu UV-1601 spectrophotometer. Calibration curves for each compound were prepared over the range 0.01–0.10 μmol dm^{-3}. All samples were diluted as necessary to ensure measurements fell within this linear range.

Determination of metal content in crude oil

Metal concentrations in crude oil before and after extraction were quantified using the emulsion-breaking method developed by de Sousa *et al.*[35] Untreated crude oil (0.5 g) was mixed with 2.5 mL of paraffin wax (mineral oil) to reduce viscosity. An extractant solution comprising 20% (m/v) Triton X-114 and 6.5 mol dm^{-3} HNO_3 (3 mL) was then added, and the mixture was vigorously shaken to form a stable emulsion.

The emulsion was broken by heating at 90 °C for 40 min, followed by centrifugation at 5000 rpm for 15 min. This yielded two distinct phases as seen in **Figure 4** below; the denser lower phase was isolated and submitted for ICP-MS analysis.

For ICP-MS preparation, an aliquot (0.1 g) of the bottom phase was diluted with xylene to a total mass of 10 g. A subsample (0.5 g) of this solution was further diluted to 5.0 g with xylene, and indium was added as an internal standard to obtain a final concentration of 50 μg kg^{-1}. Calibration standards were prepared by dilution of an organic metal standard in xylene.

ICP-MS analyses were performed using a PerkinElmer NexION 300X instrument equipped with a micro-nebulizer and cooled spray chamber. Oxygen was supplied as an auxiliary gas to facilitate direct introduction of the xylene-diluted samples into the plasma.

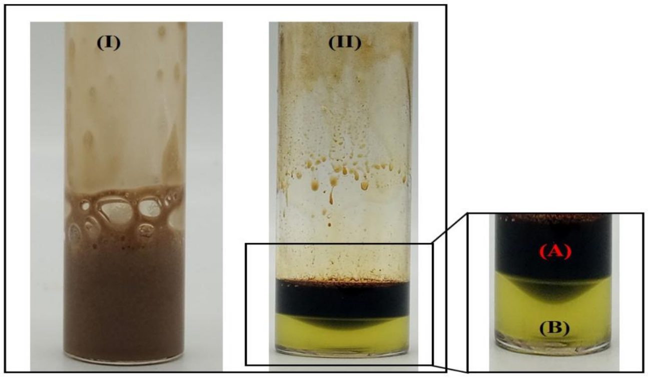


Figure 4 *Emulsion (I) before and (II) after centrifugation for the emulsion breaking. (A) Crude oil phase and (B) aqueous phase*

pH of adsorbents

If the extraction of the metal phthalocyanine is related to its protonation then the extraction efficiency should be dependent on the pH of the botanical absorbents studied. It is difficult to determine a local pH of the absorbent and so a comparative study was carried out by soaking 10 g of each sample in 10 ml of water for 24 hrs. At the end of this time the pH was measured using a pH meter.

Table 3 pH of the adsorbents used

Adsorbent	pH
Orange peel	4.63
Pine bark	5.93

Table 3 shows that all of the absorbents were mildly acidic with lime peel being the most acidic and pine bark being the least acidic.

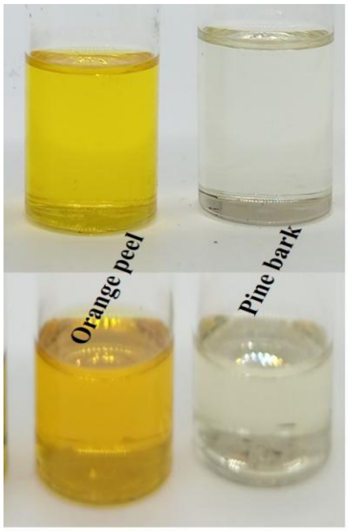
Back extraction from natural products

With natural products as the adsorbent, there are a mixture of polar and non-polar components and so there is a possibility to extract the less polar components into the toluene.

The compounds in **Table 1** have a mixture of polarities. The carboxylic acids are unlikely to be soluble in toluene and the aromatic compounds such as lignins and tannins will have too high a molar mass to be soluble. There are several compounds which will have some solubility such as limonene, myrcene and α – pinene. The aroma of these could be detected in the extract. The other obvious class of compounds is the pigments from the peels. Lime and lemon get their distinguishing colors from chlorophylls, carotenoids, and anthocyanins.

Figure 5 below is a photo of toluene after being in contact with wet and dry orange peel and pine bark. These all show the characteristic yellow and orange pigments from β-carotene, chlorophyll-b, and lycopene respectively. These compounds are only present in low concentrations and should not significantly affect the combustion characteristics of any fuel that they are extracted into.

The UV-Vis absorbance spectrum of wet orange and pine bark, dry orange and pine bark in toluene as seen in **Figure 6** below shows particularly strong signals at 450 and 500 nm which are characteristic of β-carotene and compounds with similar structures such as lycopene. [36,37] So, all this absorbance which are in the B bands (Soret) reveal the presence of poly-phenolics. [38,39] A strong peak was also observed at a wavelength between 400 nm-500 nm in orange peel but not too strong in pine bark. There does not appear to be a significant difference between the wet and dry peels and barks although it is naturally preferable to have dry samples as the water content of the oil does affect its combustion characteristics and the likelihood to aid incomplete combustion and produce smoke. Extraction from the dried sample yields more of the colored components in the toluene phase but this is expected as they are more concentrated when the water has been removed.



a wet

a dry

Figure 5 *Photograph of toluene, wet, dry orange peel and pine bark in toluene*

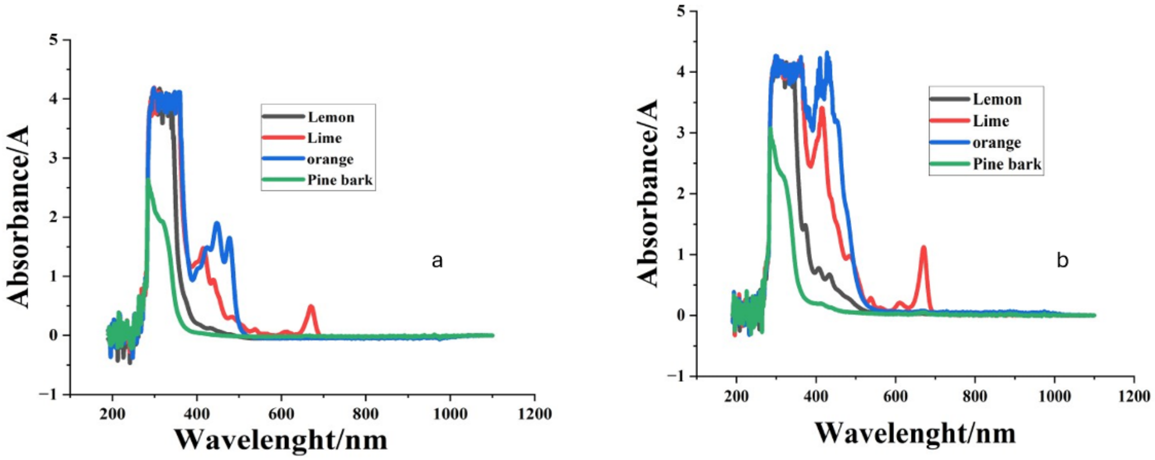


Figure 6 *UV-Vis spectra of (**a**) wet, (**b**) dry orange peel in toluene.*

Physical characterization of crude oil

Thermogravimetric analysis (TGA) of untreated and organic waste treated Samabiri/Biseni crude oil samples was conducted from 25 to 1100 °C under controlled heating conditions. Dynamic Light Scattering (DLS) measurements were performed using a Zetasizer Nano-ZS (Malvern Instruments). Surface tension measurements were obtained using a Krüss K9 tensiometer (model K9MK1) equipped with a Pt–Ir plate (part no. PL21). Density was determined gravimetrically by measuring the mass of a known volume of oil in a calibrated volumetric flask, with reported values representing the average of five measurements.[40] Specific gravity was determined using the standard American Petroleum Institute (API) gravity method (API gravity = 141.5–131.5 per SG).[41]

Table 4 *General properties of the crude oil obtained from Samabiri/Biseni flow station Bayelsa State, Nigeria. *Average of three determinations at 23° C*[40]

Surface tension (mN/m) *	29.7
Density (g/cm^3) *	0.917
Viscosity (cP) *	128.66
API gravity	22.81
Specific gravity	0.917
Refractive index	1.66
Water and sediment (vol. %)	< 1%

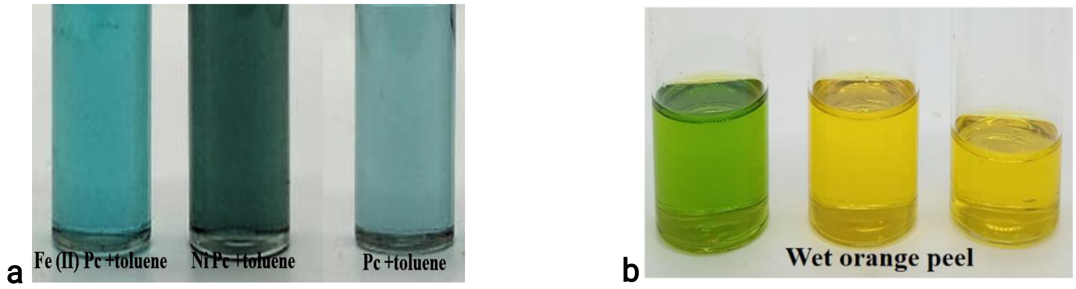
RESULTS AND DISCUSSION

Extraction Fe (II)Pc, NiPc and Pc using wet and dry orange peel (*Citrus sinensis*)

Orange peel is mainly made up of cellulose, pectin, hemi-cellulose, lignin, chlorophyll pigments and some hydrocarbons low in molecular weight. However, it should be noted that the exact chemical composition of orange peel varies based on the location, types, condition of planting, maturity etc. [42] It contain multiple hydroxyl functional groups which are present in the phenolic compound as such it is the most preferred extractant for many pollutants. [43] Many researchers have studied and carried out comprehensive research on it as a good sorbent for removal of marine pollutants and metals because of its availability. [44] Using orange peel for metal removal is eco-friendly because it repurposes agricultural waste. It provides an alternative to synthetic adsorbents and reduces the environmental impact of heavy metal pollution.

Adsorption Mechanism: Pectin molecules contain functional groups (such as carboxyl groups) that can attract metal ions. When orange peel comes into contact with metal ions in a solution, these functional groups interact with the metal ions. The metal ions adhere to the surface of the orange peel through electrostatic interactions and hydrogen bonding as shown in **Figure 7** below.

Figure 7 below is a photo of the extraction of Fe (II)Pc, NiPc, and Pc in toluene using wet and dry orange peel.



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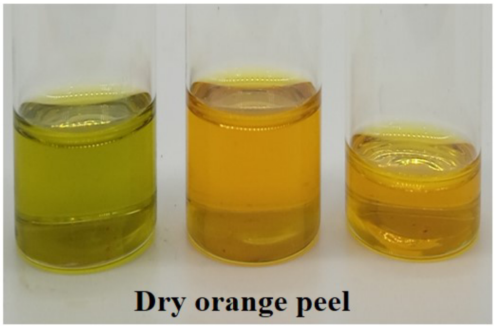

Figure 7 *0.08 mmol Fe (II)Pc, NiPc, Pc in (a)toluene and after extraction with (b) wet orange peel, (c) dry orange peel*

It can be seen from the photos in **Figure 7** above that, there is reasonable extraction of metals complexes with both the wet and dry orange peel

Results obtained so far as seen in **Table 5** and **Table 6** below, shows there is a high percentage of extraction by orange peel. This can be observed both for the dry and wet peel. For the wet orange peel, it was 71.81 % for Fe (II)Pc, 85.24 % for NiPc, and 85.16 % for the Pc. Also, it was 75.44 % for Fe (II)Pc, 45.99 % for NiPc, and 96.17 % for Pc in that of the dry orange peel. This result can be likened to the results of research carried out by Pornsawai Praipipat *et al* in 2023. [45] Studies of the lead extraction efficiency was done by many researchers and it was discovered that at a pH of 5, orange peel powdered and orange peel treated with iron (III) oxide hydroxide lead removal efficiency where, lead 72.60% and 96.27% respectively. [45] This corresponds to results obtained by other studies which reported the highest lead extraction efficiency of orange peel powder and dopped orange peel at a pH > 4.[46] They concluded that, pH of 5 was the best pH of orange peel and dopped orange peel when studying the effect of concentration. Marin et al (2010) investigated the role of three major functional groups (amine, carboxyl and hydroxyl) on the extraction of chromium using a dopped orange peel which (orange peel) was chemically modified by esterification, acetylation and methylation in order to selectively block the functional groups. It was observed that the extraction capacity was decreased by esterification. Thia may be due to the fact that the esterification of the orange peel will stop the functionality of the carboxyl functional group since it is taking part in the esterification reaction. This clearly indicate the importance of the carboxylic functional group present in the orange peel. The amine and the hydroxyl group have minimal effect. They reported 40.56 mg/g as the highest adsorption capacity.[47] Lugo-Lugo *et al* (2012) extract chromium using a dopped orange peel in both single (only chromium present) and binary mixtures (chromium and iron presence). They discovered that in the binary mixture, there was interference in the removal of chromium in the presence of iron as more than one heavy metal in the mixture may increase, decrease or may not affect removal performance of the extractant. The extraction per cent and extraction capacity obtained in the presence of chromium only was 51% and 4.79 mg/g. 79 % and 7.60 mg/g for that of chromium alongside with iron. That is an indication that the presence of iron increased the percentage extraction of chromium which is not surprising because the presence of more than one metal in the mixture may increase, decrease or not affect at all the extraction efficiency of an adsorbent.[48] In same vein, Lopez-Tellez *et al* (2011) extracted chromium from a prepared composite mixed with nanoparticles of iron and orange peel. It was discovered that for this composite the percentage extraction and the adsorption capacity were 71% and 5.37 mg/g, respectively, as compared to untreated orange peel which was 34% and 1.90 mg/g, respectively.[49] Kumar, et al. (2018) studied the physical characterization of orange peel and discovered that, increase in surface area increases the sorption capacity of the orange peel. [50] In this case, one would have expected that the extraction efficiency for the dry orange peel would be larger than that of the lump because of its low water content absence of many volatile compounds but that was not the case. The extraction percentage was relatively the same for both dry and wet orange peel except for NiPc which shows a lower extraction percentage with the dry peel. This is contrary to other work done by researchers where a bigger surface area of orange peel adsorbs more chromium and lead than the smaller surface area.[51] The effect of surface area was minimal when applied to metal porphyrins. This may be due to the fact that the walls of the orange peel attract molecules rather than the surface area covered because the walls of the orange peel are invariably destroyed in the dried orange peel.[52] It clearly shows that the metal ion in the porphyrin is attracted to the surface of the orange peel than the other peripherals in the porphyrin ring. [51] Even though the specific surface area of orange peel increased with decreasing particle size, Pc, Fe (II)Pc and NiPc were adsorbed on both wet and dry orange peel. Hydration can increase the density of particles with decreasing particle size and this could reduce the abundance of adsorption sites with enough size to retain Fe (II) and Ni (II) ions. Pc is adsorbed on the swelled bio-adsorbents (smaller particle size) because Pc has a lower ionic radius than Iron and nickel. [51] Ajimal et al studied the capability of orange peel to remove Zn, Ni, Cu, Pb, and Cr from aqueous medium and found out that the order of metal adsorption was Ni (II) > Cu (II) > Pb (II) > Zn (II) > Cr (II). [53] Sha et al also studied the adsorption of Pb^{2+} and Zn^{2+} from aqueous solution using sulphured orange. [49] Certain parameters such as metal ion concentration, adsorption time, and pH were used to verify the efficiency of extraction. It was observed that the kinetics of adsorption for both metals progressed rapidly.[54, 55] studies have shown that the carboxylic and pectin groups in the orange peel is responsible for the removal of metals and as such chemical characterization of the orange will increase the carboxylic group in the orange peel thus increasing the extraction efficiency. [52, 56, 57] Studies have also shown that, an increase in the volume of orange peel, results to an increase in extraction of metals. [58]

Extraction using wet and dry pine bark (*Pinus Radiata D. Don*)

Pine bark is abundant, renewable, and low-cost, making it an excellent alternative to ion-exchange resins and activated carbon for industrial applications. It is produced as a waste product from the paper making industry. The physical and chemical properties of pine bark that are important to it functionality.

1. Aging and Freshness: Aging refers to stockpiling and weathering bark in windrows before use, without fertilizer additions or pH adjustments. It is common in the south-eastern U.S.

Fresh Pine Bark: This is increasingly used due to its lighter weight, reducing transportation costs. However, it has distinct properties compared to aged bark. Fresh pine bark has higher air space (AS), lower container capacity (CC), and lower available water content than aged bark.

Aged pine bark theoretically holds more water due to increased fines, uniform particle sizes, and reduced hydrophobicity. The suggested Best Management Practices (BMP) of pine bark are as follows; Total porosity (TP): 50% - 85%, Air space (AS): 10% - 30%, Container capacity (CC): 45% - 65%, Bulk density (BD): 0.19 - 0.70 g/cm³.[59]

2. Chemical Composition: Non-amended pine bark typically exhibits the following chemical properties: pH (hydrogen ion concentration), low calcium, magnesium and zinc.[60] Fresh pine bark is identifiable, has undecomposed organic matter coupled with high lignin content. It should be noted that continually changing the physical and chemical properties of pine bark make it unstable.[60, 61]

Figure 8 below is a photo of the extraction of Fe (II)Pc, NiPc and Pc from an organic phase using wet and dry pine bark. It can be seen that, there is a relatively good extraction using pine bark. It should be noted that the bark does not color the toluene to the same extent as the fruit peels because the color of bark is due to tannins and lignin which are too polar and have too high a molar mass to be soluble in toluene.

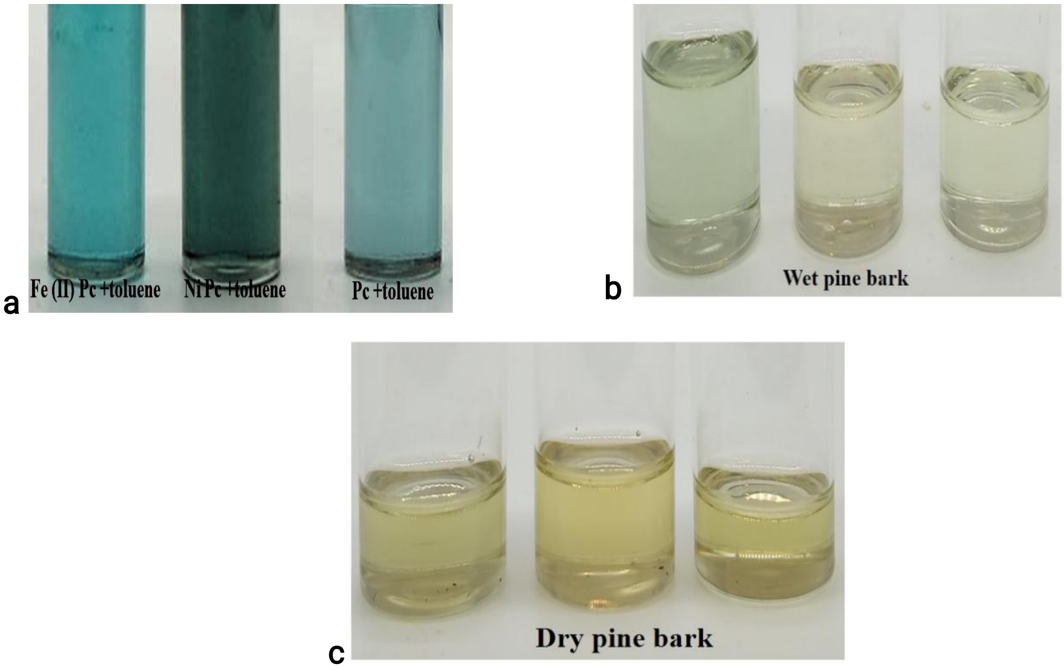

***Figure 8** 0.08 mmol Fe (II)Pc, NiPc, Pc in (a) toluene and after extraction with (b) wet pine bark, (c) dry pine bark*

Table 5 The percentage extraction of metal Fe (II)Pc, NiPc, and Pc with orange peel and pine bark (wet)

Reagents	% Fe (II)Pc Extracted	% [NiPc] Extracted	% [Pc] Extracted
Orange Peel	72	85	85
Pine Bark	92	78	92

Table 6 The percentage extraction of metal Fe (II)Pc, NiPc, and Pc with orange peel and pine bark (Dry)

Reagents	% Fe (II)Pc Extracted	% [NiPc] Extracted	% [Pc] Extracted
Dry orange Peel	75	46	96
Dry pine Bark	60	52	78

Application to Nigerian Crude Oil

Figure 9 shows sample of crude oil after extraction with lemon peel. There is no visible change in the appearance of the oil although this is not surprising. There was also no change in the aroma of the oil. The crude oil sample was sent for ICP-MS analysis after extraction to determine the metal composition.

a. before **b. after**

Figure 9 *orange peel and pine bark (a) before treatment (b) after treatment in crude oil*

The efficiency of the orange peel and pine bark for the extraction of the metals from crude oil have been clearly shown from the ICP-MS analysis as shown in **Table 7**

Table 7 *ICP-MS analysis of metal concentration in Crude Oil before and after extraction with lemon peel, using Extraction Induced by Emulsion Breaking (EIEB) Procedure in a 1:5 fruit peel to oil ratio*

Extractant	**Metal concentration (ppb)**				
	Mg	V	Fe	Ni	Cu
No extract Crude oil	13307	972	104340	10116	2914
Pine bark extract	762	73	3357	849	1144
Orange peel	940	101	<1990	1008	909

extract					

This can be seen from the initial concentration of metal ions such as magnesium, vanadium, iron, nickel, and copper in the crude oil before the extraction. These metal ions are found in the crude oil in the form of a porphyrinic complexes. The Mg will be from the original chlorophyl and some Fe will exchange from surrounding rock strata. These complexes are mainly associated with the asphaltenes fractions in the crude oil. To remove the metal ions from the crude oil, the total asphaltene must be broken so as to expose the metal ions for extraction. Due to the amphiphilic properties of fruit peel and pine bark, the asphaltene phase could have been adsorbed on hydrophobic sectors enabling a significant amount of the metal ions to be extraction from the crude oil.

Recovery of the extractant after extraction

The extractant was recovered with a simple method as shown in **Figure 9** below. After extraction for 40 minutes at 25^{o}C, the crude oil was recovered with decantation. The remaining extractant which is mixed with crude was washed with cyclohexane and dried in the fume cupboard for 30 minutes to get a clean and dry extractant. Cyclohexane was used because initial studies show that, the porphyrin was not soluble in cyclohexane. Although this method was not tested to be efficient, safe and reliable, it surely recovered a crude oil free extractant after extraction from its physical look.

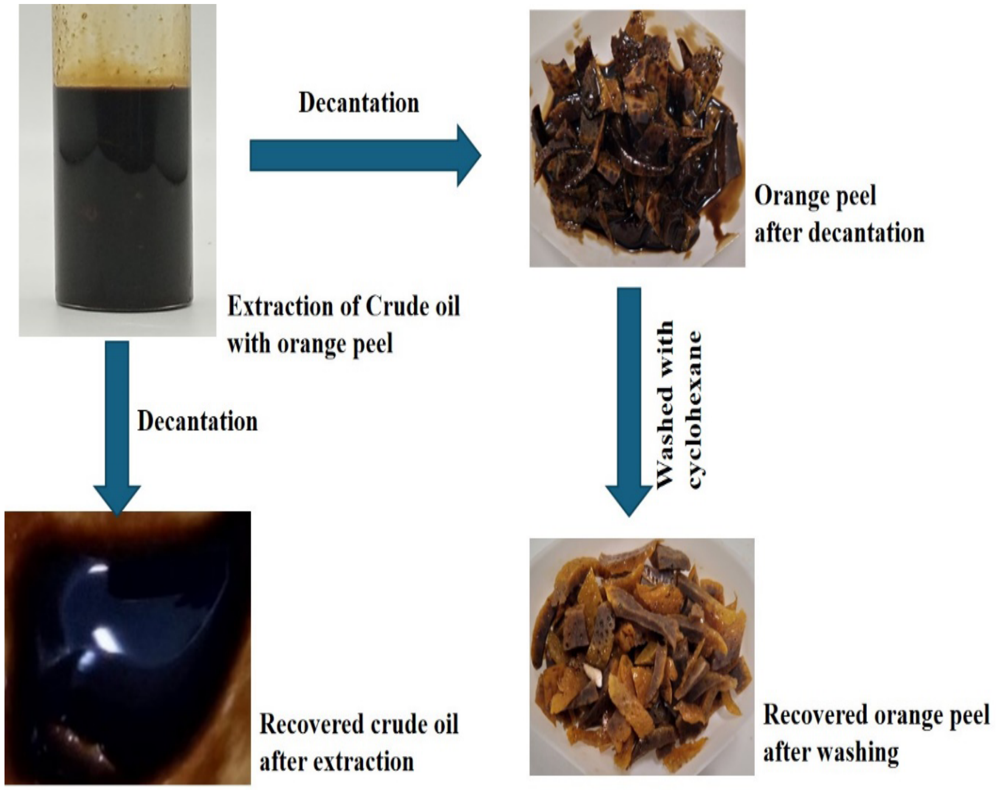

Figure 10 *Diagram for the recovery of extractant after extraction*

This is possibly not a viable method for processing the botanical waste after extraction and a more useful approach may be, to use the botanical/oil mixture for combustion in a combined heat and power plant fitted with a scrubber to capture any metal particles produced.

Conclusion

Adsorption is a very reliable and sustainable method in heavy metal removal compared to coagulation, flocculation, ion exchange, precipitation, osmosis, flotation etc. These conventional methods mentioned above are not good for the extraction of heavy metal ions from organic medium like crude oil at trace concentrations. These methods lead to increase in cost of extraction and degradation of environment, hence, scientists are studying and focusing on the use of botanical, environmentally benign low-cost extractants for metal extraction. Cellulose containing agricultural waste products are promising extractants for metal extraction, because of their availability and they are renewable natural resources. Most of these wastes are rich in lignin, cellulose, hemicelluloses and organic acids content which bind to heavy metals on the surface. This work studied the extraction of metal phthalocyanines (Fe (II)Pc, NiPc) and metal free phthalocyanine (Pc) and some metals from an organic medium and crude oil using various adsorbents from agricultural wastes. After a thorough selection, two agricultural wastes in terms of percent metal removal, viz. orange peel and pine bark, were selected, and then, their possibility of achieving maximum metal removal under similar conditions was tried. Although the physico-chemical characteristics and the chemical composition of the agricultural wastes were known from relevant literature, they were characterized with pH meter for identifying the pH. From the UV-Vis analysis of the solution before and after extraction, it was observed that there is a high affinity of Fe (II)Pc, NiPc and Pc towards the orange peel and pine bark substrate. Over the years, there has been a great interest in the use of barks and other biomasses for the extraction of heavy metals. All of them shows relatively good extraction for metal free phthalocyanine. Hydroxylated species and free ions coupled with the pH of the extractant were suspected as the major factors responsible for extraction. It is clear that most of the agricultural wastes used for metal extraction in this work exhibited good extraction capacity as such these materials can serve as an alternative to other available methods applied for metal extraction from organic medium. Although the research work looks pretty fantastic, further research is needed to look into some parameters like, the recovery of the metals, the reuse of the extractants, multi-metal studies and the optimization of adsorbents. Also, researchers should give attention to the heterogeneity of the pine bark which is made up of the phloem (with inner functional region for conduction and an outer non-functional region), the periderm (with phelloderm, phellogen and phellem) and the rhytidome, the complexity of the structure and its attendant chemical composition. They should also focus on the studies of their mechanism, this includes but not limited to their coordination chemistry, metal speciation and their binding sites.

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Notes

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ABBREVIATIONS

Phthalocyanato (2-), Pc; Iron phthalocyanine. FePc; Nickel phthalocyanine, NiPc; thermogravimetric analysis, TGA; dynamic light scattering, DLS; American Petroleum Institute, API; extraction induced by emulsion breaking, EIEB; inductively coupled plasma mass spectroscopy, ICP-MS; million metric tons, MMT.

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