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Lemon and Lime Peel Organic Waste as Media for Metal Removal from Crude Oil

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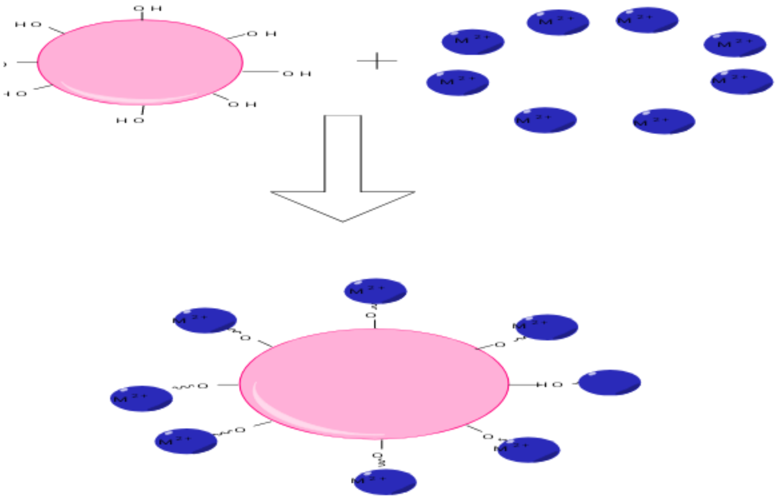
KEYWORDS: Organic waste, Sustainable crude oil processing, Solid -liquid extraction, Metal adsorption, Metalloporphyrin, Metallo phthalocyanines, Electrostatic interaction



Possible mechanism of metal adsorption on orange peel

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 lemon and lime peel were evaluated as alternative media for extracting metal-containing complexes from crude oil. Model experiments using copper, iron, and nickel 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 lemon and lime peel 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 mainly comprised of alkanes, cycloalkanes, aromatic hydrocarbons and a higher molecular mass fraction of complex molecules called asphaltenes. It also contains other organic compounds containing elements such as nitrogen, oxygen, and sulphur. Some trace metals are found in petroleum, including but not limited to iron, copper, nickel and vanadium. The short chain hydrocarbons burn very efficiently and smoothly so are vital compounds for the production of diesel and petrol. Alkanes are made up of single carbon bonds with the general formula C_nH_{2n+2}. Alkanes are nonpolar molecules that have only London dispersion forces as a means to attract one another. As a result of this, they have relatively low melting and boiling points. They make up a homologous series, which is a group of molecules which share the same general formula, undergo the same chemical reactions and show trends in their physical properties. Crude oil is made up of a greater amount of longer chain alkanes compared to shorter chains. Cracking which is a process of breaking down large hydrocarbon molecules in crude oil into smaller, more useful molecule, can be used to solves the problem between supply and demand for short chain alkanes.

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^-).[1,2] 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. [6] 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. [3,4]

At present, the most widely applied method for removing sulfur-, nitrogen-, oxygen- and metal-containing species is catalytic hydrotreating.[5-7]

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.[8,9] 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.[10-12] 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.[13]

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.[13] 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.[14-17] 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.[13]

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.[18]

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.[19-22] 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.[23] 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.[24] 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 can speed up the process of metal complexation which result in biosorption of metal ions from wastewater.[25] 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, lime peel, orange peel, and pine bark as sorbents. They contain active compounds.[26] These components can also chelate with metal ions.[26] The ability of fruit peel to act as an absorbent also depends on its form and water content.

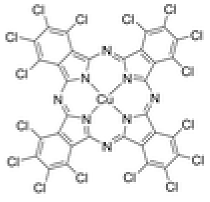
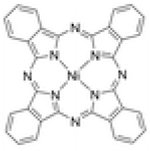
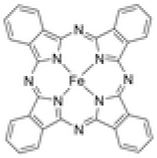
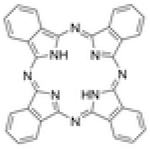
The aim of the present study is to establish whether lemon and lime peel can be used to extract metals directly from crude oil *via* solid–liquid extraction. Our working hypothesis is that protonation of the macrocyclic ligand framework—specifically porphyrinato metal complexes—facilitates efficient 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.[27]

EXPERIMENTAL SECTION

Materials

All reagents and solvents used in this study are listed in **Table 1** 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 1 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 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). 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 deep-frozen at -80°C until analysis. Part of the homogenates were oven-dried for the determination of extraction efficiency of the dried peel.[28]

Extraction experiments with metallophthalocyanines

Copper (II) phthalocyanine green ([Cu (Pc^{Cl16})]), 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 metallophthalocyanine solution with the organic 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.*[29] 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 1** 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.

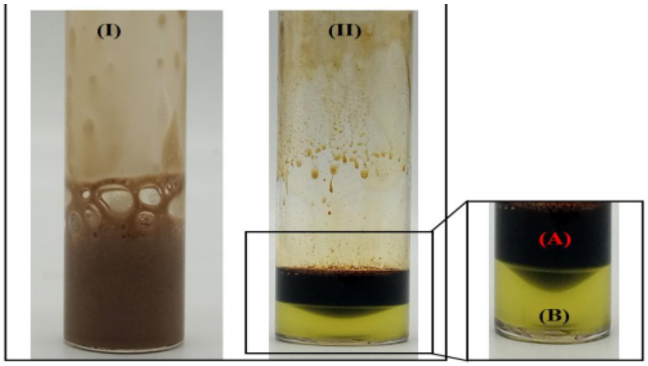


Figure 1 *Emulsion (I) before and (II) after centrifugation for the emulsion breaking. (A) Crude oil phase and (B) aqueous phase*

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 2 pH of the adsorbents used

Adsorbent	pH
Lemon peel	4.82
Lime peel	4.45

Table 2 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

The compounds in **Table 2** 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, lemon and orange get their distinguishing colors from chlorophylls, carotenoids, and anthocyanins.

Figure 2 below is a photo of toluene after being in contact with wet and dry lemon peel and lime peel. These all show the characteristic yellow, green 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 lemon and lime fruit peel, dry lemon and lime fruit peel in toluene as seen in **Figure 3** below shows particularly strong signals at 450 and 500 nm which are characteristic of β-carotene and compounds with similar structures such as lycopene. [30,31] So, all this absorbance which are in the B bands (Soret) reveal the presence of poly-phenolics. [32,33] A strong peak was also observed at a wavelength between 400 nm-500 nm in lime but not too strong in lemon. Ultraviolet/visible absorption spectroscopy can be used to determine low levels of calcium. Although, aqueous solutions of calcium salts are colorless and therefore do not absorb in the near UV and visible region, it is possible to detect it in this case since it is found in a colored organic medium. [34] There is another strong absorbance for lime peel at 670 nm which is found in the Q band region. This is suspected to be potassium or magnesium.[35]

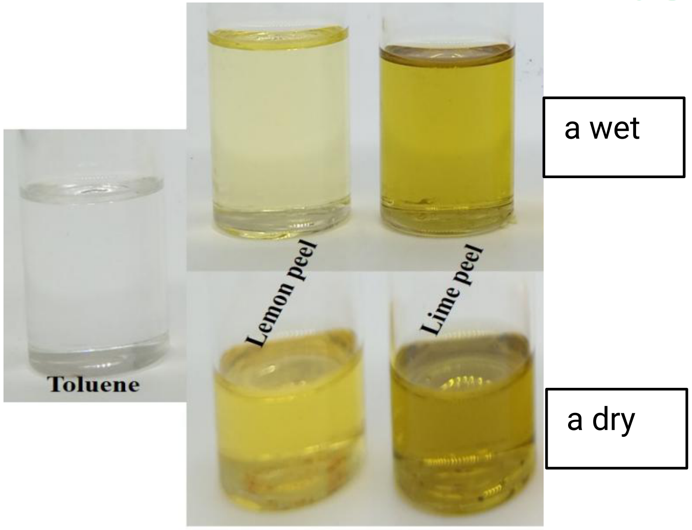
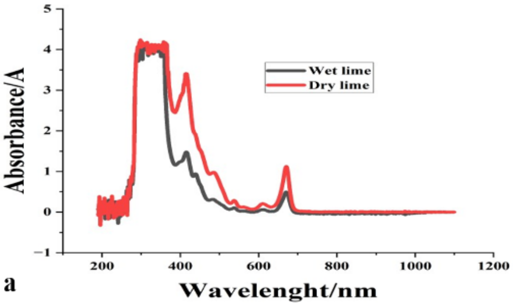
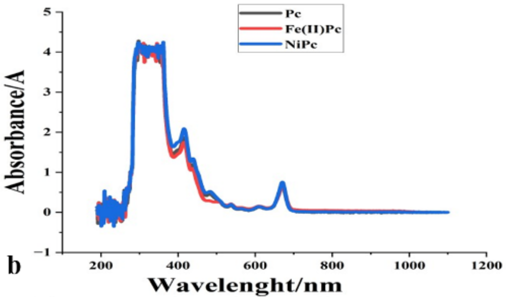


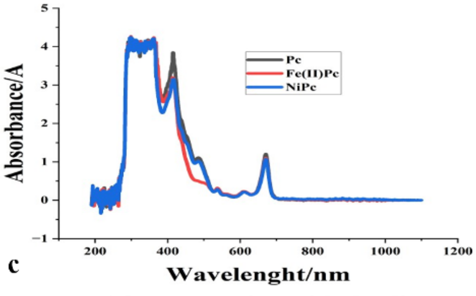
Figure 2 *Photograph of toluene, wet, dry lemon peel and lime peel in toluene*



Wet and dry lime in toluene



After extraction with wet lime



After extraction with dry lime

Physical characterization of crude oil

Thermogravimetric analysis (TGA) of untreated and DES-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.[36]

Specific gravity was determined using the standard American Petroleum Institute (API) gravity method (API gravity = 141.5–131.5 per SG).[37]

RESULTS AND DISCUSSION

Extraction Fe (II)Pc, NiPc and Pc using wet and dry lemon peel (*Citrus limon*)

Lemon peels are known to contain many bioactive compounds. They have high concentrations of ascorbic acid, citric acid, malic acid, fiber, calcium, potassium, D-limonene, hesperidin, coumarins, polyphenols, terpenes, tannins and magnesium. [38]

Figure 4 below shows the extraction of Fe (II)Pc, NiPc and Pc in toluene using wet and dry lemon peel. The extraction was carried out using a solution of 0.08 mmol of Fe (II)Pc, NiPc and Pc in toluene at 50wt % (5 g/5 g) for 40 minutes at 25°C and the remaining concentration of the metal phthalocyanine in the toluene was calculated after analysis with UV-vis spectrometer using Beer Lambert law.

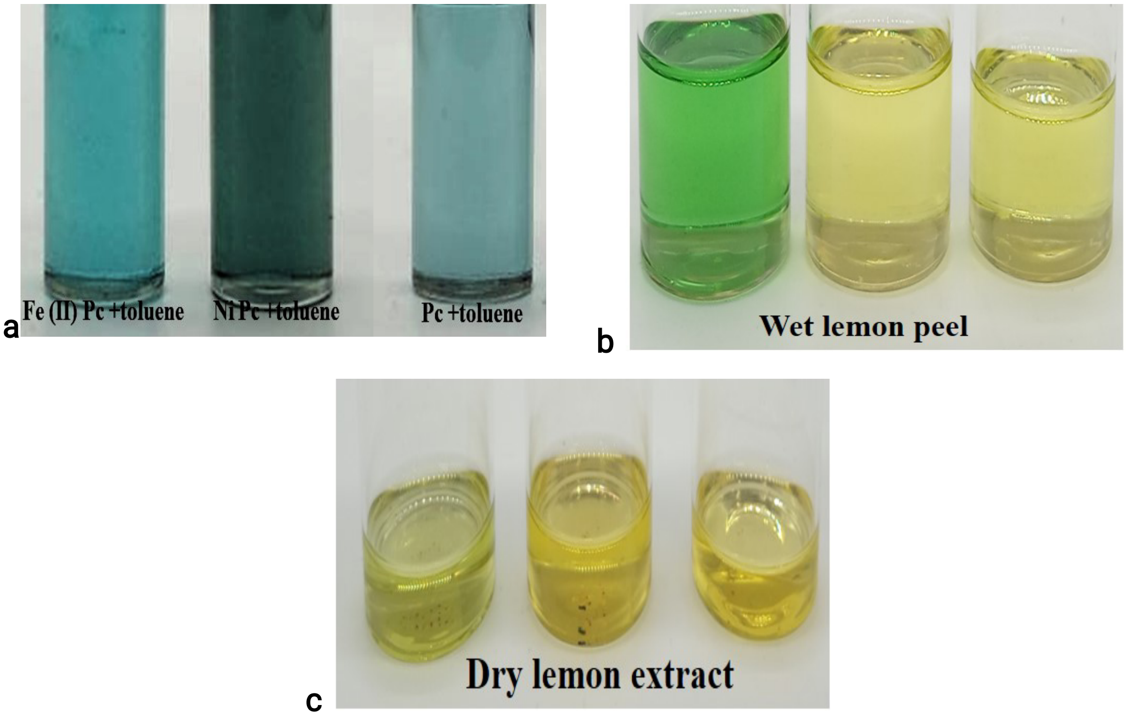


Figure 4 *0.08 mmol Fe (II)Pc, NiPc, Pc in (a)toluene (b)after extraction with wet lemon peel, (c) dry lemon peel*

The absence of blue color in most of the samples shows that the Fe (II)Pc, NiPc and Pc were adequately extracted and the majority of the metal porphyrin was extracted into the solid phase of the lemon peel. The yellow color of the toluene shows that the carotenoids have been back extracted and in the case of Fe (II)Pc with wet lemon peel the green-colored solution shows that some of the phthalocyanine is still remaining. As seen from the results in **Table 3** below, the percentage extraction for Fe (II)Pc, NiPc and Pc using wet lemon peel is 76.4 %, 97.8 %, and 100 % respectively. These numbers should however be treated with caution as the absorbance at 400-450 nm will be affected by the carotenoids which will also absorb at this wavelength so the actual amount of metal extracted will be higher.

Studies have shown that lemon peel have been very efficient in removing Cu (II), Cr (VI), Pb (II), and Zn (II) ions from industrial affluents, chemical industries etc. [39] The relatively high percentage of extraction may be due to the fact that lemons are rich in three organic acids: citric, malic, and ascorbic acid. Among these, citric acid is the most abundant, giving lemons their characteristic sour taste. [40] It is not surprising that, the metal free porphyrin has 100 % extraction as clearly seen that metals have significant effect on extraction efficiency. Also, in the ionicity of metals, (The ability of a **metal** to combine with a more electronegative element by the formation of an **ionic** (or heteropolar) bond), nickel is higher than iron hence the higher extraction efficiency of nickel to iron.

Table 3 The percentage extraction of metal Fe (II)Pc, NiPc, and Pc with lemon and lime peel (wet)

Reagents	% Fe (II)Pc Extracted	% [NiPc] Extracted	% [Pc] Extracted
Lemon peel	76	98	100
Lime Peel	94	85	100

Table 4 The percentage extraction of metal Fe (II)Pc, NiPc, and Pc with lemon and lime peel (Dry)

Reagents	% Fe (II)Pc Extracted	% [NiPc] Extracted	% [Pc] Extracted
Dry lemon peel	60	83	94
Dry lime Peel	99	88	100

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