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Eco–Friendly Refining of Petroleum Wastewater Via *Banana Musa L.* Peel

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ABSTRACT

This project investigate the ability of *banana musa L* peel for adsorption of lead and copper ions from refinery petroleum wastewater. The main functional groups in banana peel were identified by FTIR, Elements composition of used medium has been characterized by Inductively Coupled Plasma (ICP). Lead and copper were determined in refinery petroleum wastewater and their standard solutions before and after passing on banana peel medium by using Atomic Absorption Spectrophotometry technique (AAS). The adsorption isotherm fitted by Freundlich model at 38 ^oC and pH=5.5. The FTIR spectrum revealed that the main functional groups in banana peel are OH, C-H stretching, carboxylic acids and amino groups. Elements composition of banana peel medium was found to be Fe, Cu, K, Li, Mg, Mn, Mo, Na, Ni, P, Pd, Sr, Ti, V and Zn. The banana peel showed high ability to uptake lead and copper ions from refinery petroleum wastewater and their standard solutions. The R^2 of leaner shape of adsorption isotherm for lead and copper ions was found to be 0.999 and 1 respectively. The concentration of lead and copper ions in refinery wastewater was reduced from 0.091, 0.060 ppm to 0.027 , 0.013 ppm respectively, after being passed through banana peel medium.

1. Introduction

Petroleum refining utilize large quantities of water for desalting, distillation, thermal cracking, catalytic and treatment processes to produce useful products [liquefied petroleum gas (LPG), gasoline, jet fuel, diesel, asphalt and petrochemical feedstock][1][2][3]. Refining process generates wastewater (0.4-1.6 times the volume of crude oil processed)[4]. Discharge of untreated petroleum refining wastewater (PRW) into water bodies results in environmental and human health effects due to release of toxic contaminants (hydrocarbons, phenol and dissolved minerals)[5][6]. Hydrocarbons [benzene, toluene, ethyl benzene and xylenes (BTEX) are of serious concern due to their toxicity and as carcinogenic compounds [3][7][8]. High exposure for long periods to these compounds can cause leukemia and tumors in multiple organs[3]. Phenol and dissolved minerals are also toxic to aquatic life and lead to liver, lung, kidney and vascular system infection[9][10] .Therefore, according to Environmental Protection Agency (USEPA), PRW have to be sufficiently treated for quality to meet the established regulations[11].

Several technologies have been proposed to treat wastewater contaminated with metal species. Among several technologies, the extraction of metal ions using solid materials such as modified silica, alumina, activated carbon, and resins has been extensively investigated [3][7]. These materials have been subjected to functionalization reactions to anchor molecules containing Lewis bases in its structure, which acts as a metal collector[12][13]. In the case of silica, the main advantages are its high surface reactivity, the possibility to anchor molecules with desirable selectivity to ward metals ions[14,15] and the high stability of legend molecules on the silica surface, enabling the matrix to be used over a number of cycles. Despite these advantages, preparing modified silica gel with organic molecules is expensive because high-purity chemicals are required to enhance the efficiency of the reaction; moreover, the solvents used in the modification reaction are usually toxic[16][17]. This standpoint, therefore led to natural solid material that can be considered more attractive, besides being aligned with the concepts of green chemistry. Natural products usually considered waste, such as sugar cane bagasse, peanut shells, and apple waste, have been employed to extract metals from water[18][19]. This is possible due to the presence of acid groups such as carboxylic and phenolic groups[20]. This type of product can also be used in metal speciation, as in the case of Cr(VI) sorption by coconut coir[19].

The project analyzed banana peel and characterized by FTIR thought identify of main functional groups and elements composition of medium was carried out by ICP. The banana peels were tested for the adsorption of lead and copper into refinery petroleum wastewater and their standards. The adsorption isotherm was fitted by Freundlich model at 38 ^oC and pH= 5.5.

2. Materials and Methods

2.1. Materials

All chemicals used were of analytical reagent grade (AR). Nitric acid, Copper II Nitrite, Sodium Hydroxide, Lead nitrate, Refinery petroleum wastewater, Deionized water and Banana peel.

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2.2. Procedures

The experimental works were conducted at chemistry lab – Omdurman Islamic University, Central lab – University of Khartoum and chemistry lab – Ministry of Minerals, Khartoum – SUDAN.

2.2.1. Samples Collection

Banana Peels

Banana was collected from Blue Nile State (Admazien area) and have been ripened under controled ethylene friezing Refrigerator at Omdurman industrial area for 7 days. Taxonomic authentication of the plant has been carried out in the Botany Department - Faculty of Science and Technology - Omdurman Islamic University - SUDAN.

Refinery Petroleum Wastewater

The used refinery wastewater was collected from Khartoum Refinery at El-Gili- Khartoum north- Sudan.

2.2.2. Preparation of Banana Peels as Adsorbent Medium

A 500g of banana were weighed and washed well with distilled water then the peel were dried at 80 ^{o}C for 24 hours[15].

2.2.3. Preparation of standard solutions of Lead and Copper

Lead nitrate and copper nitrate salts were used to prepare standard solutions of (1, 10, 20 and 30 ppm) of Pb II and Cu II ions in 100mL volumetric flasks, according to standard methods of preparations of standard solutions.

2.2.4. Identification of Banana Peels

Identification of main Functional Groups by Fourier Transform Infrared Spectrophotometer (FTIR)

Dried powdered banana peel was used for FTIR analysis using KBr disk methodology. 1 mg of sample was encapsulated in 100 mg of KBr pellet. The powdered sample was loaded in FTIR spectroscope (Shimadzu, IR Affinity 1, Japan), with a scan range from 400 to 4000 cm $^{-1}$ with a resolution of 4 cm $^{-1}$ [21].

Identification of Elementary Composition of Banana Peels by using ICP technique

a. Instrumentation

The analytical determination of metals was carried out by ICP (Inductively Coupled Plasma): ELAN 9000 (Perkin Elmer Sciex Instrument, Concord, Ontario, Canada) [18].

b. Calibration

The ICP calibration was carried out by external calibration with the blank solution and three working standard solutions (10, 20 and 30 μg/L) for all elements[18].

c. Sample Preparation

A 0.5 mg of dried banana peel was weighed and transferred into a clean gosh crucible , then the peel was burned using muffle furnace at 550 ^{o}C for 2 hours. The ash peel was transferred by 10 ml concentrated hydrochloric acid into 100 mL volumetric flask, finally the volume was completed to the mark by deionized water.

2.2.5. Preparation of the Raw Wastewater Sample

The sample of refinery petroleum wastewater was subjected to a digestion procedure to oxidize organic substances such as humic acids, that bind metal ions in solution and influence the pre - concentration results. In this procedure, concentrated HNO_3 (5mL) was added an aliquots of 50 mL of wastewater in a beaker. The mixture was then subjected to evaporated on hotplate. The colour of the solution became dark. Further HNO_3 conc (5mL) was added and the mixture was heated for 1 h at 95 ^{o}C. The pH of the digested extract was adjusted to 5.5, the sample's volume was adjusted to 100 mL in a volumetric flask [20].

2.2.6. Passing of Standard Solutions of Lead and Copper on Banana Peels (Adsorption process)

Banana peel (2g) was placed in adsorption column. Prepared wastewater (100mL) was passed through the peel for adsorption of lead and copper ions. Then standard solutions of lead II and copper II ions (1, 10,20 and 30 ppm) were being passed separate through different banana peel (2g). The pH was adjusted at (5.5). Experimental data has been analyzed by Freundlich model (eq 1)[17].

$$\text{Log } a = \text{Log } K + n \text{ Log } C \qquad \text{……….. (Eq1)}$$

Where:

a ≡ Adsorption efficiency

C ≡ Standard concentration of metals before adsorption process.

K and n ≡ Freundlich constant.

2.2.7. Investigation of Lead and Copper Concentration

The lead and copper ions concentrations were investigated in refinery petroleum wastewater before and after passing through banana peel and in the four standard solutions of lead and copper ions using Atomic Absorption Spectrophotometry technique (AAS) [20].

3. Results and Discussion

The percentage yield of dry banana peel is shown in Table 1.

Table 1. Yield of dry Banana Peel.

Weight of raw banana peel (g)	Weight of dry banana peel (g)	percentage Yield (% $_{g/g}$)
500	150.73	30.1

The percentage yield of dry peels is higher than percentage yield of renata *et al* since 2011[20], they found that the percentage yield of dry Brazil banana peel is 20.3 %. The comparison between obtained result of percentage yield in the current study and renata *et al* results is shown in Fig 1.

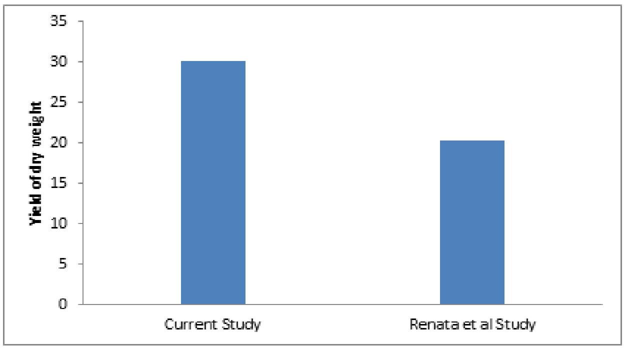

Fig 1. comparison Between current Study and Renata *et al* Results.

The main functional groups in dry banana peel were identified by FTIR technique, the IR spectrum is shown in Fig 2. and the main functional groups found in banana peels were tabled in Table 2.

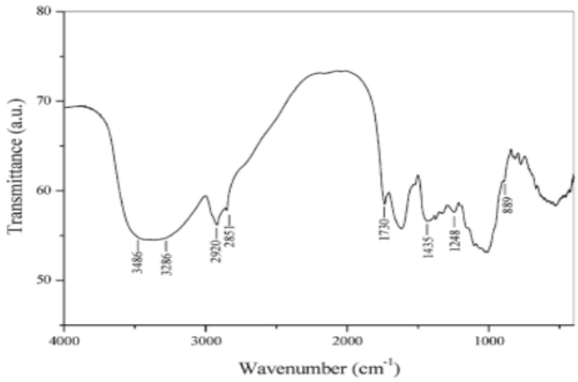

Fig 2. IR Spectrum of Banana Peel.

Table 2. The Main Functional Groups in Dry Banana Peel.

Wave Number (cm^{-1})	Functional Group
3486 - 3286	O-H
2920 – 2851	C-H
1730	Carboxylic acid
889	Amino groups

The elements composition of banana peels are shown in Table 3 and Fig 3..

Table 3. Elements Composition of Banana peels

Element	Concentration (PPm)
Cu	0.0579
Fe	3.779
K	403.3
Li	0.0424
Mg	8.887
Mn	0.2341
Mo	0.0171
Na	1.215
Ni	0.3344
P	13.24
Pb	0.0458
Sr	0.1086
Ti	0.0306
V	0.0019
Zn	0.1180

The obtained Results in table below revealed that the highest metals concentration in banana peels is K, P, Mg and Fe. The concentration of heavy metals very lower except the concentration of Iron is 3.779 ppm.

Copper and lead concentration in banana peel were found to be 0.0579 and 0.0458 ppm respectively , the low concentration of lead and copper in peel showed a good evidence for the ability to remove these mineral ions from their solutions.

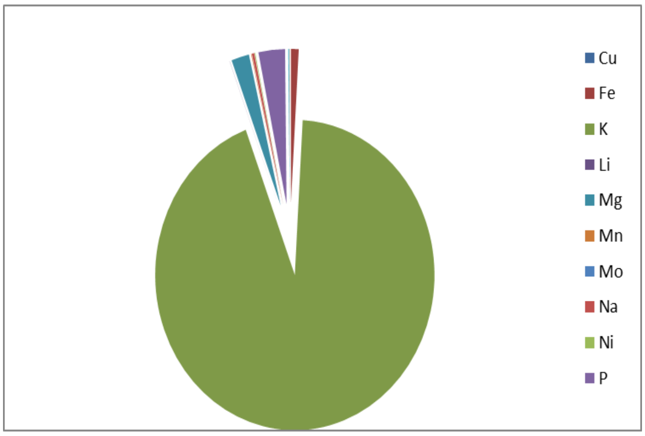

Fig 3. The elementary composition of banana peels

The concentration of lead and copper in refinery petroleum wastewater before and after passing on banana peel was shown in Table 4.

Table 4. The concentration of lead and copper in refinery petroleum wastewater before and after passing on banana peels.

Metals	Before Passing on Banana Peels	After Passing on Banana peels
Lead	0.091	0.027
Copper	0.060	0.013

The concentration of lead and copper in refinery petroleum wastewater were found out of limits assigned by ASTM, the permissible range of lead and copper in petroleum wastewater is 0.03 and 0.02 ppm respectively. The obtained results revealed that the banana peel have shown high abilities of adsorption of lead and copper from refinery petroleum wastewater , the concentration of lead and copper in wastewater after passing on peels medium were found to be lower than ASTM limits. The comparison between the concentration of lead and copper in refinery petroleum wastewater before and after passing on banana peel are shown in Fig 4 and Fig 5. Respectively.

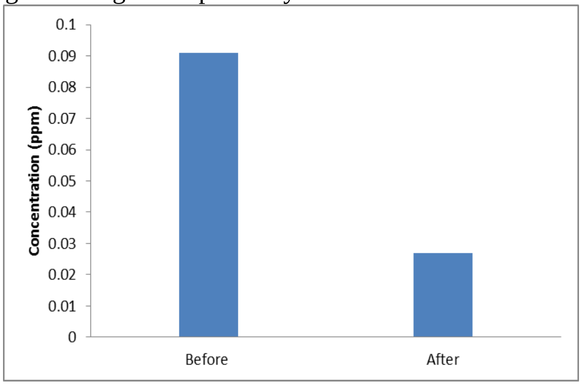

Fig 4. Concentration of Lead in Refinery Petroleum Wastewater Before and After Passing on Banana Peel.

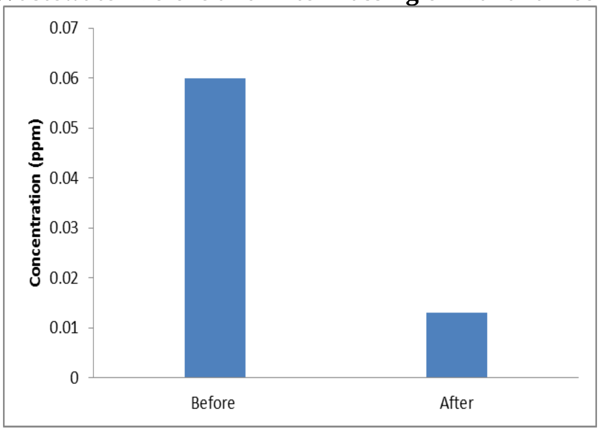

Fig 5. Concentration of Copper in Refinery Petroleum Wastewater Before and After Passing on Banana Peel.

The results of standard solutions of lead and copper before and after adsorption isotherm are shown in Table 5and Table 6 respectively.

Table 5. Concentration of Standard Lead Solutions Before and After Passing on Banana Peels Medium.

Before (ppm)	After (ppm)
1	0.232
10	0.208
20	0.334
30	1.06

Table 6. Concentration of Standard Lead Solutions Before and After Passing on Banana Peel Medium.

Before (ppm)	After (ppm)
1	0.020
10	0.389
20	0.455
30	0.847

The obtained results revealed that the banana peel showed high uptake ability of lead and copper from their solutions , the concentration of lead and copper after adsorption isotherm were investigate by sensitive and valuable technique (AAS) [20].

The Concentration of lead and copper in all standard solutions (1, 10, 20 and 30 ppm) were reduced after being passed through banana peels medium. The Freundlich isotherm models[17] were used to analyze the experimental data, the adsorption capacity of banana peel were investigated according to the (Eq2)[17].

$$a = ni/w \qquad \text{……………. Eq 2.}$$

Where :

a ≡ Adsorption Capacity (mole/g)

ni ≡ Adsorbed Number of Moles (mole)

w ≡ weight of medium (g)

$$ni = nb - na \quad \text{………….. Eq3.}$$

Were

nb ≡ Number of moles for ion before the adsorption process[17].

na ≡ Number of moles for ion after the adsorption process[17].

The leaner shape of adsorption isotherm of lead and copper are represent in Fig 6 and Fig 7 respectively.

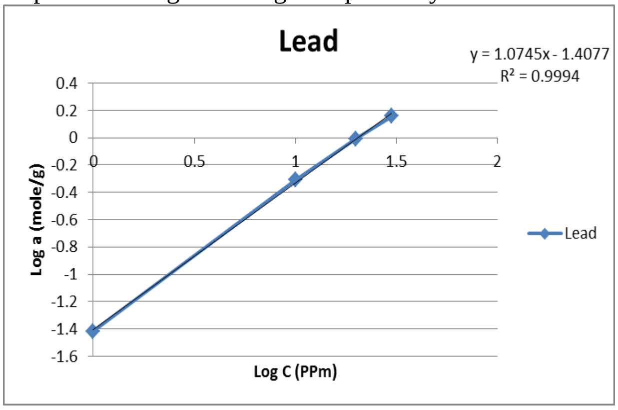

Fig 6. Leaner Shape of Adsorption Isotherm for Lead

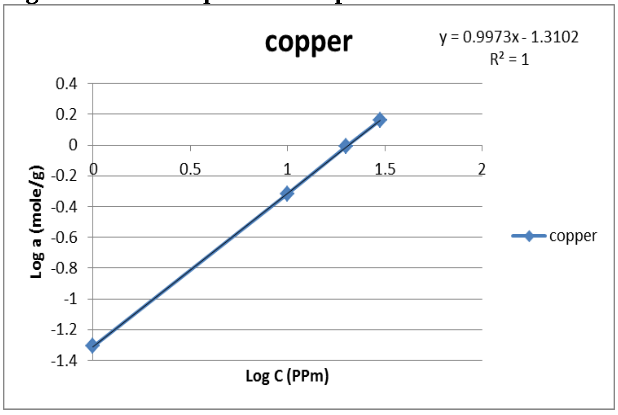

Fig 7. Leaner Shape of Adsorption Isotherm for Copper

The (R^2) of leaner shape of adsorption isotherm for lead and copper was found to be 0.999 and 1 respectively, these results revealed that the banana peel showed different uptake abilities of lead and copper from their solutions.

The higher extraction capacity of Cu(II) ions can be explained by the fact that carboxylic acid groups[20], which are considered hard bases, have a stronger affinity for hard or intermediate acids such as Cu(II) ions. Pb (II) ions that are considered soft due to their large ionic radius and high polarizability, which cause their extraction to occur to a higher extent[20].

4. Conclusion

This research led to the conclusion that minced banana peel can be applied in the extraction and pre - concentration of lead (II) and copper (II) ions in refinery petroleum wastewater. The adsorption isotherm was fitted by Freundlich model and R^2 of leaner shape of adsorption isotherm for lead and copper ions were found to be 0.999 and 1 respectively. The uptake ability of banana peel can be explained by the fact that carboxylic acid groups which are considered hard base , have a strong affinity for interacted with lead and copper ions. The high retention percentage of Cu(II) and Pb (II) in acid medium is an important aspect of the adsorption process because it can be applied to the purification of wastewater. In our opinion, this biomaterial is also very attractive due to its low cost and the fact that it does not require modification reactions such as those required by other materials used in this type of work.

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