Study of the bioadsorption of heavy metals (Pb and Cu) in the waters of the Puyango river, using orange and apple banana peel.

Estudio de la bioadsorción de metales pesados (Pb y Cu) en las aguas del río Puyango, utilizando cáscara de naranja y plátano manzano.

Stefanie Michelle Bonilla Bermeo, 1 *; Eliza Yisabel Ortiz Sánchez 2; Lady Germania Vega Calero 3

Abstract

Bioadsorbents are a new alternative to remove heavy metals, low cost compared to conventional methods. In this research work, the adsorption capacity was evaluated with a particle size of 0.3150 mm of apple and orange banana peel powder in water contaminated with lead and copper, carried out under normal conditions of ambient temperature and constant agitation at 100rpm. The experimental procedure was based on two studies, the first one was carried out with 5%, 10%, 15% of each bioadsorbent powder of orange peel and apple banana with the 500ml sample of raw water. The second was based on the preparation of standard solutions with different concentrations starting with 5000ppm, 8000ppm, and 10,000ppm, with each bioadsorbent from which aliquots of 10ppm, 20ppm y 30ppm. The best removal results were obtained with the standard solution of 8000ppm, taking an aliquot of 30ppm. With the orange peel powder, a removal percentage of 91.60% of Lead and 78.11% of Collection was obtained, with a maximum adsorption capacity (q mg/g) 0.075 of Copper and 0.1284 of Lead. While with the apple tree banana, a removal percentage of 93.47% of Lead, and 85.71% of Copper with a maximum capacity (q mg/g) 0.082 of Copper and 0.1311 of Lead was obtained. In addition, with the mixture of both bioadsorbents, a removal percentage of 72.27% Copper was obtained, with a maximum capacity (q mg / g) 0.069 Copper.

Keywords: Bioadsorption, orange peel and apple tree, lead, copper removal.

Resumen

Los bioadsorbentes son una nueva alternativa para remover metales pesados, de bajo coste en comparación con los métodos convencionales. En el presente trabajo de investigación se evaluó la capacidad de adsorción con un tamaño de partícula de 0,3150 mm de polvo de cáscara de plátano manzano y naranja en agua contaminada con plomo y cobre, realizados en condiciones normales de temperatura ambiente y agitación constante a 100rpm. El procedimiento experimental se basó en dos estudios, el primero se realizó con 5%, 10%, 15% de cada bioadsorbente en polvo de cáscara naranja y plátano manzano con la muestra de 500ml de agua cruda. El segundo, se basó en la preparación de soluciones patrón con distintas concentraciones partiendo con 5000ppm, 8000ppm y 10000ppm, con cada bioadsorbente de los cuales se tomó alícuotas de 10ppm, 20ppm y 30ppm. Los mejores resultados de remoción se obtuvieron con la solución patrón de 8000ppm, tomando una alícuota de 30ppm. Con el polvo de cáscara de naranja, se obtuvo un porcentaje de remoción del 91,60% de Plomo, y 78,11 % de Cobre, con una capacidad máxima de adsorción (q mg/g) 0,075 de Cobre y 0,1284 de Plomo. Mientras que con el plátano manzano, se obtuvo un porcentaje de remoción del 93,47% de Plomo, y 85,71 % de Cobre con una capacidad máxima (q mg/g) 0,082 de Cobre y 0,1311 de Plomo. Además, con la mezcla de ambos bioadsorbentes se obtuvo un porcentaje de remoción del 72,27% de Cobre, con una capacidad máxima (q mg/g) 0,069 de Cobre.

Palabras claves: Bioadsorción, cáscara de naranja y plátano manzano, plomo, cobre remoción.

1. Introduction

Water is a vital liquid for life. Over the years there has been an increase in its contamination due to anthropogenic activities, making many of its uses impossible and generating great concern. For this reason, research has been promoted and new environmentally friendly technologies have been developed to address this issue [1].

Heavy metals are currently considered one of the main pollutants of water bodies in places with greater mining exploitation, damaging the environment and the health of those who consume it, causing severe and irreversible damage [2].

Prolonged contact with small amounts of lead can cause irreversible damage in children. It has been discovered that at concentrations of 7 micrograms of lead per deciliter of...
blood causes irreversible damage to children's nervous systems [3].

Heavy metals are highly hazardous contaminants for the aquatic environment since they have low biodegradability and a great ability to accumulate in different organisms. Processes to treat waters contaminated by metals generally use activated carbon, solvent extraction, membrane technology, ion exchange, among others, but most of these processes become very costly, causing them to be discharged into rivers without any treatment [4].

Bioadsorption is a new alternative to remove heavy metals from water. One of its main advantages is that it is low cost because its raw material comes from agricultural waste such as orange peel, banana peel, apple peel, plantain peel, grapefruit peel, etc., and it has high efficiency [5].

Orange and plantain peels have biosorption properties because they contain functional groups called (carbonyl, carboxyl, sulfhydryl hydroxyl alkyl, phosphates) in their composition, allowing ion exchange [6].

Therefore, the objective of this research is to determine the adsorption capacity of orange and plantain peels for the treatment of waters contaminated by heavy metals (Pb and Cu) present in the River.

1.1. Background of the Puyango River
The Puyango River, located between the Provinces of El Oro and Loja, remains permanently polluted, due to the presence of heavy metal waste from mining production in the upper stretch of the Province of El Oro, whose waters are unsuitable for human use, livestock, and agriculture. Its basin covers 4,700 square kilometers and is where the binational Puyango-Tumbes plan will be executed, which will enable 40,000 hectares. Some fish species have vanished, and others have migrated to other places with less pollution. It is unavoidable that through a regulation the Government prohibits miners from throwing waste into the tributary, but rather that it be purified beforehand with chemical processes so that purified and clean water free of pollutants flows into the river basin. It is regrettable that to this day the Ministry of the Environment does absolutely nothing to decontaminate this great river [7].

1.2. Impacts of mining activity
The main acidification problems in the Province of El Oro occur in the rivers and groundwater, due to drainage from gutters, underground corridors, tailings, slag, oxidative leaching and leaching of metal sulfides, especially pyrite. The rivers that present oxidative leaching and leaching of metal sulfides, especially pyrite, with the greatest pollution generation are the Pindo and Puyango rivers. The dissertation carried out by the Ministry of the Environment of Ecuador (MAE) determined that in summer the likelihood of returning heavy metals in suspended solids to the human body and fish is much higher than in winter. A clear example occurs in Puyango, where Pb concentrations in summer range between 3,972 and 5,080 μg/g and in the rainy season Pb decreases to 269 and 345 μg/g [2].

In the rivers of the Province of El Oro, discharges of pollutants resulting from mining activity negatively affect all life forms, causing severe environmental impacts and damage to human health. The Cantons of Portovelo and Zaruma are the main affected sectors due to the intake of contaminated water and food.

Currently, there are very few studies in relation to the consequences caused by mining activity on human health [2].

1.3. Sources of heavy metal contamination in food

<table>
<thead>
<tr>
<th>Source of contamination</th>
<th>Heavy metal involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural, from soil</td>
<td>Cadmium, bromine, fluoride, copper</td>
</tr>
<tr>
<td>Use of insecticides, disinfectants, and medications.</td>
<td>Arsenic, copper, lead, mercury</td>
</tr>
<tr>
<td>From sandy soil and glass packaging</td>
<td>Silicon</td>
</tr>
<tr>
<td>From processing equipment</td>
<td>Copper, iron, nickel, tin, lead, cadmium</td>
</tr>
<tr>
<td>Due to storage</td>
<td>Iron, nickel, tin, lead, cadmium, strontium</td>
</tr>
<tr>
<td>From oxidation in packaging</td>
<td>Iron and copper</td>
</tr>
<tr>
<td>Due to processing</td>
<td>Copper, cadmium, arsenic</td>
</tr>
<tr>
<td>Dietary supplements in animal feeds</td>
<td>Copper, cadmium, iron, zinc, arsenic</td>
</tr>
</tbody>
</table>

Source: [8].

1.4. Sources of emission and generation of heavy metals
Metals belong to the earth's crust. These large proportion pollutants which manifest in the environment through human activities, causing environmental damage. Mining is one of the main causes of heavy metal pollution due to the extraction of large amounts of material, through the refining of precious metals or also by the discharge of industrial effluents into the environment and vehicle
emissions. The inappropriate distribution of metal waste has thus caused soil, surface and groundwater contamination and aquatic environments [9].

1.5. Heavy metals in wastewater
The increase in concentration of these compounds in wastewater is mainly due to industrial or mining pollution. Landfill leachates or wastewater discharges are sources of contamination [10].

These sources are also emitted by domestic, commercial, and industrial wastewater:
- Chemical products
- Mining activity
- Petroleum combustion
- Wastewater

1.6. Chemical composition of orange peel

<table>
<thead>
<tr>
<th>Component</th>
<th>Conceptual content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble sugars</td>
<td>16.9%</td>
</tr>
<tr>
<td>Cellulose</td>
<td>9.21%</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>10.5%</td>
</tr>
<tr>
<td>Pectin</td>
<td>42.5%</td>
</tr>
</tbody>
</table>

Source: [12].

1.7. Orange peel as a bioadsorbent
Adsorption through residual biomass is quite promising, which is why it is very important to highlight orange peel as a bioadsorbent with great potential. Orange waste such as its peel contains cellulose, pectin, hemicellulose, and lignin. They also contain other lower molecular weight compounds including limonoids. They therefore contain active functional groups such as carboxyl present in pectins and hydroxyls found in cellulose. Phosphate and thiol are also able to bind to metal ions in solution [13].

1.8. Cation exchange capacity of orange peel
This cation exchange capacity (CEC) is the total sum of cations that an adsorbent material has available to be exchangeable. The results obtained in the triplicate determination of this parameter indicated an average of 8.04 (meq/100g sample). This value was compared with those obtained for other types of materials used as adsorbents [6].

1.9. Orange production in Ecuador

According to the Ministry of Agriculture, orange production in Ecuador in 2011 was 84 thousand metric tons in warm climate locations in the province of Bolivar where 40,706 tons were taken to market. When harvesting ends, Ecuador stops importing this crop. The provinces with the highest production are Manabí and Los Ríos [14].

Orange production in Ecuador is represented as one of the 25 most representative crops in the country. This plant, with proper harvest management, can produce 15 oranges per year. Ecuador is estimated to have 55,953 orange plantation hectares, of which 10,639 hectares belong to the province of Bolivar and 2,650 hectares belong to the Caluma canton, representing 4.73% of its national production. The most common orange production is white orange [15].

Orange production in Ecuador is located in the province of Bolivar and in the Caluma canton belonging to the province of Bolivar, containing different cultivated varieties such as: Valencia, Lime orange, Valencia tadia, Sour orange, Valencia delta and Pomelo orange. The highest production is that of Valencia orange [15].

1.10. Characteristics of the banana plant
The stem of the tree measures approximately 2-5 m and the height can reach up to 8 m with the leaves. The fruits are berry-shaped without seeds, cylindrical distributed in hands of 30-70 bananas measuring 8 to 13 cm in length and 3 cm in diameter, its pulp is ivory colored and buttery, and its skin is yellow [16].

1.11. Functional properties of banana peel
The main byproduct of banana productive development is the peel; therefore, it represents around 30% of the fruit's weight; the tenacity and capacity of the banana peel depend on its chemical structure. Banana peel is rich in dietary energy, proteins, essential amino acids, polyunsaturated fatty acids, and potassium; among the efforts to use the peel, proteins, methyl alcohol, ethanol, pectins and enzymes have been emanated [17].

1.12. Natural polymers that have bioadsorbent properties

According to the Ministry of Agriculture, orange production in Ecuador in 2011 was 84 thousand metric tons in warm climate locations in the province of Bolivar where 40,706 tons were taken to market. When harvesting ends, Ecuador stops importing this crop. The provinces with the highest production are Manabí and Los Ríos [14].

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Below we describe the following steps for preparing the raw material:

- **Collection of raw material**: Waste orange peels (Citrus sinensis L.) were collected from the juice sales establishment at the University of Guayaquil and plantain (Musa sapientum) waste peels from a banana plantation located in Los Ríos.

- **Cleaning**: The peels were washed with plenty of distilled water to remove impurities and compounds such as tannins and reducing sugars.

- **Chopping**: After cleaning, the peels were cut into small pieces to facilitate the drying process and size reduction.

- **Drying**: Drying was carried out at a temperature of 60°C in the oven for 48 hours until a constant mass was obtained.

- **Grinding**: They were ground to reduce and pulverize the particle size.

- **Sifting**: Once pulverized, they were sifted by size using the Tyler sieve which consists of a series of sieves from which only particle sizes of mesh #9 equivalent to 0.3150mm were collected.

### Common name | Extracted from | Part where it is obtained
---|---|---
Alginate | Brown sea algae | The whole plant
Pectin | Orange peel | All the peel
Starches | Corn, potato, cassava, wheat | The grain or tuber
Nopal pectin | Opuntia Ficus Indica | The leaves
Nirmali seeds | Strychnos potatorum | The seeds
Carob | Quebracho, acacia or carob Schinopsis lorentzi | Tree bark
Carboximeticelulosa | Trees | Tree bark
Guar gum | Cyanopsis psoralioides | Seeds

Source: [18].

### 1.13. Plantain peel as a biomaterial

The ability of lignocellulosic residues to adsorb heavy metal ions is of great importance for developing effective and low-cost technologies to treat water. Plantain peel contains cellulose, pectin, hemicellulose, and lignin as well as other lower molecular weight compounds including limonoids. They therefore contain active functional groups such as carboxyl, hydroxyls and amines [9].

### 1.14. Plantain cultivation

This type of cultivation occurs with greater production in temperate climates. After planting, its first production occurs at 1 year and its stem is used as fertilizer due to its high-water content. Its product is well received in the local market and is also imported in smaller proportions to other countries [19].

### 1.15. Main characteristics for cultivation

The plant is described as a large herb and is said not to be a tree. Its leaves are very elongated and has the following crop characteristics:

- **Plant**: It is large and is composed of several leaves that develop on the stem.
- **Bulb or rhizome**: (described as a stem containing several buds). It is an underground stem that helps produce several points in plant growth.
- **Roots**: It has superficial roots, white in color if buried, and yellowish and hard when emerging on the surface.
- **Stem**: The stem is large and is buried. When a bud forms it will become an inflorescence (flower).
- **Leaves**: They are produced in the elevated part of the rhizome. The flowers sprout from the leaf axis.
- **Flowers**: Its flowers are yellowish and accompanied by six stamens.

- **Fruit**: It is an elongated berry, yellowish green in color [17].

### 1.16. Plantain production in Ecuador

The production of this product is very small in Ecuador because it is a rare species, and its fruits are small. The country that imports the most is Colombia because of its characteristic flavor. Ecuador only imports 10% of this product. Peasants take advantage of this product to make flour and later porridge because of its high nutrient content, being a breast milk substitute [19].

Ecuador is one of the main banana exporters and only 10% are plantains. Most of its production remains locally because it is grown on a larger scale in other countries in Asia and Africa [20]. The traditional production of this banana is in the Cucay area of the Guayas province, Azuay, El Oro, Bolivar, Cotopaxi, and Chimborazo, in charge of marketing the product nationwide and internationally, but in smaller quantities than bananas [21].

### 2. Materials and Methods

Procedure to obtain orange peel and plantain peel powder biomaterial.

Below we describe the following steps for preparing the raw material:

- **Cleaning**: The peels were washed with plenty of distilled water to remove impurities and compounds such as tannins and reducing sugars.
- **Chopping**: After cleaning, the peels were cut into small pieces to facilitate the drying process and size reduction.
- **Drying**: Drying was carried out at a temperature of 60°C in the oven for 48 hours until a constant mass was obtained.
- **Grinding**: They were ground to reduce and pulverize the particle size.
- **Sifting**: Once pulverized, they were sifted by size using the Tyler sieve which consists of a series of sieves from which only particle sizes of mesh #9 equivalent to 0.3150mm were collected.
Storage: They were stored in sterilized bags separated according to particle size to prevent moisture uptake and contamination until subsequent testing.

2.1. Physicochemical characterization of bioadsorbents

➢ Determination of the pH of the bioadsorbents.
➢ A 10 g sample dissolution was made in 90 ml of distilled water with constant stirring, the resulting solution pH was measured.
➢ A pH of 4.27 was obtained for the orange peel powder and 6.05 for the plantain powder.
➢ Determination of the moisture percentage of plantain and orange peel powders.
➢ Approximately 3073.756 g of orange peel and 3860.854 g of plantain peel were weighed and introduced into an oven at 60°C for 48 hours. After this time, the samples were passed to a desiccator until cooled to room temperature for subsequent weighing and obtaining the moisture percentage.

Calculation of moisture percentage

\[
%H = \frac{\text{weight}_{\text{initial}} - \text{weight}_{\text{final}}}{\text{weight}_{\text{initial}}} \times 100
\]

Calculation of moisture percentage of dehydrated orange peels

\[
%H = \frac{3073,756g - 798g}{3073,756g} \times 100 = 74.03\%
\]

Calculation of moisture percentage of dehydrated plantain peels

\[
%H = \frac{3860,854g - 518g}{3860,854g} \times 100 = 86.58\%
\]

2.2. Preparation of the solution with the bioadsorbents

The obtained bioadsorbent is weighed on an analytical balance to prepare a 5000 ppm, 8000 ppm, and 10000 ppm solution separately for each bioadsorbent to carry out the necessary experimentation in the flocculator equipment and find the optimal dose to treat the raw water. The experimental design details the process conditions to define the effective result for the capture of heavy metal ions (lead and copper), using orange peel and plantain peel powder with a single particle size corresponding to 0.315 mm.

A total of 27 experiments will be carried out. In the first 6 experiments, equal percentages of 5%, 10%, and 15% of each bioadsorbent will be used and they will be taken to the flocculator where the samples to be treated will be.

This will be followed by 18 more experiments which will be carried out from the preparation of a separate standard solution of each bioadsorbent of 5000 ppm, 8000 ppm, 10000 ppm from which dosages of 10 ppm, 20 ppm and 30 ppm will be taken and placed in a precipitation vessel with sample to be treated.

Finally, 3 experiments will be carried out in which a mixture of the bioadsorbent will be used in a 1:1 ratio of the powder, an 8000 ppm solution was prepared from which dosages of 10 ppm, 20 ppm and 30 ppm will be taken and placed in a precipitation vessel with sample to be treated, the best adsorption results will be selected.

The experimental design is detailed below:

<table>
<thead>
<tr>
<th>Orange peel powder (%)</th>
<th>Volume of raw water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1= 5</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 10</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 15</td>
<td>500</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plantain peel powder (%)</th>
<th>Volume of raw water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1= 5</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 10</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 15</td>
<td>500</td>
</tr>
</tbody>
</table>

Source: [22].
Table 5. Experimental design of copper and lead bioadsorption using orange peel and plantain peel powder.

<table>
<thead>
<tr>
<th>Standard solution (5000ppm)</th>
<th>Volume of raw water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peel powder</td>
<td></td>
</tr>
<tr>
<td>Sample 1= 10ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 20ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 30ppm</td>
<td>500</td>
</tr>
<tr>
<td>Plantain peel powder</td>
<td></td>
</tr>
<tr>
<td>Sample 1= 10ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 20ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 30ppm</td>
<td>500</td>
</tr>
</tbody>
</table>

Source: [22].

Two 5000 ppm standard solutions were prepared, one of the bioadsorbent from orange peel powder and the other from plantain peel powder bioadsorbent, with a particle size of 0.3150 mm. Aliquots of 10ppm, 20ppm, and 30ppm were dosed in each of the precipitation vessels containing 500ml of water to be treated. Subsequently, the experiment was carried out in the flocculator equipment with stirring for 12 hours at 100 rpm.

Table 6. Experimental design of copper and lead bioadsorption using orange peel and plantain peel powder.

<table>
<thead>
<tr>
<th>Standard solution (8000ppm)</th>
<th>Volume of raw water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peel powder</td>
<td></td>
</tr>
<tr>
<td>Sample 1= 10ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 20ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 30ppm</td>
<td>500</td>
</tr>
<tr>
<td>Plantain peel powder</td>
<td></td>
</tr>
<tr>
<td>Sample 1= 10ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 20ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 30ppm</td>
<td>500</td>
</tr>
</tbody>
</table>

Source: [22].

Two standard solutions of 8000 ppm were prepared, one of the bioadsorbent from orange peel powder and the other from plantain peel powder bioadsorbent with a particle size of 0.3150 mm. Aliquots of 10ppm, 20ppm, and 30ppm were dosed in each of the precipitation vessels containing 500ml of water to be treated. Subsequently, the experiment was carried out in the flocculator equipment with stirring for 12 hours at 100 rpm.

Table 7. Experimental design of copper and lead bioadsorption using orange peel and plantain peel powder.

<table>
<thead>
<tr>
<th>Standard solution (10000ppm)</th>
<th>Volume of raw water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peel powder</td>
<td></td>
</tr>
<tr>
<td>Sample 1= 10ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 2= 20ppm</td>
<td>500</td>
</tr>
<tr>
<td>Sample 3= 30ppm</td>
<td>500</td>
</tr>
</tbody>
</table>

Two standard solutions of 10000 ppm were prepared, one of the bioadsorbent from orange peel powder and the other from plantain peel powder bioadsorbent with a particle size of 0.3150mm. Aliquots of 10ppm, 20ppm, and 30ppm were dosed in each of the precipitation vessels containing 500ml of water to be treated. Subsequently, the experiment was carried out in the flocculator equipment with stirring for 12 hours at 100 rpm.

3. Results

Table 8. Characterization of orange peel (Citrus sinensis L).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Orange peel</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.27</td>
</tr>
<tr>
<td>Moisture (%) of orange peel</td>
<td>74.03</td>
</tr>
<tr>
<td>Moisture (%) of orange peel powder</td>
<td>1.88</td>
</tr>
<tr>
<td>Total ash of bioadsorbent</td>
<td>10.38</td>
</tr>
</tbody>
</table>

Source: [22].

Tables 8 and 9 present the results obtained from orange and plantain peels:

- **pH**: The obtained pH values are within the range for both plantain 6.05 and orange 4.27 bioadsorbents, which are similar to those obtained in the research of [23], they obtained pH values in ranges between 5.4 to 6.9 for the plantain bioadsorbent and 4 to 5 for the orange peel bioadsorbent.

- **Moisture**: The moisture content of the orange peel was 74.03% and the plantain 86.58%, while for the orange and plantain powder bioadsorbents it was 1.88% and 2.32% respectively, like that reported by [24].

- **Total ash percentage**: The values obtained for total ash percentage for orange bioadsorbents 10.38 g and for plantain 15.79 g are like those reported by [24].
3.1. Copper bioadsorption with orange peel and plantain powder

Fig. 1. Copper bioadsorption with respect to g/ml concentration
Source: [22].

Figure 1 shows the evaluation of copper removal at different grammages. The best results were obtained with a dosage of 5g/ml in both cases, however, with the plantain peel powder the highest removal percentage of 73.05% was obtained with an adsorption capacity of 0.112 mg/g, that is, 6% more removal was obtained.

3.2. Copper bioadsorption with orange peel and plantain powder.

Fig. 2. Copper bioadsorption with respect to ppm concentration
Source: [22].

Figure 2 shows the evaluation of copper removal with a 5000ppm solution, taking different aliquots. The best results were obtained with a 30ppm aliquot in both cases, however, with the plantain peel powder the highest removal percentage of 67.40% was obtained with an adsorption capacity of 0.103mg/g.

3.3. Copper bioadsorption with orange peel and plantain powder

Fig. 3. Copper bioadsorption with respect to ppm concentration
Source: [22].

Figure 3 shows the evaluation of copper removal with a 10000ppm solution with different dosages, carried out in the flocculator for 12 hours of stirring at 100 rpm with a particle size of 0.315mm. The best results were obtained with a 30ppm aliquot in both cases, however, with the plantain peel powder the highest removal percentage of 60.19% was obtained with an adsorption capacity of 0.046 mg/g, that is, 5.32% more removal.

3.4. Copper bioadsorption with orange peel powder

Fig. 4. Copper bioadsorption with respect to ppm concentration
Source: [22].

Figure 4 shows the evaluation of copper removal using 3 different standard solutions of 5000ppm, 8000ppm and 10000ppm with the 30ppm aliquot of each of them with the orange peel bioadsorbent, it was determined that with the
8000ppm solution it offers greater removal, reaching a removal percentage of 78.11%.

3.4. Copper bioadsorption with plantain peel powder

Fig. 5. Copper bioadsorption with respect to ppm concentration
Source: [22].

Figure 5 shows the evaluation of copper removal using 3 different standard solutions of 5000ppm, 8000ppm and 10000ppm with the 30ppm aliquot of each of them with the plantain peel bioadsorbent. It was determined that with the 8000mg/l solution it offers greater removal, reaching a removal percentage of 85.71%.

3.5. Copper bioadsorption with a mixture of orange peel and plantain peel powder

Fig. 6. Copper bioadsorption with respect to ppm concentration
Source: [22].

Figure 6 shows the results obtained from the 8000-ppm standard solution, this being the optimal concentration that presented the highest percentage of removal working with the bioadsorbents separately. For this reason, solutions were prepared from said concentration in equal proportions with both bioadsorbents, obtaining the highest removal with 30ppm taking a 15ppm aliquot from each bioadsorbent, reaching a removal percentage of 72.27%.

3.6. Lead bioadsorption with orange peel and plantain peel powder

Fig. 7. Lead bioadsorption with respect to ppm concentration
Source: [22].

Figure 7 shows the evaluation of lead removal with an 8000ppm solution, carried out in the flocculator for 12 hours of stirring at 100 rpm with a particle size of 0.315mm. The best results were obtained with a 30ppm aliquot in both cases, however, with the plantain peel powder the highest removal percentage of 93.47% was obtained with an adsorption capacity of 0.1311 mg/g.

4. Conclusions

The physicochemical characterization of the samples taken from the Puyango River was analyzed and the presence of heavy metals with concentrations above the maximum permissible limits was mainly determined based on Agreement Annex No. 097 A Environmental Quality Standard for Water Resources, with 2.2444 mg/L of Lead and 1.54 mg/L of Copper. In addition to 58.4 NTU Turbidity, pH of 5.13.

In obtaining orange peel powder, the yield reached was 26% from 3.1kg of orange peel with a particle size of 0.315mm and a moisture percentage of 1.88%. While with 3.8 kg of apple banana peel, a yield of 13.41% was obtained, obtaining a 0.315mm powder with a moisture of 2.32%.

According to the results obtained, the apple banana peel biosorbent offers the highest absorption capacity of both heavy metals, being 0.082 mg/g for Copper and 0.1311 mg/g Lead, reaching a removal of 93.47% of Lead, and
85.71% Copper respectively. However, with the orange peel biosorbert, an adsorption capacity of 0.075mg/g was determined for Copper and 0.1284 mg/g for Lead, reaching a removal of 91.60% of Lead, and 78.11% of Copper respectively.

Through the experimentation carried out, it was determined that the best results regarding the adsorption capacity and removal of the heavy metals under study, copper, and lead, were based on the apple banana peel biosorbent powder. Thus, the water resulting from the use of the biosorbent showed a decrease in Lead concentration to 2.098 mg/L and Copper to 1.32 mg/L. It should be noted that these values are below the maximum permissible limit for discharges to a freshwater body receptor, according to Annex 097-A Limits for discharge to a freshwater body.

**Recommendations**

Continue with the present investigation making variations in concentration, with a particle size less than 0.315mm, which allow replicating the present work on an industrial scale.

When drying the orange and apple banana peels, it is recommended to place them in the oven at a maximum temperature of 60°C to avoid alteration or change in their functional groups which cause adsorption.

**References**


[18] B. Ticonia, «Estudio de la determinación de la actividad de floculantes en aguas provenientes del Río Chili contienen As, Pb, y Cr tratados con pectina obtenido a partir de la cáscara de naranja, limón, y mandarina,» Repositorio Institucional Unsa Investiga, Arequipa- Perú, 2018.


