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**Bioadsorption by coffee leaves in polluted river
Mantaro water at Central Peru**

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Bioadsorption by Coffee Leaves in Poluted River Mantaro Water at Central Peru

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Abstract. The biosorption of heavy metals is the property of some types of biomass, a process that captures or accumulates metal ions, allowing their removal or immobilization. The present study was carried out in the Mantaro river, following the recommendations of the ANA (National Water Authority), the experimental process was carried out in the laboratories of the Universidad Continental and the Volcan Mining Company, for this purpose the drying of the coffee leaves of the species (*Caturra-arabic coffea*) and its subsequent grinding, then it was added in 4 different proportions for samples of 250 ml of water. The first results showed that the water contains lead (0.1 mg / l), copper (4.12 mg /l), iron (0.01 mg / l) and zinc (0.42 mg / l) with a pH (7.53) and electrical conductivity (671 μ S).which are not recommended according to the Environmental Quality Standards, after adding the coffee leaf allowing it to act in a period of 48 hours, the best result was with the second sample adsorbing lead (0%), copper (95.15%), iron (0%) and zinc (52.38%) with a pH of 7.05 and electrical conductivity (664 μ S). Coffee leaves were more effective in reducing copper by up to 95.15%.

1. Introduction

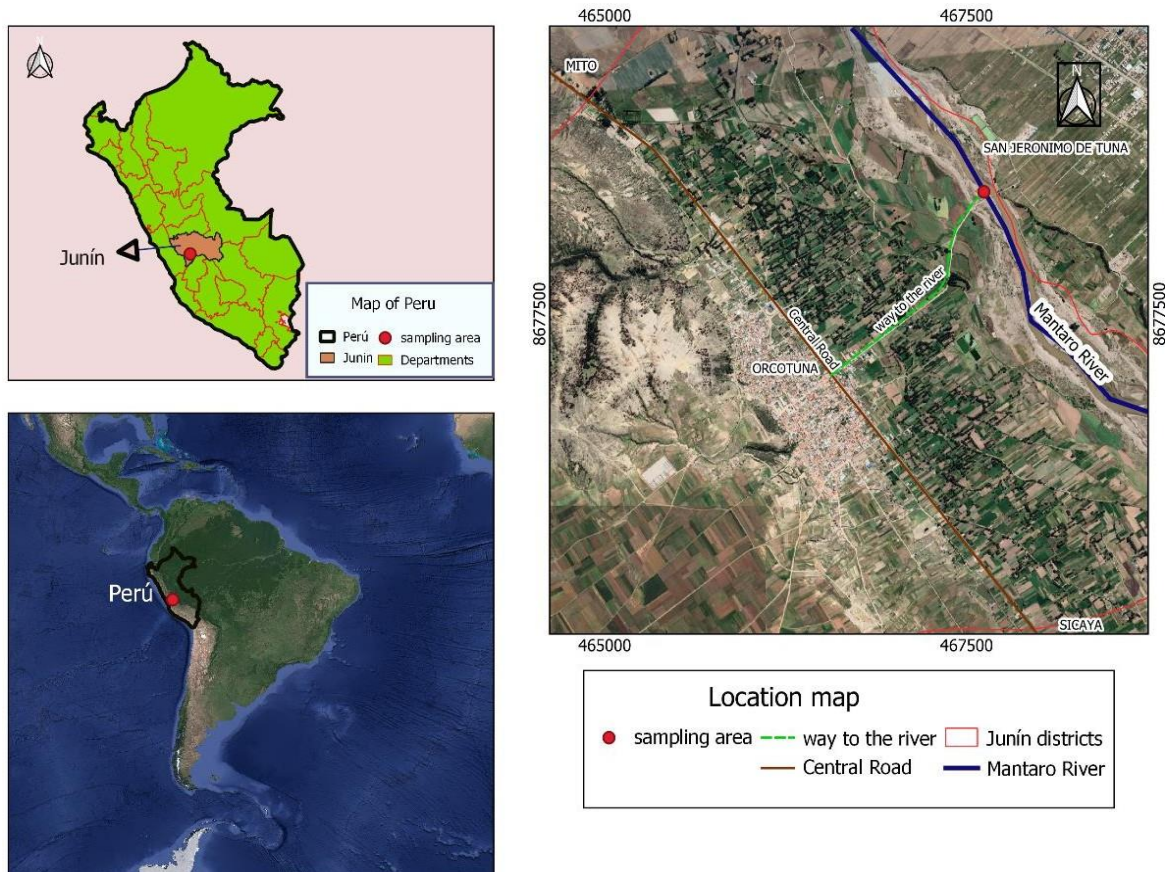
Today, there is great concern about the high increase in pollution that the Mantaro River presents thanks to mining and industrial effluents loaded with heavy metals. .that come to this river. In a study carried out by the project team "El Mantaro revive" with its 53 control points located at strategic points along the river, resulting in the presence of toxic elements such as chromium, copper, nickel, aluminum, lead and mercury [1], these substances can be very harmful to the human body or the flora in the river [2]. This leads us to consider various solutions to control the quality and potability of water, one of them being the adsorption of copper by means of a coffee leaf of the caturra variety (*Coffe arabica*), since this method, in addition to being one of the most practical, it is also one of the least economic resources compared to other methods [3]. To carry out this process, the water of the Mantaro River is 100% polluted from Lake Junín; At the beginning of its journey, it is flowed by the polluted waters of the Antícona River, bringing the polluting substances from the Huarón and Animón mines, reaching La Oroya the contamination deepens as it flows through the Yauli River and the Oroya Metallurgical Complex. The La Oroya complex, according to its PAMA eliminates toxic liquids through 37 tributaries, only monitors 12 (Cederstav 2002) and in daily tons it eliminated around 3,000 sulfur dioxide, 2,500 lead, 2,500 arsenic, 20 cadmium, 20 particulate matter and others.just because of the largest chimney at 167,500 meters high; it also removes 24,000 tons of toxics from the coke factory, plus what the 94 small stacks and the industrial incinerator remove (PAMA 1996). Another source that increases pollution near La Oroya is the Kingmill Tunnel through which the mines that operate in the vicinity of the Huascacocha lagoon eliminate their toxic agents; it



has an average flow of acidic waters of 1.16 cubic meters per second, which flows into the Yauli River. The Yauli River is dammed for energy purposes and every month this dam is opened at the height of Corte, removing sediment and stored water; the pollution intensifies even more and the river turns an orange-brown color. In man, when it comes into contact with contaminated water, with heavy metals, it can produce ulcerations on the skin and if ingested it can cause gastrointestinal irritations and promote the appearance of cancer and other degenerative diseases and induce genetic mutations. thus affecting their offspring. Materials of biological origin are used in the biosorption process such as: algae, fungi, arthropod shells, bacteria, plant remains, etc., which are found in great abundance and are easily transformable biosorbents. The heavy metal and metalloid ions bind to the active biosorption centers of the biological material through the formation of complexes, chelates, ion exchange, microprecipitation in the internal part of the material, etc. In an investigation carried out in 2009 by students from the University of Colombia, they achieved a removal of chromium, with the Arabica variety coffee leaf 82% [4]; for this reason, we use the caturra coffee leaf as an innovative proposal in the absorption of copper from the Mantaro River.

1.1. Study place

The water samples for the present investigation were extracted from the Mantaro River of the Orcotuna district located in the province of Concepción in the department of Junin -Perú, at the location 11 ° 58 '8' 'S and 75 ° 18' 35 " Or at 3,250 m asl and the coffee leaves were extracted from the San Martín de Pangoa district, Satipo province, Junin department.



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Figure 1. sampling location

1.2. Sampling method

In this research, the parameters to be measured in the field are pH and electrical conductivity. According to ANA (2011), it is recommended that a clean and transparent bucket be used to take the sample in situ, which before taking the sample, rinse the bucket with water from the sampling point at least twice and the reading of the parameters should be taken immediately and recorded in the field data record sheet, this procedure is carried out where the current is homogeneous and not very turbulent, submerging at a depth of approximately 20 to 30 cm from the surface

The development of the research is evaluated with a variety of coffee leaf; the coffee leaf is obtained from the Junin region (Satipo). For the tests, they were sterilized and put to dry at 70 ° C: then they were crushed with a home mill.

The dissolution of each sample was put in different proportions to be able to determine the percentage of adsorption in relation to the amount dissolved. The determination of the concentrations of heavy metals was carried out in the volcano mining, likewise the variants of the pH and electrical conductivity were carried out at the Universidad Continental with a multiparameter.

1.3. Laboratory analysis

In table 1, we show the standards applied in the research.

They were carried out in the volcano mining located in the department of Cerro de Pasco with the collaboration of Ing. Pablo Cesar Espinoza Tumialán from the Universidad Continental -Huancayo.

In the investigation, four tests have been elaborated taking into account different proportions of biomass particles of the coffee leaf for the samples of 250 ml of water from the Mantaro-Orcotuna River.

Determining the absorption capacity in each sample to compare with the water quality standard through supreme decree No. 004-2017-MINAM. [5]

Table 1. Standards used in the study.

Standards	description	Formula
Specific Research Method	it will help to determine the concentrations of heavy metals in the water sample of the Mantaro river using the coffee leaf in the caturra variety; The experimental methodology consists of determining the adsorption capacity of metal ions in solution, it is determined by each initial value [6], with experimental data of equilibrium concentration and initial concentration, using the following equation:	$Adsorption\ capacity = \frac{C_i - C_f}{C_i} \times 100$ <p>Where: Ci: Initial concentration Cf: Final concentration</p>
Water quality standard Supreme decree No. 004-2017-minam	The ECA parameters for Water are determined considering the pollutants that characterize the effluent, natural conditions that have not been altered, background levels of the effluent bodies, among others. [5]	<p><i>Category 3 : irrigation of vegetables and animal beverages</i> <i>sub. Riego de vegetales</i> PH: 6.5 - 8.5 Ce: 2500 us / cm Pb: 0.05 mg / l Cu: 0.2 mg / l Fe: 5 mg / l Zinc: 2 mg / l</p> <p><i>sub. Bebida para animales</i> PH: 6.5 - 8.4 Ce: 5000 us / cm Pb: 0.05 mg / l Cu: 0.5 mg / l Fe: 0 mg / l Zinc: 24 mg/l</p>

2. Results and discussion

2.1. Laboratory samples

Table 2. Initial parameters

Show	PH.	Electrical conductivity (μS)	Pb (mg / l)	Cu (mg / l)	Fe (mg / l)	Zn (mg / l)
<i>Mantaro River Water</i>	7.53	671	0.1	4.12	0.01	0.42

Table 2 shows the first results obtained in the laboratory of the water sample without biomass, obtained from the Mantaro River of the Orcotuna district, Concepción province, located in the Junín department.

Table 3. Solution with biomass of the coffee leaf to a teaspoon dissolved in 250ml of water from the Mantaro River.

Species	PH.	Electrical conductivity (μS)	Pb (mg / l)	Cu (mg / l)	Fe (mg / l)	Zn (mg / l)
<i>Caturra- Coffea Arabica</i>	8.26	639	0.1	1.18	0.05	0.2
<i>Percentage of adsorption</i>	-	-	0%	71.36%	0%	52.38%

In table 3, it can be seen that copper has reduced its concentration by 71.36%, zinc by 52.38% while iron increased its concentration by 4% and finally lead remains the same.

Table 4. Biomass solution of the coffee leaf at two and a half teaspoons dissolved in 250ml of water from the Mantaro River.

Species	PH.	Electrical conductivity (μS)	Pb (mg / l)	Cu (mg / l)	Fe (mg / l)	Zn (mg / l)
<i>Caturra- Coffea Arabica</i>	7.05	664	0.1	0.2	0.01	0.2
<i>Percentage of adsorption</i>	-	-	0%	95.15%	0%	52.38%

In table 4, it can be seen that copper has reduced its concentration by 95.15%, zinc by 52.38%, while iron and lead remain.

Table 5. Solution with biomass of the coffee leaf to three teaspoons dissolved in 250ml of water from the Mantaro River.

Species	PH.	Electrical conductivity (μS)	Pb (mg / l)	Cu (mg / l)	Fe (mg / l)	Zn (mg / l)
<i>Caturra- Coffea Arabica</i>	7.03	696	0.1	2.2	0.43	0.2
<i>Percentage of adsorption</i>	-	-	0%	46.60%	0%	52.38%

In table 5, it can be seen that copper has reduced its concentration by 46.60%, zinc by 52.38%, while lead is maintained.

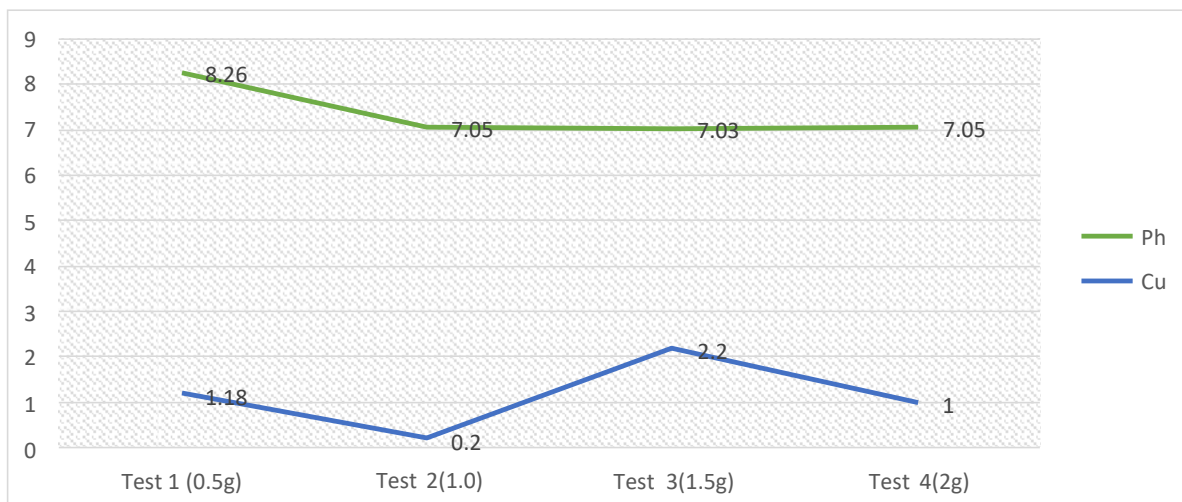
Table 6. Solution with biomass of the coffee leaf to four teaspoons dissolved in 250ml of water from the Mantaro River.

Species	PH.	Electrical conductivity (μS)	Pb (mg / l)	Cu (mg / l)	Fe (mg / l)	Zn (mg / l)
<i>Caturra- Coffea Arabica</i>	7.05	690	0.1	1.0	0.12	0.2
<i>Percentage of adsorption</i>	-	-	0%	75.73%	0%	52.38%

In table 6, it can be seen that copper has reduced its concentration by 75.73%, zinc by 52.38% while lead is maintained.

2.2 Effect of the pH of the Cu solution

The pH of the aqueous solution is a primary parameter that controls the course of adsorption of metals on different adsorbents, due to the reason that hydrogen ions compose into a vigorously competitive adsorbate. This adsorption of metal ions depends on the nature of the adsorbing surface as well as on the division of the chemical classes of the metal in the aqueous solution. The pH value of the aqueous phase is the most important cause in the adsorption of cations and anions, the result being different in both cases. Thus, while cation adsorption is usually favored for pH values above 4.5, anion adsorption prefers a low pH value, between 1.5 and 4 [7] the evaluation of the effect of pH with respect to the adsorbate, by means of different metal ions elucidates the great complexity of the aqueous chemistry of metal ions, whose predominant chemical species strongly depends on the acidity of the medium, without neglecting the importance of the acidity of the cation, necessary to compete with other ions for active sites on the adsorbent surface. [8]



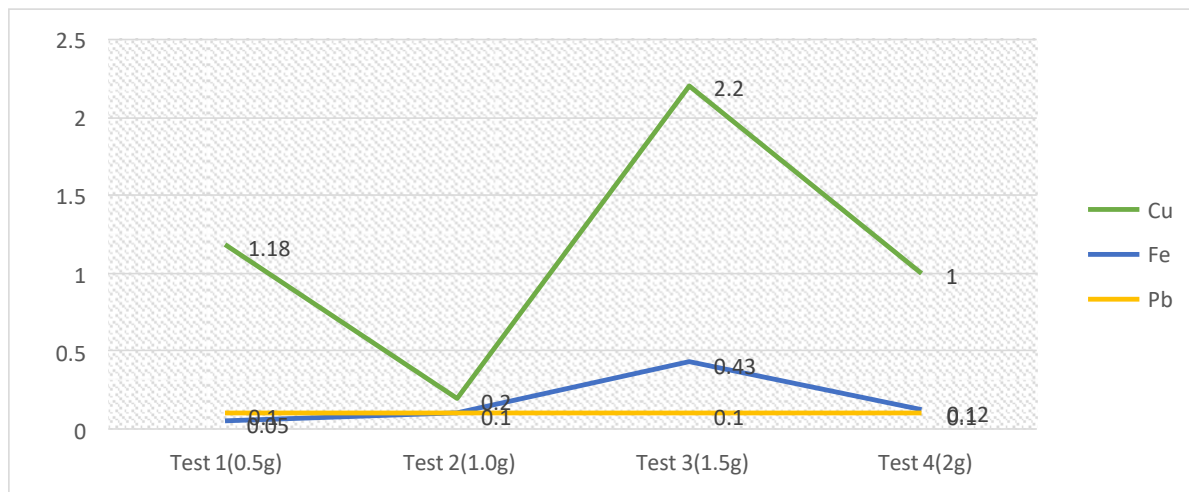
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Figure 2. Effect of the pH of the Cu solution

2.3 Effect of Fe on the dissolution of Cu and pH

Giving an absorption result of 95.2% of Cu; efficiencies were also obtained in the removal of chromium, with the coffee leaf variety Castillo-Coffea arabica of 82% for synthetic solutions of 1,000 mg / L. [9] In another research review, it mentions that the different residues from the benefit and consumption of coffee are used as biosorbent material in the removal of heavy metals from aqueous solutions, likewise a removal efficiency greater than 90% was reported. [10]; the Cu adsorption index of the investigation is similar to that obtained in the different referenced investigations.

Although the adsorption is affected by the pH and the total concentration of metal ions [11] in the tables it is possible to appreciate the level of adsorption of heavy metals, being the concentration of Fe and Ph the determinants of the degree of adsorption of the Cu; as can be seen in table 4, Fe remains stable, while the pH decreases slightly, thus obtaining an optimal value for copper adsorption; however, in the table the percentage of Fe increases with 33% being affected in the adsorption of Cu, obtaining the minimum adsorption of the investigation.



Source: self made

Figure 3. Effect of Fe on the dissolution of Cu and Ph

3. Conclusion

It is concluded that the study showed that the coffee leaf variety Caturra-Coffea Arabica can be used for copper adsorption relating to pH and Fe as shown in the following table.

It was possible to identify that of the 4 samples tested, the highest efficiency is obtained with 2 + 1/2 teaspoons of coffee biomass for 250ml of water, as can be seen in Table 4, this being the results obtained from the laboratory highlighting the most efficient result with the absorption of 95.15% of Cu; this would allow us to reduce the concentrations of the heavy metal Cu in the mining tailings treatment plant in order to obtain optimal parameters matched to the ECA water in category 3. In this way, give an economic value to the coffee leaf due to its organic waste It has the property of desorbing heavy metals and thus prolonging the useful life of the coffee leaf.

Table 7. Summary table between the initial parameters and the results of the samples obtained.

	Initial parameters	Sample to 1	Sample at 2+1/2	Sample 3	Sample 4	Degree of adsorption			
						M1	M2	M3	M4
PH	7.53	8.26	7.05	7.03	7.05				
Electrical conductivity (μS)	671	939	664	696	690				
Lead quantity (mg / l)	0.1	0.1	0.1	0.1	0.1	0%	0%	0%	0%
Amount of copper (mg / l)	4.12	1.18	0.2	2.2	1.0	71.3 6%	95.1 5%	46. 6 0%	75. 7 3%
Amount of iron (mg / l)	0.01	0.05	0.01	0.43	0.12	0%	0%	0%	0%
Amount of zinc (mg / l)	0.42	0.2	0.2	0.2	0.2	52.3 8%	52.3 8%	52. 3 8%	52. 3 8%

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