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Tesis

**Development of a Biodegradable Detergent Based
on Quinoa as an Alternative to Minimize
Eutrophication**

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Tesis



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Developmente of a biodegradable detergent based on quinoa as an alternative to minimize eutrophication

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Resumen. Synthetic detergents were created more than a century ago and their use has been essential, however, during the SARS-CoV-2 pandemic, the Ministry of Health issued recommendations for hygiene and disinfection in which the use of these detergents was further enhanced. Due to this problem, it was proposed to develop a biodegradable detergent with low concentrations of compounds containing phosphorus and nitrogen, in order to minimize eutrophication in surface bodies that cause ecosystemic imbalances. The experiment consisted of washing two garments in the same conditions (dirty) and each one with each detergent (conventional and biodegradable), as a result it was obtained that both garments were clean after washing. For the laboratory analysis, wastewater samples were taken from each container. The results obtained from the laboratory were as follows: the conventional detergent had the following concentrations: pH (11.25), T° (12.3 °C), Conductivity (11 350 uS/cm), Phosphorus (4.11 mg/L) and total Nitrogen (20. 16 mg/L); while for the biodegradable detergent the resulting concentrations were: pH (7.02), T° (12.6 °C), Conductivity (445 uS/cm), Phosphorus (0.318 mg/L) and total Nitrogen (< 1.00 mg/L). Finally, the biodegradable detergent proved to have the same efficiency and minimize eutrophication.

Key words: Biodegradable, detergent, eutrophication, phosphorus, nitrogen.

1. Introducción

Throughout history, the chemical industry has been developed to satisfy human needs that were gradually increasing, which led to the transformation of raw materials to produce new products, such as conventional detergents. Conventional detergents were developed around 1916 and are still as important for cleaning today. However, in the process of evolution to improve the effectiveness of the dirt remover, the product was intensified by adding more compounds to its formula, opening a large gap with the environment. It should be noted that in the past, products were not as sophisticated and effective, but their environmental impact was not as significant as it is today. For example, in the 19th century, the first detergent used was "urine" because of its ammonia content; today, the most important compound in detergents because of its dirt removal power are "surfactants".

The surfactant, also called surfactant (surface active agent), the main component of synthetic detergents, is a chemical substance characterized by minimizing the surface tension of a liquid, its function is to break the interface between water, grease and dirt. There are four types of surfactants: anionic, cationic, nonionic and amphoteric. Soaps and detergents have the same group of anionic

surfactants because these are the most appropriate for dirt removal by washing. However, the anionic surfactant in its toxicity classification is classified as: very toxic, toxic or harmful to aquatic organisms based on EC50 (effective concentration) and LC50 (lethal concentration at 50%).

These surfactants are widely used in household industry products, for example, in Europe 10 years ago, about 4.2 tons of detergents were used annually, where the concentration of surfactants was in the range of 15% to 40% of the detergent composition. The degree of contamination of the detergent depends on the concentration of the surfactant, which, when released into surface waters, tends to expand. The most serious aspect is that these waters often do not undergo prior treatment (i.e. a wastewater treatment plant), which can reduce the concentrations of surfactants. That is why in order to degrade surfactants that are massively used in detergents, it is recommended that these surfactants should be of ecological composition. [2]

The environmental impact is mainly caused by the exacerbated discharge of wastewater into surface bodies where there is a high concentration of phosphorous compounds that are components of detergents (sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ (STP), sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$, etc.), the accumulation of these compounds leads to the overnutrition of surface bodies causing algae proliferation (producing hypoxia, lower oxygen), persistence in the environment and because they are not easily decomposed by bacterial action, the foam that forms on the surface prevents the passage of light to the interior of the receiving body, leading to water putrefaction (foul odor), loss of aquatic biodiversity, and these consequences inevitably lead to the destruction of the ecosystem [3].

It should be noted that phosphorus compounds are used in the preparation of the detergent because it is a sequestering and chelating agent that makes the detergent have greater cleaning power, it also eliminates calcium and magnesium ions that are already in the drinking water and reduce the cleaning action of the detergent. The phosphate increases the efficiency of the detergent and makes the final product (commercial detergent) cheaper [1].

On the other hand, the increase in water pollution by nitrogenous compounds has been deserving special attention, as it is becoming a worldwide problem, because nitrogen is dispersed in the environment, causing water contamination with nitrate and other nitrogen compounds, then it can pass into the air contaminating it with ammonia and nitrous oxide, causing negative impacts to the environment. [4] Nevertheless, nitrogen compounds in health produce adverse health effects such as blue baby syndrome, which is a disease caused by ingesting nitrate-contaminated water.

In other countries such as Germany, Austria, Italy and Norway, detergents containing phosphorus and nitrogen in their composition were banned because of high concentrations of these elements, because high concentrations of these elements are often toxic and consequently hazardous to human health and aquatic life, since some animals may become extinct.

While it is true that this problem is worldwide because the use of detergents is globalized, it is for this reason that it was proposed to develop an ecological detergent based on citrus peels, palm kernel oil and palm kernel oil that has quinoa peel as a surfactant, which replaces the chemical surfactants what makes this detergent biodegradable and environmentally friendly.

2. Materials and Methods

2.1 Biodegradable Detergent Formulations

The biodegradable detergent was made from quinoa peel, citrus peel (lemon, orange and mandarin) and palm kernel oil. (lemon, orange and tangerine). It should be noted that the first two inputs are discarded since they do not represent an economic value; on the contrary, they are considered solid

waste; however, they will be used in the production of the detergent. However, in the elaboration of the detergent they will be used as raw material, due to their degreasing and aromatizing properties, which is vital in a detergent. As for palm kernel oil, which serves as a surfactant and foaming agent, it is a very popular product in supermarkets, for which the price is not high. Composición del detergente biodegradable

2.2. Composition of the biodegradable detergent

2.2.1. Quinoa

The first and most important component for the elaboration of the biodegradable detergent is the quinoa husk (natural surfactant and foaming agent), it is an organic component and therefore does not generate disturbance when in contact with the environment, however, it is not used for consumption (food) because of its bitter taste, due to its saponin content; saponins are a complex mixture of triterpenic glycosides, which are soluble in water and produce foaminess, are also characterized by being antimicrobial, anti-inflammatory, anticancer and antioxidant, which is why it is being used by the pharmacological, cleaning and cosmetic industry. [5]

According to the scientific article "Obtaining detergent using saponin from quinoa (*Chenopodium quinoa* Willd), Chocho (*Lupinus mutabilis* Sweet), Cabuya (*Sisalana perrine*) and its production design", extracted the saponin using 96% ethanol and it is mentioned that among its physicochemical properties, saponin is a product free from alkali, sodium silicates, sodium sulfate, amide foam stabilizers, and a low concentration of phosphates (0.08%) and a biodegradability of 94%; therefore, they contribute to the care of the aquatic environment since the causes of eutrophication are the excess of nutrients such as phosphorus. [6]

2.2.2. Citrus peel

Citrus fruits are fruits that are grown all over the world, the world production of citrus fruits recorded in 2016 was 124.24 million tons, from which the peel is considered an agro-industrial waste, so it is presumed that citrus peel becomes a source of environmental problems due to fermentation and microbes that are a product of the deterioration process. However, these peels can be obtained as a by-product and are already being used by the food, pharmaceutical, cosmetic and cleaning industries [7].

For the elaboration of the biodegradable detergent, lemon, orange and tangerine peels were considered because of their 95% limonene content, limonene is a monocyclic monoterpene used mostly in industrial, chemical, pharmaceutical and food processes; for example: Limonene is used as a solvent in resins, pigments, inks and in the production of environmentally friendly cleaning agents. It is considered as a substitute for solvents derived from petroleum. It has high effectiveness as a solvent since it forms an emulsion with water, after a rest time the fat particles are dragged and finally separated on the surface. It is also used as a degreaser in cleaning products for cars, printing presses, upholstery oil removal, the concentration varies according to its use. On the other hand, it also has properties as flavoring and insecticide (pest control) replacing synthetic pesticides that negatively affect the environment [8].

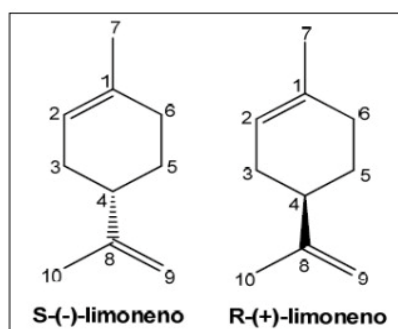


Figure 1: Chemical structure of the enantiomers of limonene [9].

2.2.3. *Palm kernel oil*

Palm oil is obtained from the palm tree, where its oil content is 45-55%, it has a white or slightly yellowish color. It should be noted that this oil is in the lauric group, a property that determines its application as an edible compound. Its composition is mainly fatty acids.

Table 1. Composición del aceite de palmiste

Fatty acids	Composición (%)
Lauric acid (C12)	48%
Myristic acid (C14)	16%
Oleic acid (C18)	15%

Source: Own elaboration.

On the other hand, the importance of this product is that it is very well known and used in the cleaning industry, both for the production of soaps, shampoos, toothpastes, etc. Its value is due to the fact that it is widely used in the detergent and surfactant industry. In the non-edible field, palm kernel oil is acquiring greater significance due to its natural composition in the cleaning products industry. For example, palm kernel oil is also used in the manufacture of soaps, due to its fast foaming properties. In countries such as Western Europe and the United States, soaps contain at least 20-25% palm kernel oil. [10]

2.4. *Inputs and quantities for making the biodegradable detergent*

Table 2 below shows the natural inputs and the quantities used for the production of the biodegradable detergent.

Table 2. Inputs for the preparation of biodegradable detergent

Ingredients	Quantity	Unit
Quinoa husk	0.5	kg.
Palm kernel oil	0.2	L
Lemon peel	0.1	kg.
Tangerine peel	0.1	kg.
Orange peel	0.1	kg.

Source: Own elaboration.

2.5. Procedures to elaborate the Biodegradable Detergent

Figure 2 shows the process of making biodegradable detergent.

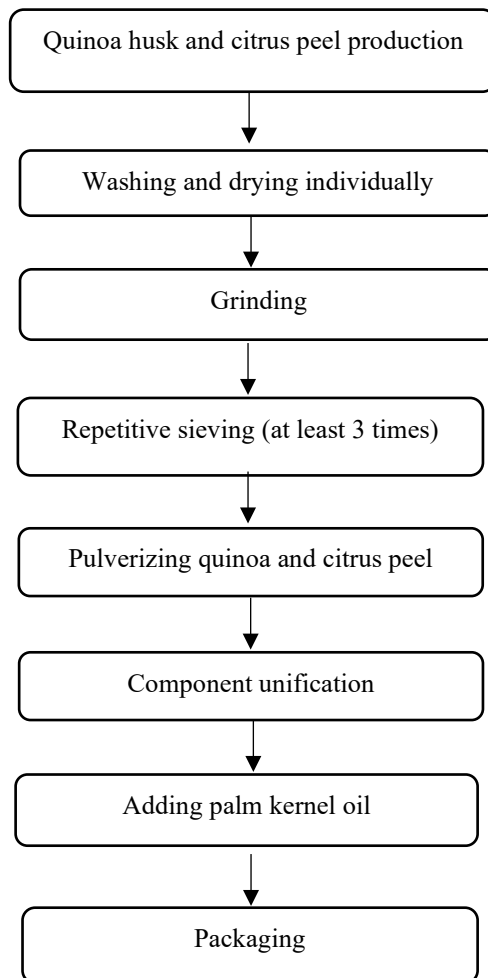


Figure 2: Diagram of Detergent production

2.6. Conventional Detergent Formulations

Nowadays, detergents are composed of different surfactants, additives, coadjuvants and auxiliary agents for their respective presentation, as shown in Figure 3.

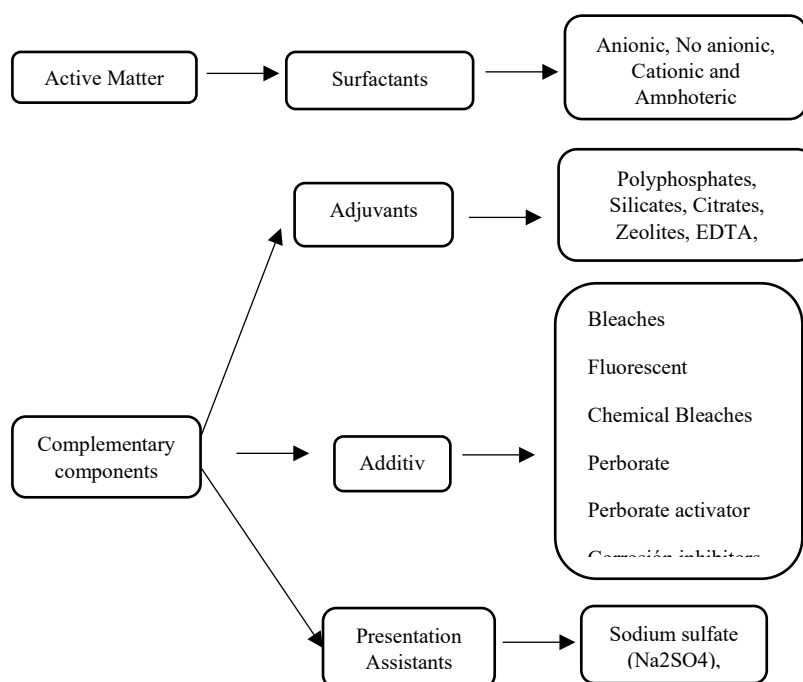


Figure 3: Components of detergent formulations.

Table 3. Comparison of the components of conventional and biodegradable detergents.

Components	Conventional Detergents	Biodegradable Detergents
Surfactant	Petroleum derivatives.	Quinoa husk (saponin)
Enhancers	Phosphates (especially tripolyphosphates), phosphonates, polycarboxylates or zeolites.	Citrus (degreasing property)
Enzymes	Obtained by chemical synthesis or from bacterial cultures.	These are obtained from bacterial cultures.
Bleaching agents	The most common is sodium perborate. .	The most common is sodium bicarbonate.
Polishers	Petroleum derivatives	They do not usually carry.
Fragrance	Petroleum derivatives	Essential Natural oils.
Filling	Sodium sulfate	Does not contain

Source: Own elaboration

2.7. Efficacy of the biodegradable detergent

After preparing the biodegradable detergent, the experiment was carried out to test the effectiveness of the biodegradable detergent against the conventional detergent. The experiment consisted of soiling two white garments homogeneously with soil, coffee and food debris, as shown in Figure 4.



Figure 4. Garments soiled with soil, coffee and food debris

Then the garments were submerged in 1 liter of water and 100 grams of biodegradable detergent and conventional detergent, left soaking for 5 minutes, followed by washing the garments simultaneously.

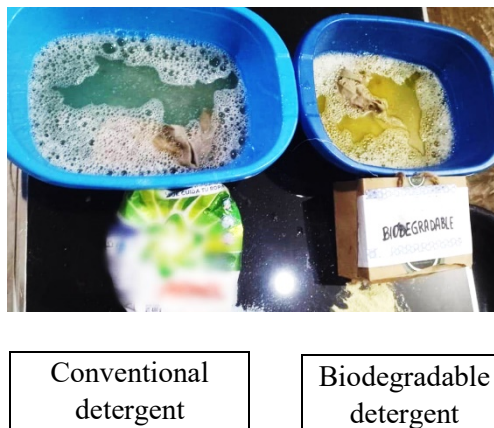


Figure 5. Soaking garments

Finally, it was proved by the experiment that the biodegradable detergent was equally effective in removing dirt and grease as the conventional detergent. The result is shown in Figure 6.

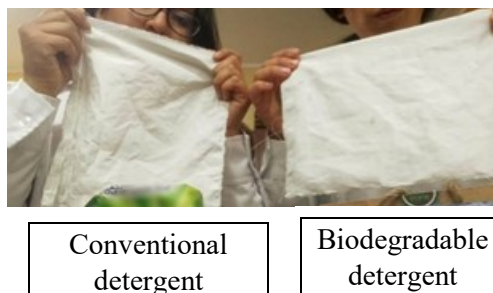


Figure 6. Results for both detergents

2.8. Sample collection

After the experiment to test the efficacy of the biodegradable detergent versus the conventional detergent, the environmental specialist proceeded to analyze the following parameters of both samples: pH, temperature and conductivity. As for the nitrogen and phosphorus parameters, samples were taken from both containers and preserved to be taken to the laboratory for on-site analysis.

3. Results and discussions

3.1. Assay Methodology.

Table 4 shows the assay methodology established by the laboratory Servicios Analíticos Generales S.A.C. where the samples were analyzed.

Table 4. Methods of Analysis

Ensayo	Método	L.C.	Unidades
Ph (field measurement)	SMEWW-APHA-AWWA-WEF Part 4500-H + B, 23rd Ed. 2017. Ph Value. Electrometric Method.	Doesn't apply	Unit. pH
Temperature (field measurement)	SMEWW-APHA-AWWA-WEF Part 2550 B, 23rd Ed. 2017. Temperature. Laboratory and Field Method.	---	°C
Conductivity (field measurement)	SMEWW-APHA-AWWA-WEF Part 2510 B, 23rd Ed. 2017. Conductivity. Laboratory Method.	---	uS/cm
Total nitrogen (NTK)	SMEWW-APHA-AWWA-WEF Part 4500-N _{org} - B, 23rd Ed. 2017 Nitrogen (organic). Macro -kjeldahl Method.	1.00	NH ₃ ⁺ -N mg/L
Total Phosphorus or Phosphorus (P)	SMEWW-APHA-AWWA-WEF Part 4500-P E, 23rd Ed. 2017. Phosphorus. Ascorbic Acid Method.	0.013	P mg/L

L.C.: Quantification limit

Table 5 shows the results obtained for the parameters analyzed for each detergent (biodegradable and conventional).

Table 5. Results of laboratory

Parameters	Unit	Biodegradable Detergent	Conventional Detergent
pH Parameters	Unit. pH	7.01	11.15
Temperature	°C	12.5	12.8
Conductivity	uS/com	448	11550
Phosphorus (P)	mg/L	0.316	4.310
Total nitrogen (N)	mg/L	< 1.00	20.34

Source: Own Elaboration

3.2. Analysis of analyzed parameters

3.2.1. Hydrogen Potential

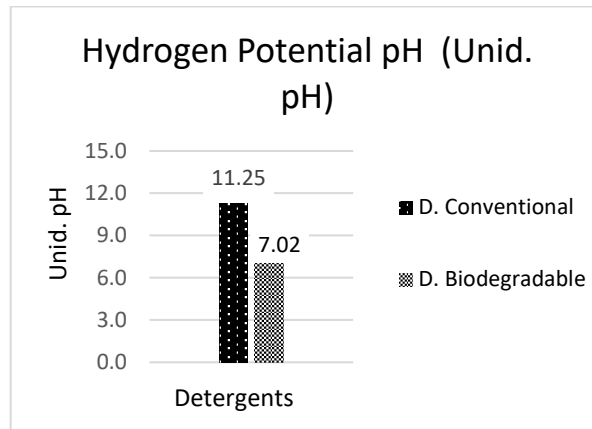


Figure 7. Analysis of pH parameter - conventional detergent vs. biodegradable detergent

According to the results obtained for the biodegradable detergent, a pH of 7.02 pH unit was obtained, while for the conventional detergent it was 11.25 pH unit. From the result we can state that the pH of the biodegradable detergent is neutral, that is to say that it has no adverse effect on the environment; however, if the pH turns out to be acid or alkaline like the conventional detergent, it can cause damage to health and the environment. In general, pH is one of the most important parameters for determining water quality and is also an essential parameter for determining the hydrochemical composition of water. [11]

3.2.2. Temperature

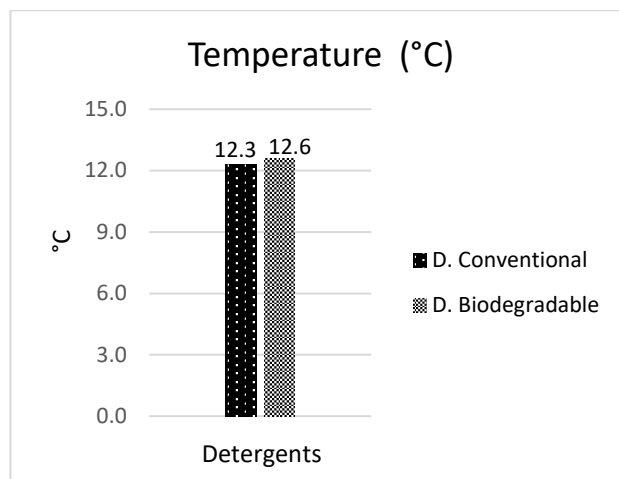


Figure 8. Analysis of temperature parameter - conventional detergent vs. biodegradable detergent

For the temperature parameter, Figure 8 shows that, for the biodegradable detergent, a temperature of 12.3 °C was obtained, while for the conventional detergent it was 12.6 °C, therefore, it is shown that both temperatures have no significant variation due to the fact that the measurement was made under

the same conditions of time and space. In other words, the temperature variable was controlled but not manipulated. [12]

3.2.3. Conductivity

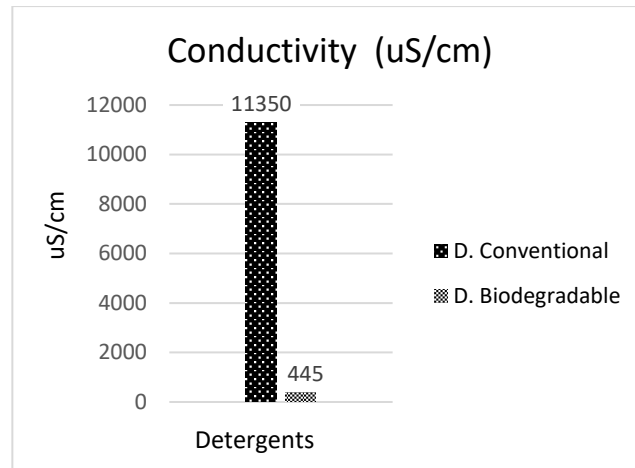


Figure 9. Analysis of the conductivity parameter - conventional detergent vs. biodegradable detergent.

The results obtained for the conductivity parameter in the biodegradable detergent were 445 uS/cm while for the conventional detergent 11 350 uS/cm. From this it can be deduced that the conductivity of the synthetic detergent is approximately 25 times that of the conventional detergent. It should be noted that conductivity is a physical property that can be used to evaluate the approximate number of dissolved ions in water, i.e., the total mineralization of water, it should be mentioned that changes in conductivity are caused by chemical fluctuations and the amount of dissolved ions in the water. [13]

3.2.4. Total Phosphorus or phosphorus

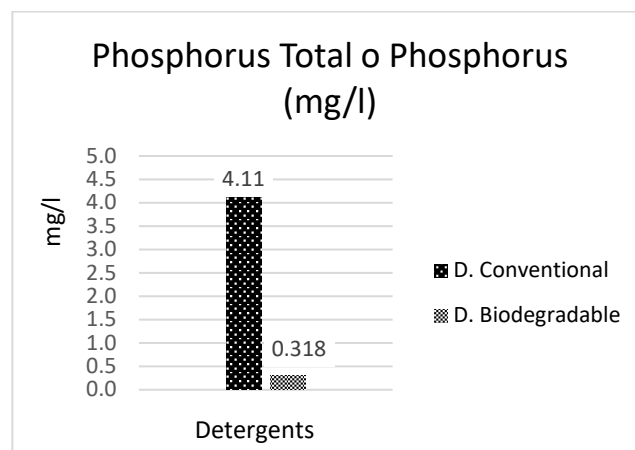


Figure 10. Analysis of the Total Phosphorus parameter for conventional detergent vs. Biodegradable detergent.

Figure 10 shows the results obtained for the parameter Total Phosphorus or Phosphorus (including all phosphorus compounds), for the biodegradable detergent a value of 0.318 mg/L was obtained and for the conventional detergent it was 4.11 mg/L. Phosphorus is one of the parameters that contributes most to eutrophication, which consequently affects water bodies and living beings [100]. In synthetic detergents, phosphorus (P) is found in higher concentration as Na₅P₃O₁₀ (sodium tripolyphosphate), which serves as a softener, auxiliary surfactant and stabilizer; properties that help to increase detergent efficiency. [14]

However, in a biodegradable detergent, the natural surfactant that can replace sodium tripolyphosphate is quinoa husk due to its saponin content, which acts as a stabilizing and emulsifying agent for hygiene products.

3.2.5. Total Nitrogen

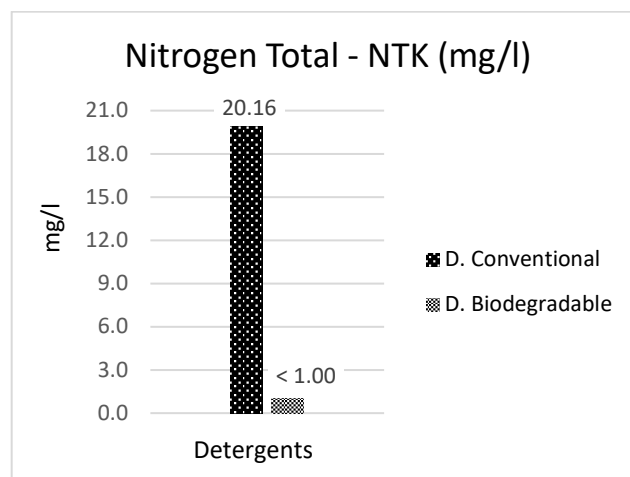


Figure 11. Analysis of the Total Nitrogen parameter for conventional detergent vs. biodegradable detergent.

The results obtained for the Total Nitrogen parameter were as follows: for the biodegradable detergent a value of < 1.00 mg/L was obtained and for the conventional detergent it was 20.16 mg/L. It can be seen that the concentration of nitrogen in the biodegradable detergent, as opposed to the conventional detergent, is approximately 20 times less in concentration, which is evidently environmentally friendly compared to synthetic detergents.

In general, the presence of nitrogen compounds in their different oxidation states is an indication of aquifer contamination and possible unsatisfactory hygienic-sanitary conditions. [15]

4. Conclusions

In conclusion, according to the research carried out, synthetic detergents are products that accelerate eutrophication in water bodies, due to their components containing phosphorus and nitrogen in their chemical composition; however, the continuous and exacerbated discharge of these waters causes the concentration of these nutrients to exceed the capacity of the surface body, leading to the destruction of the ecosystem.

In response to this problem, the development of a biodegradable detergent was proposed, and to check its effectiveness compared to synthetic detergents, washing tests were carried out to verify its effectiveness, which proved to be similar to that of conventional detergents; laboratory analyses were

also carried out to compare the concentrations of nitrogen and phosphorus parameters. According to the results obtained from the analysis of the chemical parameters, it was shown that the biodegradable detergent presented significantly low concentrations of phosphorus and nitrogen, the concentration of phosphorus was (0.318 mg/L) and total nitrogen (<1.00 mg/L) in comparison with the conventional detergent where phosphorus (4.11 mg/L) and total nitrogen (20.16 mg/L) were obtained.

It is concluded that the biodegradable detergent, in addition to being effective for cleaning, is a viable alternative solution to avoid and/or minimize eutrophication.

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