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EFFECT OF BIODEGRADABLE DETERGENTS ON WATER QUALITY

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Abstract

This research was conducted to study the chemical and biochemical contribution by the addition of biodegradable detergents when used in laundry processes which are discharged as contaminants to domestic wastewater. Three types of commercial detergents were selected (A, B, C) with different specifications in terms of biodegradability in which laboratory analyses were developed with water from the washing process to study representative parameters such as DBO5, DBO21, DQO, phosphates, pH, salinity, dissolved solids, and surfactants. The results indicated that in the use of non-biodegradable detergents there was a decisive increase in the concentration of surfactants, conductivity, phosphates and dissolved solids in wash water compared to biodegradable, while changes were found little variables in the other chemical parameters. It could also be considered that only two detergents obtained the percentage of biodegradability according to the proportion given by the ratio DQO/DBO21 and DBO5/DQO. The highest concentrations of contaminants reflect the non-biodegradable detergent, which also leaves a concern for the content of phosphates and high concentrations of surfactants, in addition to being the highest commercial consumption.

Keywords: surfactants, biodegradability, detergents

Introduction

Household detergents soaps, detergents and other cleaning products are an important source of organic and inorganic substances such as active ingredients (surfactants), adjuvants and additives. These compounds are discharged into the environment, usually through urban and industrial wastewater sewage systems, thus resulting in their wide dispersion in the aquatic environment (Ivanković and Hrenović, 2010).

The activities of everyday life have led us to dependence on these commercial products. Despite their great usefulness, these formulations have become an environmental problematic due to the emission of molecules such as surfactants (Surfactants) large sources of pollution in the water bodies of our country. These molecules, amphiphilic in character consist of two well differentiated structural parts or groups, a hydrophilic group (head group) polar, soluble in water and a hydrocarbon chain (hydrophobic tail) non-polar, which is not so soluble in water (Ivanković and Hrenović, 2010).

Since the first introduction of soap powder in the year 1907 by the Henkel company in Germany, the consumption of detergents and soaps by that time increased in an alarming way, thus making the world production of surfactants reach the order of 16 million tons, being about 44% of the detergent production (Galvañ, 2002).

This has led the environmental authorities to take action in this matter, since it is common to observe a blanket or layer of foam on the surface of water bodies, concluding that detergents, due to the different molecules that compose them, which are difficult to degrade due to their characteristics, affect the fauna and flora of aquatic ecosystems in an extraordinary way. Detergents cause several impacts on the environment, such as eutrophication, due to the high levels of phosphorus from tripolyphosphate, the main ingredient of detergent formulations. In addition, they can increase the levels of chlorine and organochlorine compounds, some of which are possibly toxic and carcinogenic (Villena and Serrano 2007).

At present, no research projects have been carried out in Colombia on the biodegradability of detergents that are discharged without any type of control into water sources, which prompted this research study on the biodegradability or behavior of some biodegradable detergents in relation to non-biodegradable detergents

Materials and Methods

Detergent Selection

For the selection of the detergents, their claim as biodegradable products was determined, in addition to their composition and demand for laundry activities, taking into account the recurrent consumption in domestic households. Table 1 shows the characteristics of the detergents selected for the research project.

Resolution 1974 (2008) requires detergent manufacturing companies to indicate the content of surfactant present in the formulation at the time of applying for sanitary registration, so the composition of detergent B and C only makes a generic mention of the surfactant.

Detergent A was chosen because it contains the exclusive and advanced BIOQUEST FORMULA™ technology, contains ingredients derived from natural sources, contains cleaning agents derived from natural sources as stated by the manufacturer. It is also recognized by the Designed for the Environment (DFE) program and the U.S. Environmental Protection Agency (EPA), does not contain phosphates, chlorine, and other abrasive acids, provides high performance due to its concentrated and environmentally safe formula since it is biodegradable and dermatologically tested, which, due to these characteristics, serves as a model of analysis for the research project.

In the choice of detergent B, its claim as an ecological product was taken into account, as well as the contribution of surfactants for the removal of dirt with the presence of phosphorus.

Detergent C was selected because it is a common detergent used in households due to its easy accessibility and price due to the distribution logistics of the detergent company. It contains surfactants and its use in volume can give an estimate as the major contributor of pollutant loads to the discharge receiving systems.

Table 1. Characteristics of selected detergents

DETERGENT	USE	ENVIRONMENTAL DEFINITION	COMPOSITION
A	Laundry	Biodegradable	Sodium Carbonate, Ethoxylated Alcohol C 10- 16, Citric Acid, Fumaric Acid, Silica, Water, Sodium Carboxymethyl Cellulose, Sodium Chloride, Sucrose, Fragrance, Fluorescent Brightener 28 (disodium salt), Starch, Protease Enzyme, Sodium Sulfate
B	Laundry	Ecological	Processing aids, cleaning agents, anionic surfactants, non-ionic surfactants, water conditioners, anti-redeposition agents, enzymes, optical brightener, perfume and colorant, phosphorus content less than 0.15%.
C	Laundry	NA	Surfactant, optical brightener, anti-redeposition agents, processing aids, colorant, fragrances.

Source: Authors

Obtaining Water Samples for Analysis

An experimental analysis was carried out with water samples from washing clothes (blankets, towels, clothes in general) without the addition of detergents (raw water), in which, once the centrifugation process was finished. The water samples were collected in containers with a capacity of 8 liters.

Subsequently, the detergents were dosed with the concentrations recommended by the manufacturers according to the water capacity used in their cleaning processes. Of detergent A, 12 g were added while detergent B and C, 36 g were added.

Determination of Biodegradability

For the determination of the Biochemical Oxygen Demand (BOD), which determines the relative oxygen requirements of the samples during a specified incubation period (5 and 21 days) at a specified temperature, standardized procedures based on the Standard Methods (Federation and Association, 2005) were used. Dissolved oxygen (DO) was measured before and after incubation and BOD was calculated as the difference between the initial and final dissolved oxygen (DO).

For the determination of Chemical Oxygen Demand (COD), a measurement of the oxygen equivalent of the content of the samples susceptible to oxidation of matter using potassium dichromate as oxidant in the presence of sulfuric acid and silver ions as catalyst was used. The aqueous solution was heated under closed reflux for 2 h at 150 °C. Then the amount of unreacted dichromate was evaluated by titrating with an iron(II) solution. The Chemical Oxygen Demand was calculated from the difference between the initially added dichromate and the dichromate found after oxidation. This procedure was also based on the procedures of the Standard Methods (Federation and Association, 2005).

The determination of the percentage of environmental biodegradability was carried out using the ASTM D 2667 standard, which is based on the ratio between COD (Chemical Oxygen Demand) and BOD5 (Biological Oxygen Demand) of the test samples for 21 days for the evaluation of the biodegradability of the product by biological action (bacteria) and biochemical action by oxidation. According to this standard, a substance is considered biodegradable according to the BOD/COD ratio in 21 days, and if this ratio is higher than 60%, the detergents evaluated will be considered biodegradable (Gender Cevallos and Ramírez, 2005).

Physical-Chemical Parameters

With the SAAM parameter, methylene blue active substances were determined for the formation of an extractable ionic pair in blue chloroform by the reaction of cationic methylene blue and an anionic surfactant of the detergent using the analysis method established in the Mexican Official Standard NMXAA-039-SCFI-2001 (Pereza and Delgado-Blas, 2012).

For the determination of salinity, its respective analysis was determined under the capacity of water to conduct electricity. Thus, by measuring the electrical conductivity (EC) of water using a conductivity meter, its salinity, which depends on temperature, can be estimated; therefore, to make valid comparisons, the electrical conductivity was expressed in relation to a reference temperature of 25°C.

Analyses were performed on other factors that influence the determination of the established parameters in order to determine the correlation with the biodegradability of the detergents, among these are: pH, orthophosphates, salinity and dissolved solids, all these analyses were performed by an external contracted laboratory.

Samples of biodegradable and non-biodegradable detergents were measured with the same protocol described above for the biodegradability and physical-chemical parameter analyses and the dosages were checked to ensure that they were comparable according to the amount of use recommended by the manufacturers.

Results and Discussion

Ratio of Biodegradability DBO21/DQO

The biodegradation percentage is based on the calculation of the BOD/DQO ratio, which shows the behavior of the ratio of the biochemical oxygen demand versus the chemical oxygen demand, and its ratio in a time of 21 days. This ratio indicates the corresponding biodegradation percentage, so that if it is higher than 60%, the detergents evaluated will be considered biodegradable, as stated in ASTM 2667 (Gender Cevallos and Ramírez, 2005).

Table 2 shows the results obtained from the detergent products used and their BOD21/DQO ratio as an indication of the amount of organic matter present that can be metabolized and the percentage of matter that can be broken down by biological action in each detergent.

Table 2. BOD21/DQO Ratio

DETERGENT	RATIO DBO_{21}/DQO	DBO_{21} mg O_2/L	DQO mg O_2/L	* CONSUMPTION
A	0,72	527	731	+
B	0,76	893	1173	++
C	0,57	557	973	+++

*NOTE: + Low, ++ Moderate , +++ High

Source: Authors

As a first analysis of the values obtained, it can be indicated that detergent A reported the lowest concentrations of BOD21 and COD due to the amount of detergent added to the sample which was 12 g, which corresponds to 33.33% less detergent added to the sample compared to the samples containing detergents B and C.

It could be indicated that the value obtained in detergent A in comparison to the other detergents reflects that its cleaning principle does not use surfactants, which is a contributor of toxic substances to the water, but by protease enzymes, which although in comparison to surfactants, its toxic load is diminutive.

The values of the COD results obtained with the use of detergent B show that it contributes the highest concentration of COD in the generation of wastewater from domestic washing where this detergent is used. This could be reflected by measuring the organic matter in the wastewater from washing with this detergent, which contains compounds that are toxic to biological life and which are estimated to contribute to the addition of anionic and nonionic surfactants present in the product.

From the above, it can be concluded that detergent B has the greatest impact on wastewater discharge areas and discharge effluents. This indicates that there is a possibility that the microfauna in the water bodies and in many cases in the soils where the discharges from domestic washing with this product are poured, present a decrease in oxygen for their metabolic processes and that the degradation of the toxic compounds present in the discharges by biological means is lower than by chemical means.

Likewise, the COD of the water from the washing of the three detergents showed to be higher than the BOD, due to the fact that in the three detergents there are as main components a greater number of compounds whose oxidation takes place by chemical means compared to those that are oxidized by biological means.

In relation to the Colombian regulations on discharges, Resolution 0631 (2015), chapter V, article 8, where it indicates the permissible limit discharge values for discharges of individual sanitation solutions of singlefamily and two-family houses, the permissible limit value of COD corresponds to 200 mg O2/L, therefore, none of the detergents analyzed complies with the regulations as shown in Table 3.

In contrast to the permissible value of BOD5, the standard does not refer to a discharge limit value, it only requires analysis and reporting, which causes a regulatory vacuum and reflects a problem in discharges not only by effluents with detergent products, but with discharges from different processes whether manufacturing, industrial, agro-industrial, etc., whose content of high concentrations of organic matter affect the receiving water bodies and their consequent consequences to the fauna present and their subsequent treatment.

In comparison to effluents from soaps and detergents, according to the Ministry of the Environment (2002), COD values are at an intermediate value of 300 mg O2/L and BOD5 at 500 mg O2/L, which indicates that none of the detergents meet the specifications for COD values. Table 3 shows a comparison between the values stipulated by the discharge standard and the BOD5/COD ratio, which gives us an idea of the level of contamination of the samples under study.

The results for the detergents under study showed that detergent A had a ratio of 0.43 and detergent B a value of 0.67, which are within the acceptable limits, unlike detergent C with a value of 0.30 (Características de las aguas residuales, n.d.).

Table 3. Comparison of Regulations DQO y DBO

DETERGENT	DQO mg O_2/L	DBO mg O_2/L	DBO_5/DQO	BIODEGRADABLE
A	731	315	0.43	SI
B	1173	786	0.67	SI
C	973	301	0.30	NO
RESOLUTION 0631 OF 2015	200	Analysis and reporting	-	

Source: Authors

Although biodegradability is not a property that depends exclusively on the compounds that make up the wastewater, the enzymes that participate in the biodegradation of detergent A and the products derived from it do depend on the substrate.

With respect to the analysis of the percentage of biodegradation calculated with the BOD21/DQO ratio according to ASTM D 2667, detergent A, with a result of 72%, exceeded the percentage of 60%, indicating that it is biodegradable.

Likewise, detergent B, with a percentage of 76%, is considered biodegradable and its value is higher than the value obtained for detergent A. Although it should be noted that detergent B, having a higher COD value, in the relationship proposed for the determination of biodegradability, the BOD5 values were also higher than the results of detergent A, giving it a greater contribution to degradation by biological means.

It should be noted that the percentage of biodegradation by COD and BOD depends on the final BOD value obtained in relation to the metabolic activity of the microorganisms present in the sample. This is because the activity, type and concentration of these heterogeneous microorganisms are not controlled factors in the laboratory analysis. Thus, water from washing with detergent products with low activity microorganisms (e.g., in the case of toxic compounds from surfactants present in detergents B and C) may have a low BOD even if its organic content is significant.

It is well known that microorganisms in water suffer seasonal variations in their quantity and type and, therefore, we can say that the unit of measurement of BOD in classical analysis has considerable intrinsic variability (Diez, Rodríguez and Ferrer, 1999).

Finally, detergent C was the one that did not obtain an indicated percentage of biodegradability, but it transcends the fact that it is the most consumed detergent (see Table 2) for washing activities, this is due to its low economic cost and its presence in local and municipal pantries. This increased use can increase the problem in water treatment systems and receiving bodies due to the subsequent effects (e.g., increased foaming due to surfactants, increased toxicity, etc.) due to its collateral effects..

Biodegradability Ratio DQO/DBO_5

Another method to establish the biodegradability of detergent products is the comparison between Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD5) (Table 4), both indirect measures of organic matter content.

It consists of establishing the COD/BOD5 ratio. When the BOD5 has a value close to that of the COD, the biological processes are efficient in the degradation of organic matter. Otherwise, if the COD is much higher than the BOD5, the action of microorganisms on organic matter is not efficient and the wastewater would not be biodegradable by biological means.

Table 4. Relationship DQO/DBO5 – Concept

Relationship DQO/DBO_5	CONCEPT
Higher to 5,0	Non-degradable
Between 3,0 y 5,0	Conduct additional studies
lower to3,0	Degradable

Source: Authors

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Table 5. Relationship DQO/DBO5 – Concept

Relationship DQO/DBO_5	CONCEPT
Higher to 5,0	Non-degradable
Between 3,0 y 5,0	Conduct additional studies
lower to3,0	Degradable

Source: Authors

As a reference base, we use wastewater of domestic origin, which is more than 90% degradable when subjected to natural or forced aeration processes. The COD/BOD5 ratio for them varies between 1.8 and 2.5 (Ministry of the Environment, 2002).

Consequently, as shown in Table 5, when the COD/BOD5 ratio of waters with detergent products is greater than 5.0, they are difficult to treat by biological means and are considered non-degradable. For values between 3.0 and 5.0 it is necessary to carry out additional studies to establish their degradability, while when this ratio is lower than 3.0 the waters are treatable by biological means and are considered degradable.

Table 6. Relationship DQO/DBO5 – Results

DETERGENT	DBO_5 mg O_2/L	DQO mg O_2/L	Relationship DQO/DBO_5	CONCEPT
A	315	731	2,32	Degradable
B	786	1173	1,49	Degradable
C	301	973	3,23	No degradable

Source: Authors

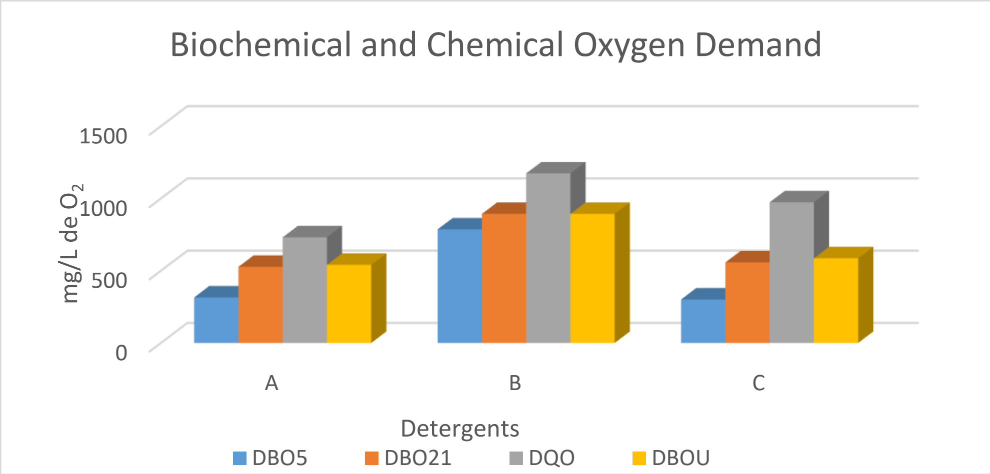
Based on the results of the COD/BOD5 ratio, detergent A with a value of 2.32 and detergent B with a value of 1.49 are among the degradable values, while detergent C with a value of 3.23 exceeds the determined ratio and is considered non-degradable.

Detergent C presents the lowest BOD5 value, although it is not considered biodegradable, due to the presence of surfactants, the concentration of oxygen consumed is due to chemical decomposition, since the microorganisms present cannot degrade some of the components of the anionic and nonionic surfactants. The results concerning BOD21, BOD5 and COD are shown in Graph 1. It can be observed that, although the biodegradability ratios were more promising for detergent B, it requires a greater consumption of oxygen, both biological and chemical, for its biodegradation.

The above represents a counterpart with detergent B, although ecological because of its biodegradability, this means higher oxygen consumption, interfering in the demand used by biological life, in addition to its effects due to the addition of surfactants. A comparison reflects that detergent B requires higher O2 consumption for BOD5 than detergent A requires for oxidation by chemical means.

Detergent C reflects that it is the least susceptible to be degraded by biological means, the means to produce degradation is feasible by chemical means because of its high O2 content in reference to that used by biological means since the chemical concentrations cannot be degraded by microorganisms. This also justifies the biodegradation results previously calculated, which show a higher degree of contamination due to the oxygen demand required by the water to degrade the organic matter content, including that necessary for biological degradation.

Graph 1. DBO5, DBO21, DBOU y DQO



Source: Authors

The values of nbDBO calculated in relation to the concentration of BODu in the COD reflect that the non-biodegradable organic matter is higher in detergent C (39.87% nbDBO), in relation to detergent A (26.12% nbDBO) and detergent B (23.87% nbDBO). The percentages of nbDBO reflected that detergent C can only degrade approximately 60% by biological means and the remaining is organic matter that is not assimilated or not biodegradable by the microorganisms present in the sample.

Likewise, these high concentrations of COD, due to their oxidation, in turn generate a higher concentration of CO2 and CH4 from the decomposition of organic matter, due to the oxygen required by the microorganisms to fully oxidize it to CO2 and H2O, generating a higher concentration of greenhouse gases.

The values of detergents A and B obtained from the COD/BOD5 ratio for the wastewater studied suggest that they can be treated through biological treatment such as activated sludge or lagooning systems to reduce pollutant concentrations

Results of Physical-Chemical Parameters

In the reports of results given by the contracted external laboratory, it is observed that the resulting values of the parameters analyzed for each detergent vary depending on the composition of the detergent and the principle that acts to remove the dirt, in addition to other factors, which intrinsically participate in the determination of biodegradability and allow participating in the determination of the proposed parameters.

- Hydrogen potential analysis (pH)

The experimental results reported by the laboratory observed in Table 6 corresponding to pH, it can be observed that the values exceed the permissible limits for domestic wastewater discharges - ARD in the Colombian regulations, Resolution 0631 (2015), as well as by existing studies on their own characteristics in which the ranges are between 6 to 9 (Ministry of the Environment, 2002).

Although a significant difference is found between detergents A, B and C, this may be due to the characteristics of the compositions, which on the one hand detergent A with its carboxymethyl cellulose content generates a contribution of hydroxyls by dissociating into its ions when they come into contact with water and contribution of salts from the dirt present in the sample.

On the other hand, for detergent B it can be estimated that its value was due to the anionic surfactants present that contain hydroxyl ions (OH-) that cause the increase in pH, although it would be important to determine other interactions that the detergent components may generate with the water and the dirt coming from the clothes. For detergent C, this same analysis of the aforementioned interactions would be important, since having so little information on its components, the class and type of surfactant used, it is not possible to define the precise origin of the result in this sample.

Table 6. Analysis de pH

DETERGENT	A	B	C
pH	10,01	10,3	10,5

Source: Authors

From the above, it can be seen that the three detergents are alkaline detergents that contain surfactants to improve rinsing power and control the foam produced during cleaning, although this has repercussions on the receiving ecosystem, affecting the soils where laundry discharges are dumped, in addition to the addition of acidic substances for treatment in wastewater treatment plants (Amaya et al., 2004).

If it is considered that a large percentage of wastewater discharges in Colombia go directly to water bodies, the values obtained act directly on the permeability processes of the cell membrane of the organisms that are part of these water resources, interfering in the intra- and extracellular ionic transport, as well as between organisms in the environment (Castañón, 2012).

- Conductivity - Salinity

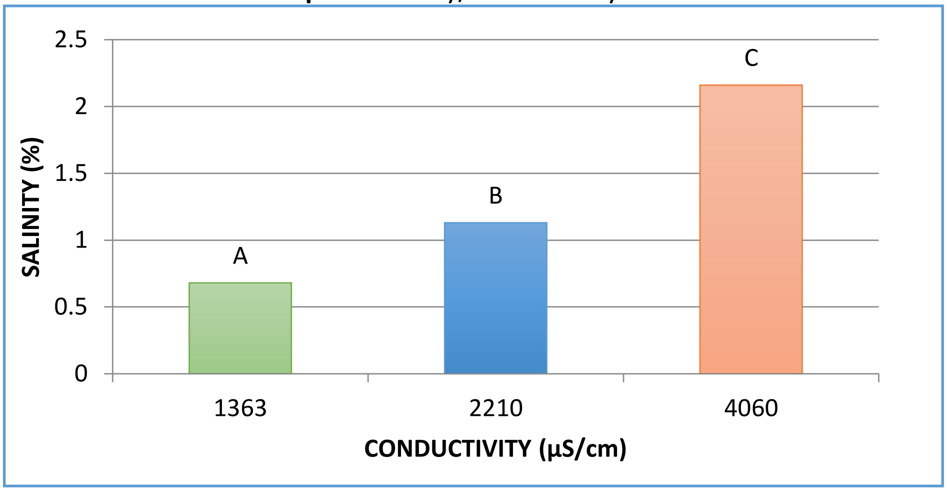
The electrical conductivity contributed by the detergents is associated with the ions present in their composition and concentration of dissolved salts in the water, which in consideration of the sum of the ions of both the water and the detergent, there was an important contribution by the detergents analyzed. There may also be a contribution from the surfactants present, which have certain special properties in relation to the concentration in solution (Lechuga 2015).

These contributions are produced by ions present in the composition of each of the detergents and of which can be included those contributed by the dirt from the laundry. In Graph 2, the significant difference in the conductivity result of the three detergents can be observed.

The highest concentration of conductivity and salinity is reported for detergent C showing the highest concentration of ions present. In addition, it is reflected that the result of detergent C is three times higher compared to the result of detergent A and almost two times higher than the result of detergent B.

Detergent C, having a higher concentration of hydroxyl [OH-] reflected in the pH results (see Table 6), its conductivity is higher due to the values contributed by this ion (199 units). The other common ions have values that vary between 40 and 80 units, and this shows that in composition, this detergent has a higher concentration of cations and anions that participate in the result of this conductivity measurement.

Graph 2. Salinity/Conductivity Ratio



Source: Authors

These values obtained can cause alteration of the conductivity of the environment, increasing or decreasing the levels of salts present, which will negatively affect the metabolic capabilities of organisms and even alter the type of ion (e.g., exchange of potassium for sodium) which can be detrimental to aquatic life if their biological processes cannot cope with these changes.

- Conductivity - Total Suspended Solids (TSS)

Detergent C, which shows a higher conductivity value and also indicates a higher content of salts than detergents A and B, as well as according to the relationship of formula 1, shows a higher presence of TSS, although there are no reliable data available on possible health effects associated with the ingestion of TSS present in drinking water and no reference value based on health effects is proposed. However, the presence of high concentrations of TSS in drinking water can be unpleasant for consumers (WHO, 2013).

An important factor in the values obtained is due to the amount of detergent added based on the concentration of the detergents and according to the manufacturers' references. In detergent A, due to its concentration, 12 g was added while in detergents B and C it was 36 g, which indicates that in the latter two there is a greater presence of ions that are part of the conductivity analysis and in their correlation a higher TSS was found as shown in the results.

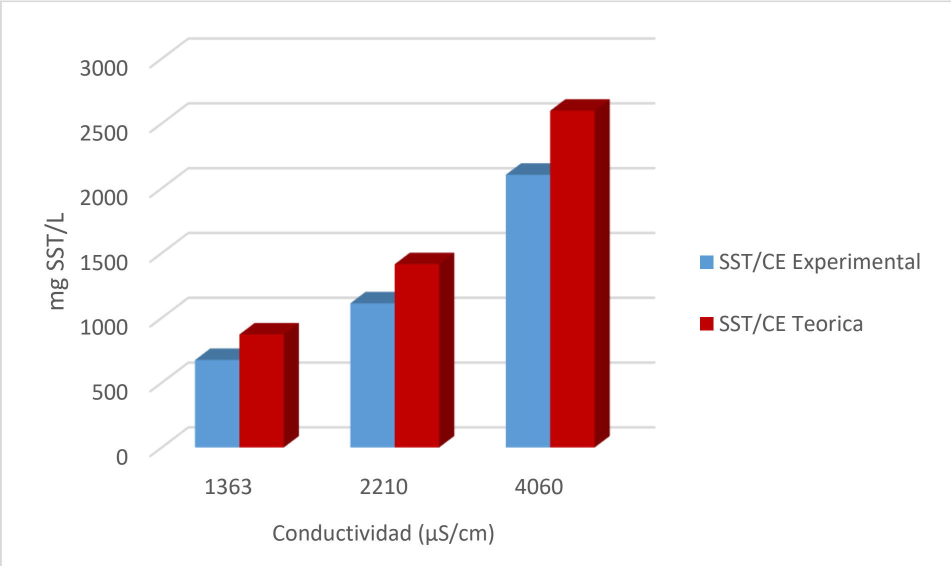
Being an analysis in aqueous solution, conductivity is directly proportional to the concentration of dissolved solids, therefore the higher the conductivity, the higher the concentration. An approximation to the above is expressed in formula 1, in which for the theoretical calculations for the comparison of the analyses supplied, FC=0.64 was taken as FC=0.64 because it is the manufacturer of the measuring equipment.

$$SST = FC * CE$$ *Formula 1. Theoretical correlation SST – CE*

As shown in Graph 4, the concentrations have a significant correlation in the reported analyses, showing that detergent C has the highest amount of TSS (4060 mg TSS/L) and this can cause limited growth of aquatic life and can cause the death of certain species that do not tolerate high TSS concentrations in the discharge sites with this detergent product.

The relationship proposed in formula 1 and shown in Graph 3, has a high difference to the laboratory analysis. This may be due to the high concentrations of anionic and non-ionic ions of the surfactants present in the detergents that increase the TSS concentration. It is also worth mentioning the correlation factor used, since in many cases it is not proportional due to intrinsic factors that affect its value, such as temperature, concentration of ions present, among others..

Graph 2. Theoretical Experimental Relationship SST/CE



Source: Authors

The concentrations obtained of dissolved solids contributed by the detergents representing the soluble and colloidal material in the treatment systems will usually require biological oxidation or coagulation and sedimentation for their removal. In the biological treatment of wastewater, a dissolved solids limit of 16000 mg/L is recommended (Gómez Rendón, 2012), which by concentration obtained, detergents A, B and C are at the threshold to be applied to the discharges coming from these washes diversity of biological treatments seeking their reduction to reduce their concentrations in discharges.

The concentrations of TSS reported by detergents can cause cells to shrink, and can also affect the ability of an organism to move in a water column, causing it to float or sink beyond its normal range, and TSS can also affect the taste of the water, and increase alkalinity or hardness..

- Salinity

The detergent A, reference in its composition that contains ions of sodium chloride salts (NaCl), which may be participating in the result of salinity obtained, although the results denote that the detergent A, obtained the lowest concentration of salts with a value of 0.68%, unlike detergent B with a value of 1, 13% and detergent C with a value of 2.16%, it is not possible to estimate the increase in these last detergents since in the composition label of these there is not enough information for a possible indication of their value, however the fact that they contain anionic and non-anionic surfactants means that these are generating the contribution.

Regarding the conductivity - salinity relationship, it was observed that the higher the conductivity, the higher the salinity (see Graph 2). This relationship was due to the fact that the salinity of the water from the laundry process is a variable that is measured by an indicator according to its electrical conductivity.

The values obtained in the laboratory analysis do not contemplate regulation in discharges or decrease in relation to conductivity or salinity according to Resolution 0631 (2015), so it can be foreseen that regardless of its contribution of positive or negative ions, in any magnitude of discharge it is allowed to be discharged into water bodies, which causes that by not having a regulation that regulates this, These ions can cause wear in soils where there is no sewage system, in addition to obtaining a large amount of salts in solution that affect several important physical processes, as well as important properties of water and substances dissolved in water that can be caused in receiving waters in rural areas by these processes in the treatment systems.

It is important to deepen studies related to the salinity provided by detergent products, particularly because it affects the solubility of dissolved oxygen. The higher the salinity level, the lower the concentration of dissolved oxygen, and this can affect metabolic and photosynthetic processes in receiving water bodies or in anaerobic and aerobic treatment systems.

- Orthophosphates

The determination of phosphate content in the detergents analyzed shows that their use in the manufacture of detergents has been decreasing, due to the high levels of phosphorus from tripolyphosphate, which is one of the main ingredients in detergent formulations, but which is also widely used as a chemical substance with a water softening effect to flocculate and emulsify dirt particles (Gender Cevallos and Ramírez, 2005).

Due to the above, restrictions have been generated for the use of phosphates in the manufacture of detergent products and it can be observed that detergents A and C, in their compositions do not show phosphorus-related ingredients, unlike detergent B, which specifies that its composition has a value of less than 0.15% (Table 1). This is shown in the results of Table 7, which reflects the presence of phosphates of less than 1% between detergent A (0.21 mg $PO4^{-3/L}$) and detergent C (0.39 mg $PO4^{-3/L}$) as opposed to detergent B (8.45 mg $PO4^{-3/L}$).

Table 7. Phosphate Analysis

DETERGENT	ORTHOPHOSPHATES mg P/L	PHOSPHATES mg PO_4^{-3}/L
A	0,07	0,21
B	2,76	8,45
C	0,13	0,39

Source: Authors

With reference to detergent B, although it has the highest phosphate value, it is still an estimate due to its low concentration because it can join other sources that contribute this phosphate ion (effluents with the presence of phosphorus, processes and discharges with phosphates, etc.) and increase its concentration in wastewater in which it is estimated that 20% of the presence of phosphates in wastewater treatment plants comes from detergent products.) and increase its concentration in wastewater in which it is estimated that 20% of phosphate presence in wastewater treatment plants comes from detergent products and therefore the sources that contribute this ion should be limited to control the growth of algae on the walls and installations of the process systems that cause algae growth (Nebel and Wright, 1999).

The regulations regarding the maximum permissible limit for orthophosphate discharges do not specify any reference value, only that they must be present in a proportion that prevents eutrophication, which leaves a regulatory vacuum for the control of discharges with phosphate content, leaving the ecosystem at the mercy of uncontrolled discharges.

It is important to mention that actions are being taken to ensure that detergent products do not have phosphates in their composition due to the consequences on the environment and specifically in water, this reduction of phosphate content in wastewater will give a respite to aquatic life and could improve water quality in general (Eliminate phosphates from detergents to improve water quality | News |

European Parliament, 2019). Phosphate-free formulas (such as those reflected in detergent A and C) are already available on the market and innovations are constantly being made to offer products that meet expectations in terms of cleanliness, but have less impact on the environment.

- Tensoactives

Currently, the most commonly used surfactants in the manufacture of detergents are anionic LAS or linear dodecylbenzene sulfonic acid, which comprise more than 40% of all surfactants used [23] and more than 80% of the use in household detergents, while the rest are nonionic, cationic and amphoteric.

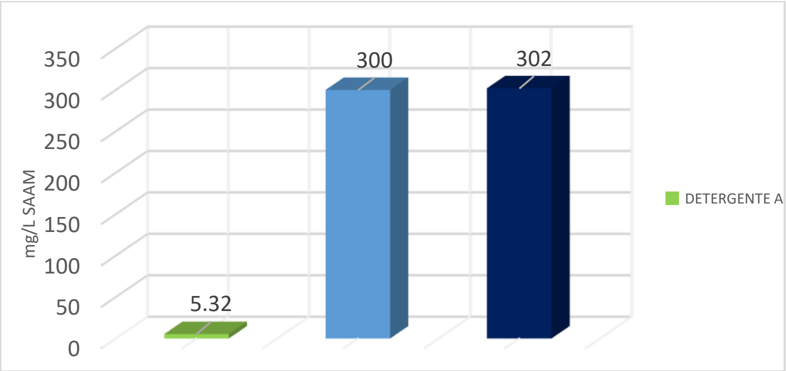
This presence of surfactants is clearly referenced in the composition of detergents B and C (Table 1), in which detergent B specifies anionic and nonionic content compared to detergent C, which does not specify the type of surfactants used for dirt removal, thus affecting receiving water bodies.

The surfactants present in detergents B and C, as shown in Graph 4, exceed the concentration with reference to the effluents from the manufacture of detergent products, which are at 200 mg SAAM/L, in addition to the maximum permissible value for discharge into water bodies, which is 5 mg SAAM/L.

In comparison to previous studies, they exceed the average specified concentration that indicates the typical concentrations of non-ionic surfactants in municipal wastewater, which is currently in the range of 3-4 mg SAAM/L.

The high concentration of surfactants reported by the analysis of detergents B and C is due to the fact that most of them, since they are not biodegradable products, have a content of 10% to 30% of surfactants of natural or synthetic origin, reinforcing agents, corrosion inhibitors, auxiliary agents, bleaching agents and perfumes, as reported by others (Cain, 1994)

Grafica 3. Tensoactives



Source: Authors

These concentrations of surfactants reported for detergents B and C would indicate that they are potentially dangerous for aquatic fauna, and the polyphosphate reinforcing agents are the most dangerous, the former for being very toxic to aquatic organisms (Pettersson, Adamsson and Dave, 2000), since their mode of action is broad, due to their amphiphilic character and their membrane solubility and endocrine disruption properties, among others (Pereza and Delgado-Blas, 2012).

From the above, it could be indicated that there is a risk in the lower part where the detergent products are discharged, since they can also alter the hydraulic characteristics of soils, which affect the circulation of contaminants through soils and groundwater (Ortega, 2009). In the lower part where discharges are made, a public health problem may be caused by those settlements where these waters are collected for human consumption and, since these waters have a high concentration of these surfactants, they could affect health.

Detergent A was the one that obtained the lowest surfactant value (5.32 mg SAAM/L), unlike the counterpart detergents. Its main reason is due to the fact that its composition does not contain surfactants, in addition to the fact that its active principle for cleaning is carried out by means of protease enzymes that replace anionic and non-ionic agents. The protease enzymes used in detergent A optimize its efficiency, while allowing cleaning at low temperatures and shorter washing periods, significantly reducing energy consumption and CO2 emissions.

A strong difference in relation to the values obtained between detergents A and detergents B and C is that the former, due to the active use of enzymes, does not produce foam when used, while the latter two, due to their surfactant content, promote foam in order to increase the surface area and to be able to be located at the interface. This foaming causes problems such as the erroneous reading of various equipment used for process control in applications such as temperature, level, dissolved oxygen, among others, in water treatment systems once the detergent discharges have reached the system..

Conclusions

According to the results obtained for the determination of biodegradability under the ASTM standard, detergents A and B were found to exceed 60% of the BOD21/CBD ratio, proclaiming themselves biodegradable. Given the COD/BOD5 ratio, detergent A and B are also between the biodegradability ranges with values of 1.6 and 2.5 being lower than 3.0, indicating that they are biodegradable. Detergent C obtained a higher value for the COD/BOD5 ratio (3.5) and a lower value for the percentage of BOD21/BOD ratio (56%), between the two not reaching the corresponding values to be considered biodegradable.

The biodegradability results agree with the specifications of the manufacturers of detergents A and B (see Table 1) in that the first one claims to be biodegradable and the next one is referred to as an ecological detergent, while detergent C's ingredients with surfactants and phosphates do not show environmental sensitivity actions, nor technologies with biodegradable products to mitigate their effects on water bodies. The results obtained by the three detergent products with reference to COD and pH, do not comply with the maximum permissible limit value of point discharges of domestic wastewater contemplated in resolution 631/2015.

The high concentrations of surfactants reported by detergents B and C, are causing great affectations to the receiving water bodies and soils, in which in many times they are little considered as main guarantors, even more concern grows since there is no maximum limit of discharge by Colombian standards. The results of detergent C were determined to be the most harmful to the environment due to the use of phosphates, although the concern increases since it is the most consumed product for laundry activities. Detergent A reported the lowest concentrations of contaminants in the water, thanks to its enzyme active principle that replaces the surfactants present in detergents B and C.

There is a gap in the Colombian regulations on discharges, since certain parameters do not contemplate maximum permissible limits, among which are: BOD5, surfactants, surfactants and other pollutants: BOD5, surfactants, orthophosphates, dissolved solids, among others. Detergent B stood out for the best results of biodegradability, which does not mean that they are totally harmless to the environment, but that they have a high and rapid degradability, although to reach such concentration it requires greater oxygen consumption, in addition to its problems due to the use of two types of surfactants: anionic and nonionic..

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