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DEVELOPMENT OF AN EDIBLE AND COMPOSTABLE BIOPLASTIC FROM FOOD INDUSTRY RESIDUES

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Abstract. The project pursues the use of waste from the Cantabrian food sector (cereal waste from the spirits industry and whey), in order to manufacture an edible, biodegradable and compostable plastic substrate, as an alternative to current plastic production, providing a solution in favor of the recovery of industrial waste. For the development of the edible plastic substrate, arabinoxylan and kefiran compounds were used, from cereal residues and milk whey, respectively. Several formulations were developed to create a pre-industrial prototype of the biocomposite for the edible plastic substrate, likewise, a search was made on the use of whey to obtain biofilm.An exploitation plan was drawn up that evidenced the need to sell 1,900 kg of bioplastic pellets per month to ensure the economic viability of the process. This production would have a unit cost of €15/kg, lower than the estimated sale price of €20/kg. Although it is estimated that the business profit margin would not be very high, the positive environmental impacts are good enough to consider the implementation of the developed solution.

Keywords: Food waste, plastic, bioplastic, environment.

DESARROLLO DE UN BIOPLÁSTICO COMESTIBLE Y COMPOSTABLE A PARTIR DE RESIDUOS DE LA INDUSTRIA ALIMENTARIA

Resumen. El proyecto persigue el aprovechamiento de los residuos del sector alimentario cántabro (residuos cereales de la industria de bebidas espirituosas y el suero de leche), con el objeto de fabricar un sustrato plástico comestible, biodegradable y compostable, como alternativa a la producción de plásticos actual, aportando una solución a favor de la valorización de residuos industriales. Para el desarrollo del sustrato plástico comestible, se partió de los compuestos arabinoxilanos y kefirán, provenientes de residuos cereales y del suero lácteo respectivamente. Se desarrollaron varias formulaciones para crear un prototipo pre-industrial del biocompuesto para el sustrato plástico comestible, asimismo, se realizó una búsqueda sobre el uso del lactosuero para la obtención de biofilm. Se elaboró un plan de explotación que evidenció la necesidad de vender 1900 kg de pellets de bioplástico al mes para asegurar la viabilidad económica del proceso. Esta producción tendría un coste unitario de 15 €/kg, inferior al precio de venta estimado de 20€/kg. Aunque se estima que el margen de beneficio empresarial no sería muy alto, los impactos ambientales positivos son suficientemente buenos como para considerar la implantación de la solución desarrollada.

Palabras clave: Residuos alimentarios, plástico, bioplástico, medio ambiente.

Introduction

Due to the increase in population, the excessive consumption of resources, and their negative effects on the environment, in the last 20 years social interest has grown towards a circular economy in which energy, resource management, as well as patterns of production and consumption, must be considered. In January 2018, the European Commission reported that recycling 1 million tons of petrochemical-based plastic is equivalent, in terms of carbon dioxide emissions, to taking 1 million vehicles off the road. Announcements by countries on the need to consider the fight against climate change and pollution, as one of the main current and future challenges of our societies, are multiplying (e.g., the declaration of "climate emergency" by the British Parliament, May 2019.).

In particular, on March 27, 2019, the European Parliament approved the directive banning from 2021 the sale of single-use plastics.

It is known that the solution to plastic pollution is not only to recycle but to reduce the use, consumption, and production of petroleum-based materials (WTO, 2018). The excessive use of unsustainable raw materials, such as petroleum, is one of the main causes of environmental pollution. Consequently, the production of consumer goods needs to be re-evaluated, with a greater focus on food packaging, one of the biggest polluters (they are 18.6% of the plastics present in the sea), that this production consumes less energy, and that plastics continue with a life cycle of minimal waste or different function (Özdamar & Ateş, 2018).

Measures such as reduction, reuse, and recycling of plastics have been taken; however, the increase in production remains constant and reuse and recycling are minimal. A study, carried out by Geyer, Jambeck, and Lavender (2017) shows that of the 6.3 billion tons of plastic turned into waste, only 9% ended up recycled, with 79% accumulated in the environment. This is why alternatives to the use of plastics of petrochemical origin should be raised.

Since the 2000s, bioplastics have emerged from scientific fields. Here we see experiences of manufacturing objects from bio-compostable materials (of vegetable, partially vegetable or fossil origin) such as flexible containers and packaging, catering articles, paper coating, agricultural mulch, shopping bags (Song et al., 2009). Today they constitute in Europe 1% of the total 335 million tons of plastics produced each year, and fortunately there is a growing interest, especially towards new bioplastics (Xu & Yang, 2012).

Bioplastics are considered to be plastics that are bio-based (the material or product is partly derived from biomass, i.e., plants), or biodegradable and/or compostable (materials that can be transformed into natural substances through a process) or both. They are made up of:

(1) biodegradable or non-biodegradable raw materials of renewable origin;

(2) raw material of petrochemical and biodegradable origin.

In the search for better characteristics of these bioplastics, the combination of elements of a biological nature has been explored, generating biocomposites of great interest. Biocomposites are mixtures of two biomaterials and are manufactured to achieve better performance, which is not possible with only one of the components.

Several companies have introduced starch/polyethylene blends as degradable materials for a number of short-life applications, such as beverage bottles, food packaging, and plastic bags. However, the impact on the environment is negative. While the starch component can degrade, the polyethylene residues remain in ecosystems and are not biodegradable.

In order to clearly set apart the different types of bioplastics, we could distinguish three main types of plastics: bio-based or organic-based plastics, biodegradable plastics, and bio-compostable plastics.

Bio-based plastics can be defined as derived from renewable biomass resources, which are largely biodegradable. They can provide functional advantages similar to those of traditional plastics, such as their use in packaging (Song, 2009). They are made of animal or plant organic matter, and very often combined with materials of petrochemical origin. Organic-based plastics depend on crops and scarce resources such as water. In some cases, and only if they do not contain materials from fossil fuels, they are edible.

Biodegradable plastics can be manufactured from renewable resources or from fossil fuels (Bastioli, 2003) since the biodegradability character is related to the chemical structure of the plastic. They also provide similar properties to plastics of petrochemical origin. Biodegradable plastics degrade by the action of microorganisms such as bacteria, fungi, and algae, without requiring human action.

Bio-compostable plastics, unlike biodegradable plastics, imply that the materials that constitute them can be converted into compost (organic fertilizer) through a process in which humans intervene, transforming the plastic through machinery.

Thus, this project was developed to achieve the use of waste from the Cantabrian agri-food sector (cereal waste from the spirits industry and whey from the production of cheese), for the manufacture of an edible, biodegradable, and compostable plastic substrate as an alternative to the production of polluting and non-recyclable plastics, providing a solution in favor of the valorization of industrial waste. Specifically, cereal bran (waste from the production of spirits) and whey (waste from the production of cheese).

Methodology and Results

First, the characterization of the two wastes involved in the project was carried out. For this purpose, the compounds arabinoxylans and kefiran, from cereal and whey wastes respectively, were analyzed since they are the two main ingredients of the edible plastic substrate proposed to be developed. The type of characterization focused on the integration of the compounds for the creation of the substrate.

As a first approach, a study of the alternatives for the pre-processing of cereal residues was carried out, for which a theoretical research on extractive techniques of compounds of interest from the cereal residue and the corresponding identification of processes and equipment to optimize the extractive process was developed. Of the cereal compounds of interest, this research focused from the beginning on arabinoxylans (AX). AX are polysaccharides present in cereal grains, located in the endosperm and bran (aleurone, cuticle, and pericarp). The interest in these polysaccharides is due to the fact that it has been shown that they can be considered as prebiotics.

AX can be water soluble (WEAX: water extractable arabinoxylans) and water insoluble (WUAX: water unextractable arabinoxylans), and it is this property that has been taken into account to adjust the extractive process.

Since AX are found as part of hemicellulose (Figure 1), we looked for hemicellulose extraction procedures that are easy to apply in the laboratory and that do not involve high reagent use, waste generation, and difficult application in green or sustainable industries.

Figure 1. Types of polysaccharides

Note: Source: Own elaboration, 2022

Taking into account the above points, the method used is the one proposed by Yadav and Hicks (2017), which is based on the soluble character of hemicellulose and AXs and separates Hemicellulose A from Hemicellulose B, being in the latter the AXs. It was decided not to separate both fractions because no references were found as to which fraction contained the AX. It should be noted that this process requires a centrifugation step as well as the use of reagents such as ethanol and sodium hydroxide. At the industrial level, these requirements are easy to implement. However, the fact that the final product is dissolved in ethanol would make it necessary to implement additional equipment in the industry for the evaporation and subsequent recovery of this solvent.

As a first step of the proposed method, it is necessary to carry out an enzymatic treatment with α-amylase. This is in order to hydrolyze the amylase and facilitate the previous process. But since in this project we start from exhausted cereal (i.e., the residue of the food industry where starch has been extracted as a source of sugar), it was decided to dispense with that process.

Figures 2 and 3 show the cellulose and hemicellulose obtained experimentally.

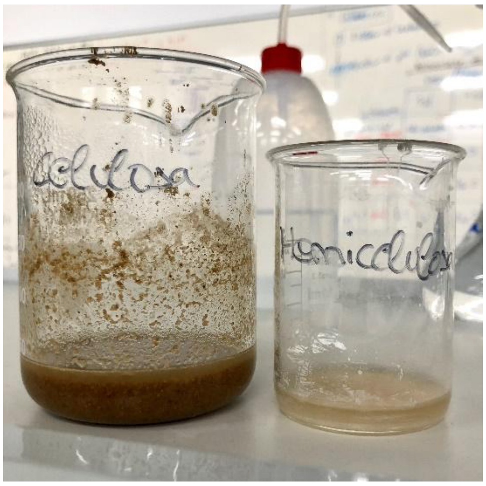

Figure 2. Extracted cellulose and hemicellulose.

Note: Source: Own elaboration, 2022

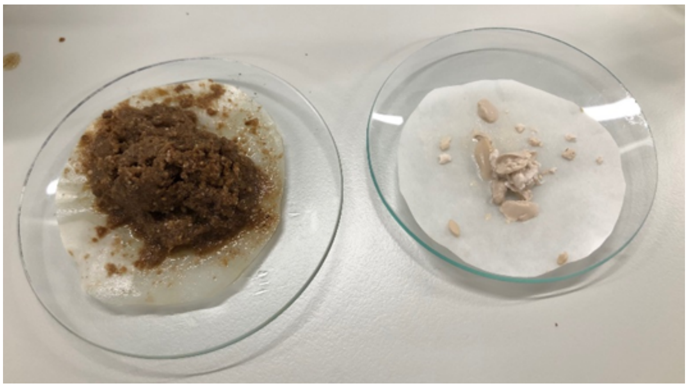

Figure 3. Cellulose (left) and hemicellulose (right) before drying.

Note: Source: Own elaboration, 2022

The characterization of kefiran was obtained from fermentation and whey purification processes by means of a laboratory-scale production protocol from whey and obtaining fresh kefir granules by growth in sterilized whey supplemented with KH_2PO_4 salts and sucrose, followed by homogenization, centrifugation, and precipitation of kefiran with ethanol.

Kefiran is the name given to a water-soluble gelatinous gum or polysaccharide released from kefir grains, formed by the monosaccharide's glucose and galactose, which is inside the matrix of the kefir granule (Piermaria et al, 2009). This kefir granule is an ecosystem inhabited by bacteria and other microorganisms responsible for the fermentation of lactose to lactic acid.

The methodology for obtaining it is that described by Joe Dailin et al. (2016), slightly modified. Said methodology is based on growing kefir in milk and identifies kefiran as the gelatinous polysaccharide that coats each granule, subsequently making several proposals for its isolation and purification.

After an analysis of this process, it was observed that it requires some factors that make the scaling up of the methodology towards a green or sustainable industry complicated. These factors were:

- Milk is required, which is not a by-product.
- Large volumes of solvents are required for kefiran washing and isolation.
- The purification process also requires a methodology and technology that do not justify the amount of waste generated and its subsequent management.
- These being the limiting factors, the following modification was proposed to overcome these drawbacks:
- Instead of using milk, residual whey from the cheese industry was used, thus working with a by-product. This whey was enriched with lactose so that fermentation could take place, the step from lactose to lactic acid.
- Instead of isolating the kefiran, the gel formed by the fermentation process itself was used as part of the biofilm. In this way, no waste is generated (Figure 4).

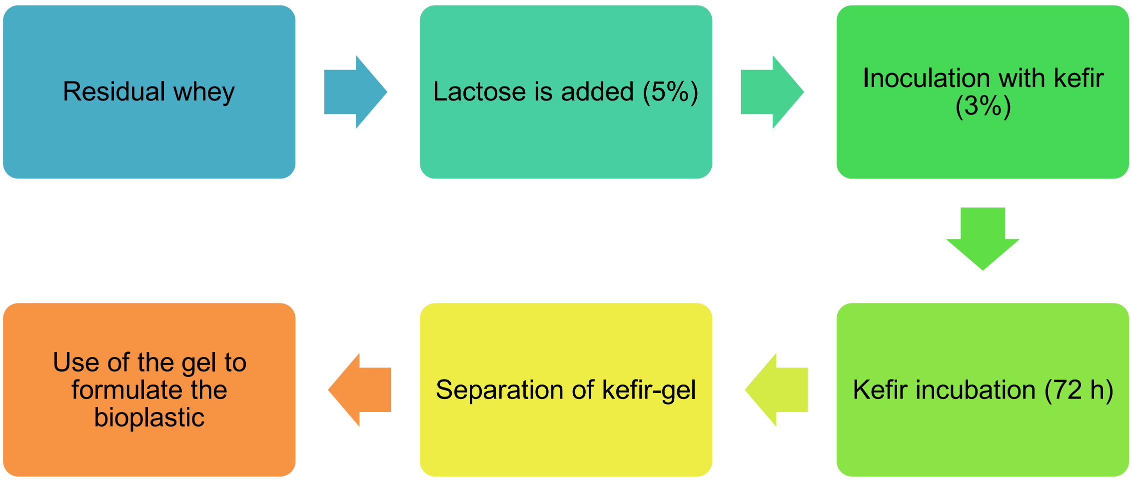

Figure 4. Process for obtaining biofilm gel at laboratory scale.

Note: Source: Own elaboration, 2022

Once the kefir is separated from the gel, it can be used for another inoculation and subsequent fermentation process, so it is a cyclic process that does not generate waste. As for lactose, it is a sugar that is easy to acquire in industrial doses. Figure 5 shows the final gel obtained after 72 hours of fermentation.

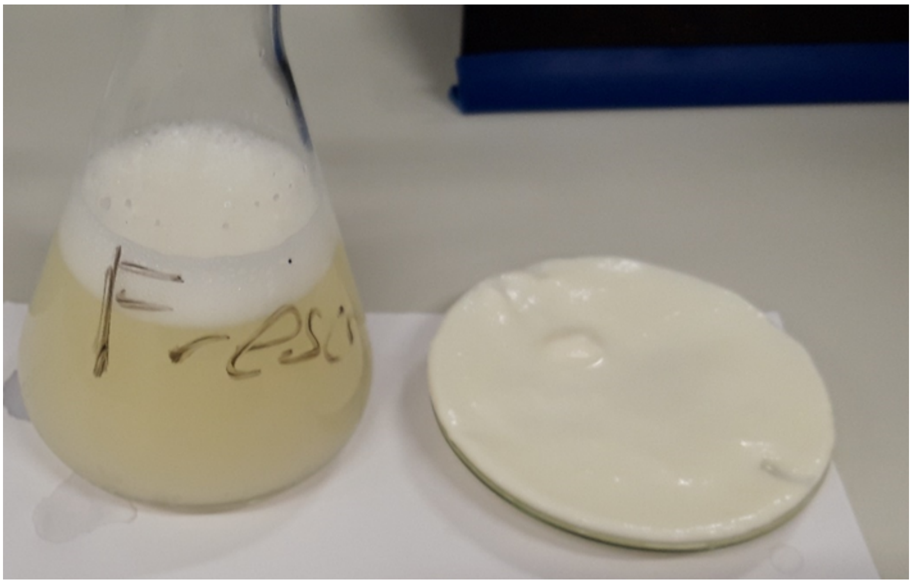

Figure 5. Kefir obtained from fermented whey.

Note: Source: Own elaboration, 2022

Kefir was inoculated at 3% on whey enriched with 5% lactose. From previous experiences of projects carried out with whey, it is known that its composition in protein and non-protein nitrogen, as well as its mineral composition, does not require adjustment of the chemical composition to facilitate the development of any microorganism. Table 1 shows the results of its analysis, which was performed on the original whey. After the fermentation process, the residual lactose, pH, and lactic acid content were measured, parameters that can have the greatest influence on subsequent use (Table 2).

Table 1
Initial composition of whey

Parameter	***L. acidophilus***
Phosphate (mg/L)	154
Protein (mg BSA/mL)	0,7
Calcium (mg/L)	62
pH	6,9
Lactose (%)	0,38

Note: Source*:* Own elaboration, 2022

Table 2
Final composition of fermented whey with kefir

Parameter	**Value**
pH	4,39
Lactic (%lactic acid)	1,50
Lactose (%)	0,20

Note: Source: Own elaboration, 2022

The separation of kefir from the gel was carried out by sequential filtration. First through larger diameter filters and then through smaller diameters. In this case, the microbiological characterization was not considered relevant because it is a pasteurized whey. It should be noted that we always worked with sweet skimmed whey.

The second characterization was of the raw cereal residues. For this purpose, the cereal residue was washed, dried, and crushed to obtain arabinoxylans. In this phase, the methodology described above was applied, and the volume of cellulose/hemicellulose was quantified, and the degree of viscosity-polymerization obtained in each working condition was characterized with a hedonic scale (Table 3). The experimental design consisted of modifying the temperatures and alkaline treatment times to separate cellulose from hemicellulose from the method described by Yadav and Hicks (2017).

The tests were carried out with 0.5 g of degassed cereal (Figure 6) that was dissolved in 10 ml of 2.3 N NaOH and subjected to heat treatment (70ºC and 40ºC in different tests). It was decided not to precipitate the hemicellulose in order to avoid a new residue and because being in a liquid medium would allow to see if it has thickening capacity or not. The thickening capacity was determined by allowing the hemicellulose suspension to cool to room temperature and observing the final result. The results are shown in Table 3.

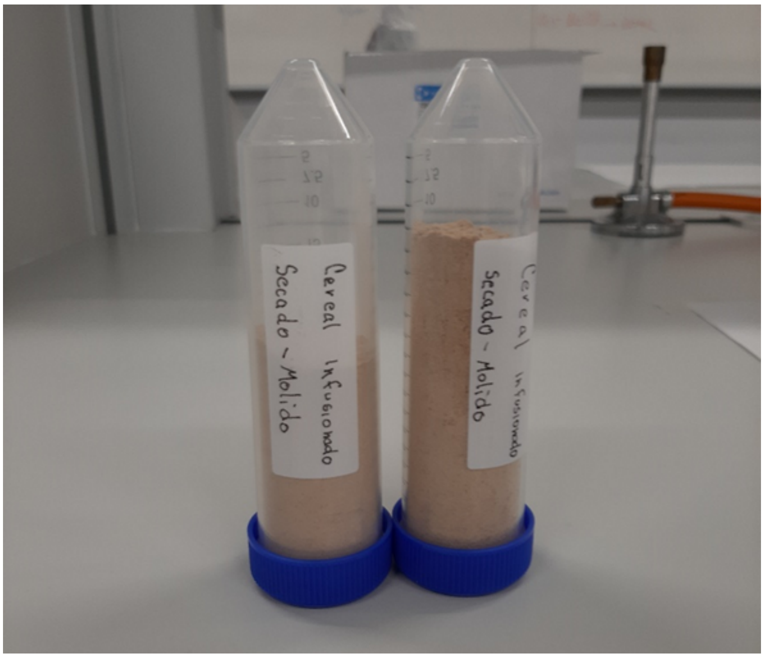

Figure 6. Degraded cereal flour
Note: Source: Own elaboration, 2022

Table 3
Results of initial alkaline treatment

Temperature (ºC)	***Time (min)***	***Cellulose (g)***	***Hemicellulose (ml)***	***Thickening capacity***
70	60	-	-	Very high
40	60	0,3	8	Medium

Note: Source: Own elaboration, 2022

At 70ºC, a highly viscous mass was formed that did not allow separation of the two fractions, so it was decided to repeat the test at 40ºC, modifying the duration of the alkaline treatment. The results are shown in Table 4.

Table 4
Treatment results at 40ºC

Time (min)	***Cellulose (g)***	***Hemicellulose (ml)***	***Thickening capacity***
60	0,3	8	Medium
120	0,4	7	High
180	0,5	6	High

Note: Source: Own elaboration, 2022

After 12 and 180 min, the final supernatant thickened upon cooling, without reaching the level observed when the temperature was 70ºC. On the other hand, the 40ºC/60 min treatment allowed a very good differentiation between the two fractions and no solidification effect on cooling, which allowed the samples to be preserved and subsequent concentration and purification treatments to be carried out.

Finally, the selection and evaluation of the biocomposite was carried out in three stages. First, different formulations adapted to the observations collected in the previous activities were carried out. As a result, no isolation of the arabinoxylans was performed, instead the hemicellulose suspension was used where these compounds and others that can facilitate the formation of the gum or biofilm are found. In this way, no waste is generated. Similarly, instead of using kefiran, the gel formed by the fermentation of whey was used.

Specifically, the experimental design consisted of comparing the following formulations:

Control: starch as structuring polysaccharide, acidification with 0.1N HCl, and viscosity adjustment agent consisting of a mixture of 50% glycerin and 2M NaOH 2M in a ratio of 1:1.25.

Formulation 1: hemicellulose from spent cereal flour, fermented whey (being acidified it replaces HCl), and 50% glycerin. NaOH 2M is not applied because it is already present in the hemicellulose suspension.

After mixing, a microwave heat treatment was applied. The heat allows the formulation to polymerize and a film is obtained. The results obtained are shown in Table 5.

Table 5
Comparison of formulations (I)

Film	***Polymerization***	***Viscosity***
Control	Yes	Adequate
Formulation 1	Very low	-

Note: Source: Own elaboration, 2022

After a first test, Formulation 1 was observed to have a very low degree of polymerization (Figure 7).

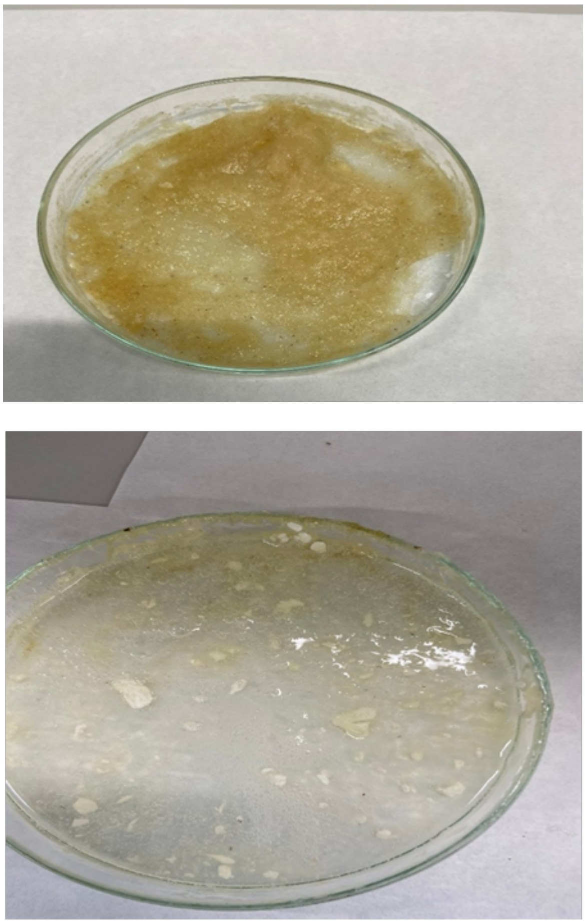

Figure 7. Comparison of the control biofilm (upper) with that of formulation 1 (lower)
Note: Source: Own elaboration, 2022

An analysis of the results led to the theory that the amount of hemicellulose is insufficient to form the film, so two possible solutions were proposed: a) enriching the formulation with starch, and b) increasing the hemicellulose content.

Choosing this second option has a practical disadvantage when it comes to implementing the process in an industry, which is the reagent and heat application requirements necessary to obtain hemicellulose, in addition to the need for an industrial centrifuge to separate it from cellulose. For all these reasons, the first route was chosen by means of starch supplementation (Figure 8).

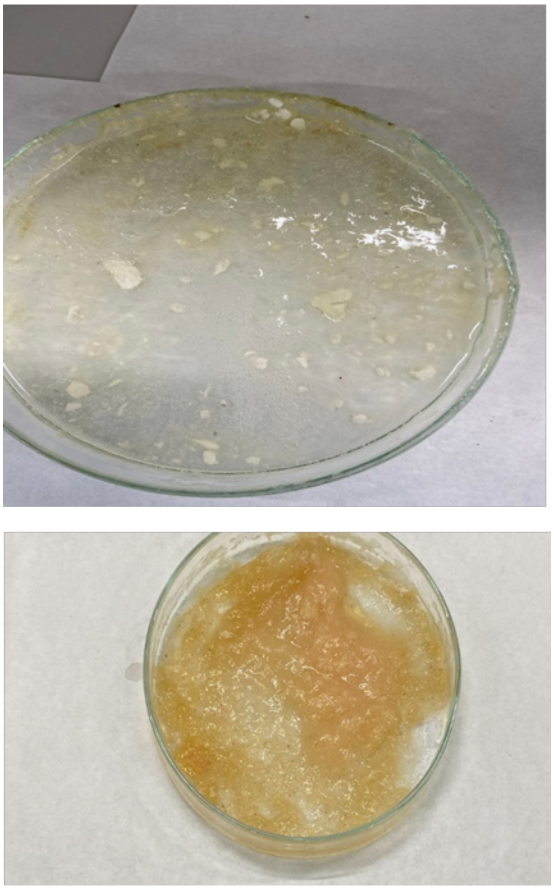

Figure 8. Comparison of formulation 1 (top) with the same formulation supplemented with 2% starch (bottom)
Note: Source: Own elaboration, 2022

Starch is a readily available product, very common in the food industry and low cost, and it would not have any technological impact or waste generation. After this first test, 2% starch was added to the new formulations. The results obtained showed a very good structure and the same behavior as the control after a few days, i.e., its consistency was maintained.

Based on these results, it was proposed to obtain bioplastic pellets since this is the usual form in which the plastics industry receives its raw material and, after an extraction process, gives it the desired shape.

Of all these compounds, the fermented whey fraction provides calcium (by its own composition), which is a structuring element that in combination with alginate has the capacity to form spheres, i.e., the desired pellets. A dose-response trial-error test was performed to determine how much alginate to add to the formulation, making the decision based on the final characteristics of the pellet, as shown in Table 6:

Table 6
Pellets characteristics at different alginate doses

Alginate (%)	***Biofilm characteristics***
0,5	No pellets are formed.
1	Pellet formation is observed but in a very limited quantity.
1,25	Unstable pellets are formed with time. As they lost their structure, it was not possible to evaluate whether or not microorganisms were growing.
1,5	Good density, good pellet formation, and stable over time. No proliferation of microorganisms.

Note: Source: Own elaboration, 2022

To obtain the pellets, a burette was loaded with the working formulation and dropped onto a bed of alginate with agitation and heat to promote the solidification process of the spheres to pellets (Figure 9).

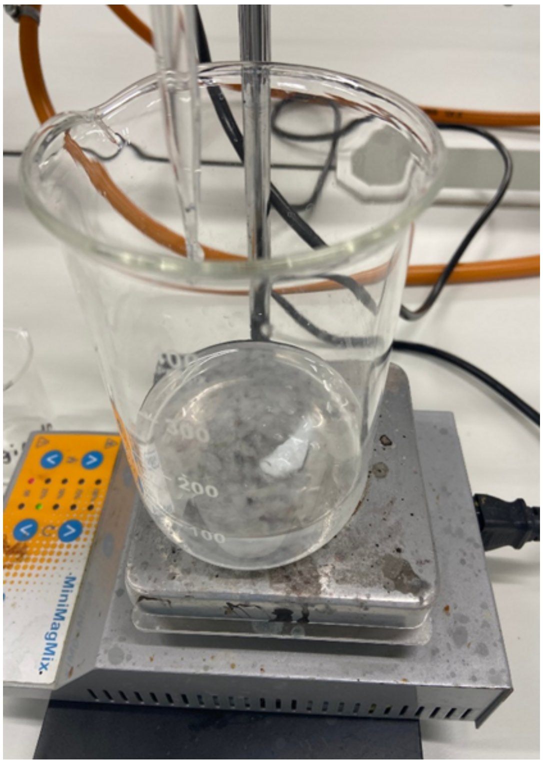

Figure 9. Formation of spheres or pellets in the laboratory
Note: Source: Own elaboration, 2022

Thus, Figure 10 summarizes the final protocol designed to obtain bioplastic pellets.

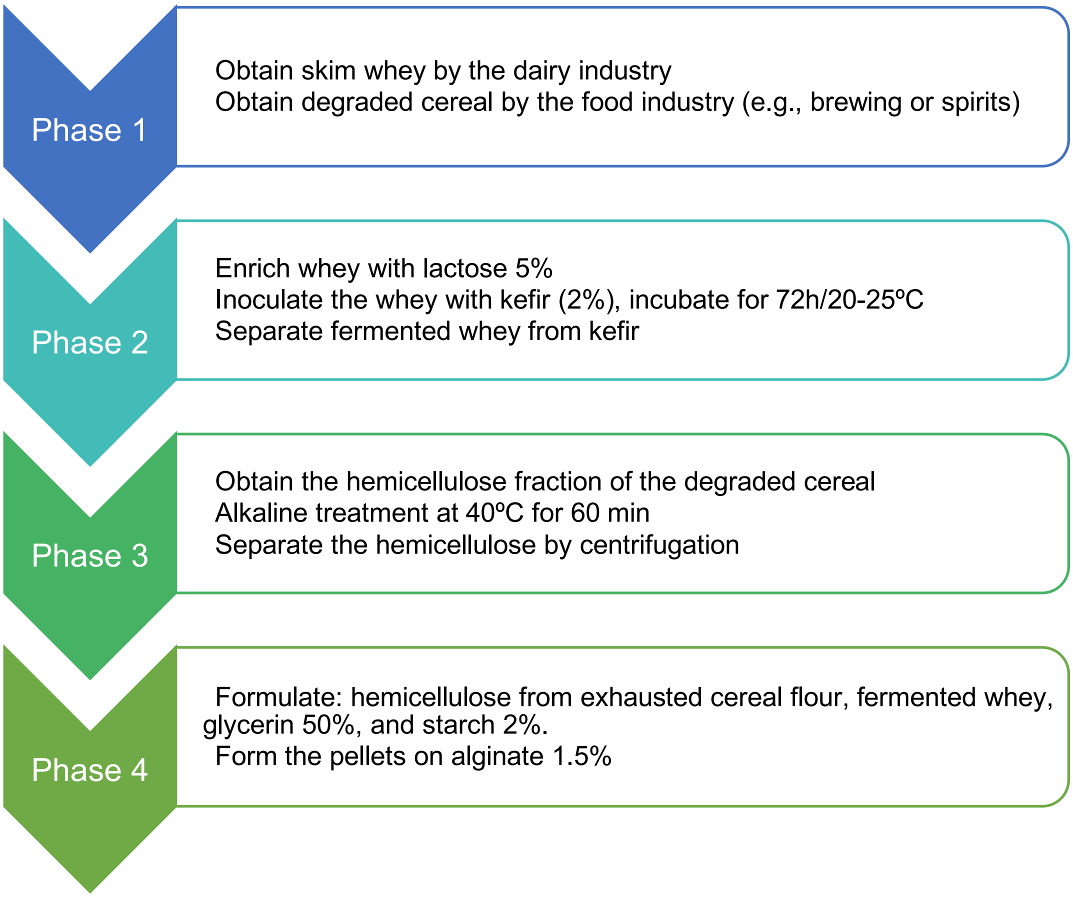

Figure 10. Bioplastic pellet production process
Note: Source: Own elaboration, 2022

A preliminary business plan was made by means of an economic estimation considering the most important costs if a start-up is created to process the industry waste to form the biofilm. Assuming that the bioplastic pellet should not exceed the price of 20 €/kg, it was estimated the quantity that should be produced monthly so that the unit cost is compensated with the selling price. The results showed that 1900 kg of bioplastic pellets should be sold per month. This production would have a unit cost of €15/kg, lower than the estimated selling price but with a low profit margin for the company.

Discussion and conclusions

As a result of this project, an edible plastic substrate was created, providing a possible solution for the valorization of industrial waste through the use of waste from the Cantabrian agri-food sector, specifically cereal waste from the spirits industry and whey from the dairy industry.

For the development of this substrate, the compounds arabinoxylans and kefiran from cereal residues and whey, respectively, were obtained by means of experimental protocols that were the result of an investigation of methodologies adapted to the objectives of the study.

Specifically, it was observed that the pellet manufacturing process should consist of the following tasks:

- Obtain the necessary components (skimmed whey and degraded cereal) from food industry waste.
- Enrich whey with lactose 5%.
- Inoculate the whey with kefir (2%), incubate for 72h/20-25ºC.
- Separate fermented whey from kefir
- Obtain the hemicellulose fraction of the dehulled cereal
- Provide an alkaline treatment at 40ºC for 60 min
- Separate the hemicellulose by centrifugation
- Formulate: hemicellulose from exhausted cereal flour, fermented whey, glycerin 50%, and starch 2%
- Form the pellets on alginate 1.5%

It should be noted that in this first stage of research, although the bioplastic generated has been obtained from waste already suitable for consumption, the necessary aseptic conditions have not been taken into account, since what was sought in this initial phase was to determine the possibility of obtaining this material. Subsequent research will include the appropriate considerations to make it edible.

With respect to economic feasibility, a business plan was developed, which led to the conclusion that 1900 kg of bioplastic pellets should be sold per month. This production would have a unit cost of 15 €/kg, which is lower than the estimated selling price of 20 €/kg. These data can be considered as the minimum reference value.

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