Analysis of a multifunctional experimental pilot plant for agricultural and dairy processing waste treatment

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Abstract

In this work a multifunctional experimental pilot plant with a reduced environmental impact which is able to process both fennel and liquid whey waste was developed and tested; such plant, using different thermal and filtration processes is able to recovery pectin and whey proteins in order to produce edible films.
An innovative feature of the proposed configuration is related to the possibility of a double type waste treatment, obtaining a final product with an higher economical value combining the two processing lines.

Keywords: Agricultural waste treatment, pectin, edible film, experimental pilot plant.

Introduction

In the past years, several changes occurred packaging industry in the food sector, following innovations and technologies of production systems. Important goals have been achieved in the production of composite multilayer films of synthetic polymers to protect foods, drugs and other products. But the accelerated growth of world population, increased consumption and the scarcity of resources, not mentioning environmental problems and climate, led research into new products equally or even more suitable in the context of renewable resources: in this framework an appealing goal is the production of edible and biodegradable films obtained from agri-food production waste that can even improve the quality of a food product, reducing the problems of resource availability and reducing the waste disposal problem.as agricultural and food processing waste disposal represents a major environmental problem for the large amount of waste produced and for their elevated BOD (Biological Oxygen Demand).

Edible films and coatings can be considered as "a thin layer of edible material, preformed or directly formed on food, used as a coating or inserted between the various components of the same" (Krochta and De Mulder-Johnston, 1997).

Available materials to form films and coatings are generally inserted in the categories of proteins, polysaccharides, fats and resins. A plasticizer agent must be often added to reduce film fragility, and a surface-active agent is often necessary to help the formation of films and coatings. Other constituent may include antioxidants and antimicrobials to improve its effectiveness.

In this context, this work aims to investigate the scale-up of a laboratory scale procedure (Giosafatto et al, 2007) for the extraction of pectin from fennel matrix (Foeniculum vulgare Mill. var. azoricum (Mill.) Thell.) and proteins recovered from the milk whey waste obtained from processing of buffalo milk. Materials used in polysaccharide films include starch and

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its derivatives, cellulose derivatives, alginates, carragenans, chitosan, pectates and different gums. Proteins can be combined with polysaccharides to change mechanical properties of film (Shih, 1994; Arvanitoyannis et al., 1996, 1997, 1998a 1998b; Arvanitoyannis and Biliaderis, 1998). Protein secondary, tertiary, and quaternary structures can be modified by various physical and chemical agents, including heat, mechanical treatment, pressure, radiation, lipidic interfaces, acids and alkalis and metal ions (Cheftel et al., 1985) and such agents are often used in the formation of films and coatings to optimize protein configuration and interactions, and properties of resulting films.

In the aforementioned categories, fennel and cheese production waste represent in Italy a significant problem, being the total amount of fennel waste estimated in Italy of 130x103 t and cheese production generates 145x106 t of liquid whey per year all over the world.

From an economical point of view, by-products are present in both wastes, and particularly fennel waste are rich of pectin and liquid whey contains a significant amount of proteins with an elevated biological value.

Many different processes have been developed in order to recovery nutrients or other components presenting an economical value, often with the aim of solving specific waste treatment problems.

Pilot plant description

The pilot plant is composed by a sequence of connected units and agitated tanks (6 jacketed tanks) in which is possible to perform mixing and mechanical breaking and degradation of agricultural and food waste matrices (variable speed rotating cutting blades are inserted into the tanks), thermal processes (heating and refrigeration units, and two plate heat exchangers), filtration processes (three different filtration units: a twin 100 μm metallic grid filter, and two polymeric variable size Millipore Polygard®-CR filtration cartridges), ultra filtration and concentration (a Millipore ultrafiltratin unit with Millipore Pellicon2® cartridges).

All units are served by four peristaltic variable size pumps, with the possibility to reverse flow direction and to move products from any of the tanks to an other selected one, and temperature and levels are digitally controlled on the control console as well as blade rotation rate.

Figure 1. Comprehensive view of the experimental pilot plant.

Pectin extraction

Fennel cultivar was chosen for the great amount of agricultural waste as residual of transformation (Italy is one of the main world production) and the relevant pectin concentration in the fennel matrix.

As first step, the possibility of using a thermo-mechanical extraction without neutral pH was investigated. In fact, in fennel pectin are mechanically structured in the fennel matrix and for the relatively soft cellular membrane they can theoretically be extracted without using acid solutions.

At the beginning, industrial fennel waste from agri-food companies were used, and then for simplicity (being almost out of fennel production season) fennels from the market were used.

In order to setup an extraction protocol, thermo-mechanical process parameter were investigated, and more in details extraction time, temperature, and fennel matrix-water dilution ratio .

Tap water at pH=7 was used, warmed up to 80 °C in order to deactivate pectin degradation enzymes; once the temperature was set, the fennel matrix was inserted into the SA1 reservoir, where the rotating blade provides the mechanical action coupled with the thermal degradation.

A first difficulty appeared in thermo-mechanical degradation using fennel agricultural waste without preliminary cleaning treatment, due to the presence of green leaves tends to interact with the rotating blade, forming a capsule around it and strongly reducing the cutting capacity.

Moreover, as the aim of the project is to build edible films by combining pectins with proteins extracted from milk whey, in presence of low pH solution precipitation of the protein component may occur.

Acid treatment is usually required in literature to separate pectin from proto-pectins or in agricultural product with a thick epicarp like in Citrus or in tomato's skin.

Simple sugars, oligosaccharides, polysaccharides and their derivatives, including methylesters, which have free or potentially free reducing groups, give a yellow-orange color when they are treated with phenol and concentrated sulphuric acid. The reaction is sensitive and the color is stable.

Through the use of this reaction with phenol and sulfuric acid, was developed a method to determine infinitesimal quantities of sugar and related substances. In agreement with the paper partition chromatography , this method is used for determining the composition of polysaccharides and derivatives methylated (Dubois et al, 1955)

This procedure was used to determine pectin concentration in the samples extracted, because in previous studies has found a large amount of pectin extracted from fennel, and then polysaccharides found by reading the spectrophotometer were considered to belong to this category, not excluding the possibility that we can treat other simple sugars or complex. At first,

It was necessary to build a line of action and then analyze the samples extracted. Industrial pectins were used as a reference with a concentration of 15 μg /μl.

In Fig.2 the extraction yield of pectin vs. time is reported for two different mass dilution ratio (fennel kg/water kg, yellow = 1/5, blue = 1/10).

In the first dilution experiments 10 kg of fennel waste vs. 50 kg of water were used, and the solution was sampled fro 5 hours of thermo-mechanical treatment.

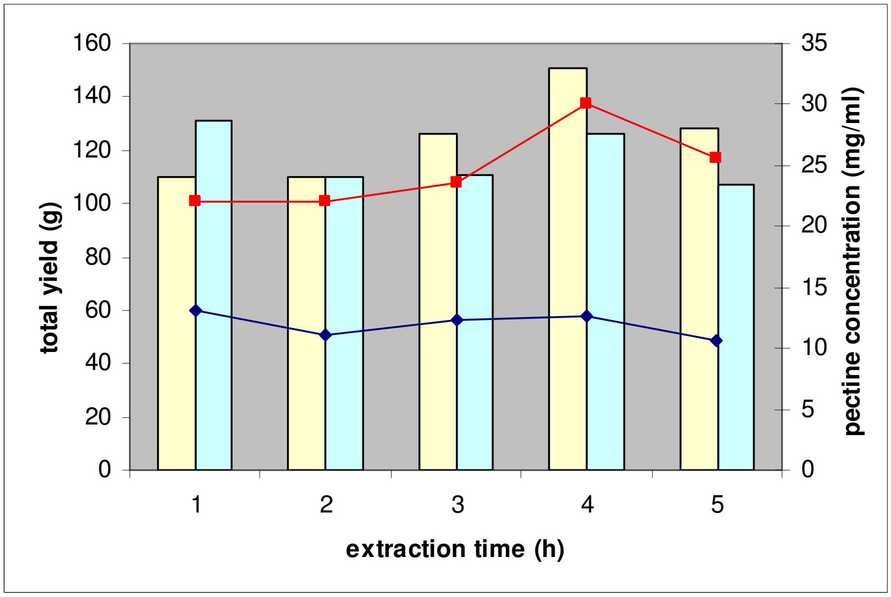

Figure 2. Total pectin yield and pectin concentration vs extraction time at 80°C

Results show that after one hour the extraction process is mostly completed, and that the final yield dos not strongly depend on the dilution ratio, at least for the considered ratio.

Further reducing the initial ratio would results in a dense solution at the exit of SA1 tank used for fennel cutting and thermal degradation, increasing filtration problems in order to obtain a clean solution before reaching the ultra filtration unit for pectin concentration process.

In Fig.3 the effect of the presence of strong cellulose residual component formation in the fennel- water solution after thermo-mechanical maceration is shown.

Figure 3. Cellulose cake formation in the twin 100 μm filters

As a matter of fact the twin 100 µm metallic cartridge filter was not sufficient to clean the solution from this component, resulting in a cake formation around the filter with a lower cut-off scale, and consequently pectin entrapment in the cake before reaching ultra-filtration concentration process.

An interesting data emerging from Fig. 2 is a pectin concentration reduction after 5 hours of thermo-mechanical treatment, that can be consequence of a degradation process linked to enzymatic process of endogen de-esterification, precipitation due to the presence of Ca^{2+} in water, or b-elimination due to high temperature. In order to reduce Ca^{2+} concentration, a water column treatment unit was included in the pilot plant.

Time history of pectin extraction (see Fig. 4) shows that after 2 hours the concentration peak is reached, with constant concentration (results averaged of 5 extraction tests).

Several test were also conducted with different time-temperature configuration, showing that higher temperature then reported in literature are required to obtain a complete deactivation of pectinase enzymes to avoid polysaccharides reduction to simpler molecules.

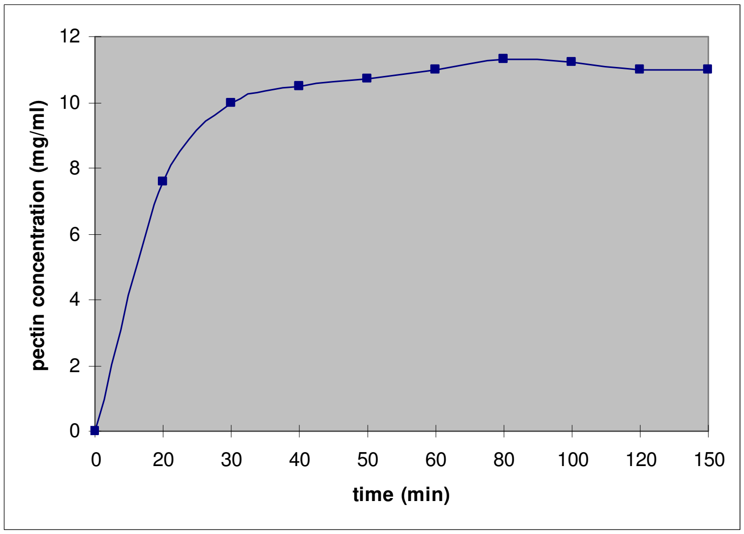

Figure 4. Time history of pectin concentration

Protein concentration

The second purpose of this type of experimental plant was to investigate the possibility of using the same configuration to extract proteins from dairy waste

Protein concentration was evaluated by using Bradford essay method (Bradford,1976, Stoscheck, 1990). Results are shown in Tab.1, where S_1 is the dairy hey at the initial concentration, S_2 after 100 mm filtration, S_3 after 25 mm filtration, P is the permeate, R_1 is the solution in the ultrafiltration tank at time t=0, R_2 at the end of filtering process.

Starting from a batch of 30 kg of dairy whey waste of buffalo milk used for mozzarella cheese production, after 1h30min ultrafiltrating with a membrane of 10k Da, 27 kg were discharged in the permeate.

Table 1 Protein concentration after ultrafiltration

Protein concentration after ultrafiltration	
Sample	g/l (min-max)
S1	0,804-1,54
S2	1,11-1,4
S3	1,05-1,4
P	0-0,06
R1	0,90.-0,96
R2	5,2-5.6

Edible film production

Combining together pectins extracted from fennel and protein obtained from dairy waste, under the action of the transglutaminase enzyme, it was possible to obtain an edible film (see Fig.5 a-b)

Figure 5 a-b. Edible film samples obtained by film casting

The first film (Fig. 5 a) was casted in a Petri plate by using pectin sampled after the thermo-mechanical treatment (before filtration), while the third using pectin obtained using concentrated and purified pectin after ultrafiltration.

As the main purpose of this work is to study the scale up properties of the experimental plant respect to the laboratory process, details of film permeability are not provided here.

Conclusions

The experiments conducted showed the possibility of using the proposed plant configuration for bio-products recovery from agricultural and food processing waste and biodegradable edible film production. Respect to the laboratory procedure, filtering and concentration seem to be relevant problems to address in order to switch from lab scale t o industrial scale production, and a layout modification of the plant, inserting a centrifuge separation unit is probably required.

Moreover, an analysis of the permeability properties of the film is further required, in order to characterize a proper use of the product.

References

Krochta, J.M. and De Mulder-Johnston, C. 1997. "Edible and Biodegradable Polymer Films: Challenges and Opportunities," Food Technol., 51(2):61–74.

Shih, F.F. 1994. "Interaction of Soy Isolate with Polysaccharide and Its Effect on Film Properties," JAOCS, 71:1281–1285.

Arvanitoyannis, I. and Biliaderis, C.G. 1998. "Physical Properties of Polyol-Plasticized Edible Films Made from Sodium Caseinate and Soluble Starch Blends," Food Chem., 62:333–342.

Arvanitoyannis, I., Psomiadou, E. and Nakayama, A. 1996. "Edible Films Made from Sodium Caseinate, Starches, Sugars or Glycerol, Part 1," Carbohydrate Polym., 31:179–192.

Arvanitoyannis, I., Psomiadou, E., Nakayama, A., Aiba, S. and Yamamoto, N. 1997. "Edible Films Made from Gelatin, Soluble Starch and Polyols, Part 3," Food Chem., 60:593–604.

Arvanitoyannis, I., Nakayama, A. and Aiba, S. 1998a. "Edible Films Made from Hydroxypropyl Starch and Gelatin and Plasticized by Polyols andWater," Carbohydrate Polym., 36:105–119.

Arvanitoyannis, I.S., Nakayama, A. and Aiba, S. 1998b. "Chitosan and Gelatin Based Edible Films: State Diagrams, Mechanical and Permeation Properties," Carbohydrate Polym., 37:371–382.

Bradford, MM. 1976, A rapid and sensitive for the quantitation of microgram quantitites of protein utilizing the principle of protein-dye binding. *Analytical Biochemistry 72:* 248-254..

Cheftel, J.C., Cuq, J.-L. and Lorient, D. 1985. "Amino Acids, Peptides, and Proteins" in Food Chemistry, ed., O.R. Fennema, New York: Marcel Dekker, pp. 245–369.
Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. 1956. "Colorimetric method for determination of sugars and related substances" Analytical Chemistry 28: 350–356.

Giosafatto C., Mariniello L., Ring S.,2007, Extraction and Characterization of Foeniculum vulgare Pectins and Their Use for Preparing Biopolymer Films in the Presence of Phaseolin Protein. J Agric Food Chem.

Stoscheck, CM. 1990, Quantitation of Protein. *Methods in Enzymology 182:* 50-69 .