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VALORIZATION OF EGGSHELLS WASTE FOR BREAD PRODUCTION

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Abstract: This paper treats the effect of addition of unconventional materials as eggshell (ES) derived products for improving the quality of bread and bakery products. The main goal of this study is to demonstrate the feasibility of eggshells macerated (ESM) that contains a high assimilable calcium source (i.e. calcium citrate) as a supplement in white bread formulation. The influence of different percentage of ESM (i.e. 2.5 %, 5.0 %, 7.5 %, 10.0 %, wt/wt) into a classical white bread recipe to some physico-chemical, textural, nutritional, microbiological properties and also to sensory quality of fresh bread is compared. The results show that the addition of ESM, promoted as a natural additive for calcium fortified breads, generates a product with potential high acceptability degree for the consumers that need to improve the calcium daily intake.

Keywords: *bread, conservation, eggshell powder, natural additive, nutritive properties, waste recovery*

INTRODUCTION

Improving the use of by-products and waste from the agri-food sector, leads to increasing and expanding opportunities for innovation by achieving a zero waste economy. Agri-food by-products / wastes are important sources of sugars, lipids, carbohydrates, minerals, inorganic compounds (e.g. silica, calcium), dietary fibers, phenols, carotenoids, tocopherols etc. These compounds are potential valuable sources for different industries as food, pharmaceuticals, cosmetics etc. [1 – 4].

The present study focuses on hen eggshell - derived compounds that are considered renewable resources with high potential for food sector but also for agriculture, building and construction industry or paper manufacturing [5].

For a long period of time these mineral-rich products have been deemed as insignificant or very low value waste and consequently hundreds of thousands of tons of hen eggshells used as plant growth promoter were disposed in landfills every year in the US alone. In the last decade, a lot of studies shown that the disposition of high quantities of eggshells in landfill leads to environmental issues and an increase of the investment on research of high-value products issued by ES was registered.

As example, in 2012 the European Commission decided to fund a project related to the mitigation of the environmental problem related to ES biowaste [6] and to produce new valuable source materials.

The development of commercial value-added ES-derived products was a high priority for food waste management in Canada too [7].

In addition, according to the United States Department of Agriculture and National Agricultural Statistics Service, massive amounts (nearly 465,000 tons per year) of eggshell produced in USA could potentially be used to generate valuable-added products for different applications notably due to the bio-ceramic nature of this by-product. [8]

Literature shown that eggshell is composed of approximately 95.0 % minerals with a major part of calcium carbonate in the form of calcite and approximately 3.5 % of proteins, proteoglycans and glycoproteins that form an organic matrix [9].

Beside a major percentage of calcium, the elemental composition of eggshell shows about 0.9 % magnesium and 0.9 % phosphorus in the form of phosphate [10].

A study concerning the relation between the structure of food consumption and the life quality in Romania reveals an unbalanced consumption of some food categories that generate calcium, iron and some vitamins deficiencies and an increase of chronic disease risks [11]. One way to reduce the low intake of calcium is represented by fortified foods. As bread and bakery products are the most consumed food products in Romania, the addition of natural calcium source as eggshell can be a natural and cost-effective solution to synthetic supplements proposed by pharmaceutical industry.

Therefore, the main goal of this research is to prove the feasibility of a waste from Romanian food industry and households, i.e. eggshell, as a natural additive in bread formulation intended for people with relatively low calcium intake.

As the acceptability of calcium fortified bread on Romanian market can be highly influenced by the physico-chemical and sensory properties, this paper proposes to use an ESM that can be easily homogenized with other compounds of a white bread recipe and the influence of the dose of natural calcium addition to the properties of the final products was reported.

The bread resulting with eggshells plays an important role for the food industry, respectively as a natural additive, so a source of minerals improving the nutritional value and with antiseptic properties with real beneficial effects on the food industry [12 – 18].
Calcium is an essential mineral for our health, which supports several functions of the body. According to the literature, it is recommended that the flour enrichment with calcium to be 900 $mg \cdot kg^{-1}$ flour. Currently, calcium enrichment can also be achieved by adding dairy products [19].
A previous study [18] proposed to valorize chemically unmodified eggshells powder to improve the calcium load of bread and the product qualities in terms of aging time and flavor, but the utilization of solid powder has presented the disadvantage that it had a gritty feeling in the mouth. To improve the texture and sensory quality of the final products, in this paper calcium carbonate powder was treated with citric acid from lemon juice, and ESM was used in bread formulations. To our knowledge, this is the first study that treats this subject. Another advantage of the citrate form refers to the bioavailability of calcium that is assimilated in the body in larger proportions, about 45 %, compared to the carbonate form, which is absorbed in a proportion of 4 % [20]. In addition, the acceptability of calcium citrate (E333) was already proved as acidity regulating agent, sequestering and synergistic antioxidant agent in the bakery industry.

MATERIALS AND METHODS

Raw materials

Hen eggshells from households were used to enrich bread with a natural source of calcium. For the conversion of calcium carbonate from eggshells to citrate, the juice obtained from fresh lemon fruit (*Citrus limon L.*) was used.
The following raw materials were used to obtain the bread samples: wheat flour type 650, yeast, water, salt, sugar, sunflower oil. For the study of the influence of ESM addition on the quality of bread and for an efficient analysis and appropriate discussions, in the experimental study are proposed the additions of ESM presented in Table 1.

Table 1. *Proportion of ESM*

Samples	*Sample 1 (B-ESM0)*	*Sample 2 (B-ESM2.5)*	*Sample 3 (B-ESM5)*	*Sample 4 (B-ESM7.5)*	*Sample 5 (B-ESM10)*
Eggshells macerate (ESM) addition (% reported to flour, wt/wt)	0.0 (reference)	2.5	5.0	7.5	10.0

Obtaining of ESM

Before the acid treatment, the ES were boiled for 10 min, to avoid possible microbiological contamination. Theoretically, this short thermal treatment presents lower risk of losing a significant amount of calcium. In the literature, it is specified that the calcium content of boiled eggshells is about 20 % lower than in untreated (uncooked) shells [10].

After the protein film was removed, the eggshells were washed with warm water (40 ºC), dried in an oven at 40 ºC, and then crushed in a blender until the powder was obtained. The powder obtained was sieved to separate particles and only particles below 180 µm (similar to the grain size of wheat flour) were used for bread formulation.

Calcium carbonate is practically insoluble in water, but it easily dissolves in acid according to the reaction:

$$2\,HCl + CaCO_3 = Ca^{2+} + CO_2 + H_2O + 2Cl^- \quad (1)$$

Calcium citrate was produced by the reaction of calcium carbonate from eggshells with citric acid from lemon juice and the protocol used was mentioned in the literature [21].

Lemon juice was used to obtain the maceration from the eggshells.

The reaction of calcium carbonate conversion into calcium citrate was stoichiometrically carried out [10]:

$$2C_6H_8O_7 + 3\,CaCO_3 = Ca_3(C_6H_5O_7)_2 + 3H_2O + 3CO_2 \quad (2)$$

The ES powder and the lemon juice mixture was kept for 72 h in a cool, dark place (Figure 1). The ESM thus obtained was used as a source of calcium in the form of citrate, in the production of bread (B).

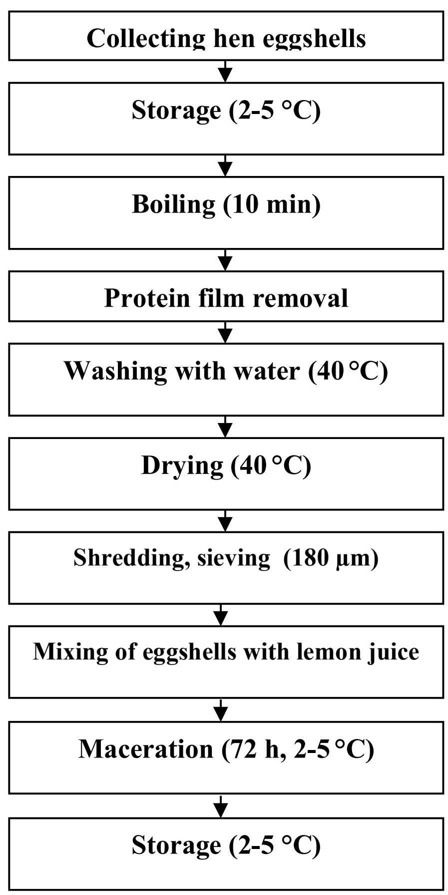


Figure 1. *Schema of ESM obtaining*

Physico-chemical characterization of eggshells

Energy-dispersive X-ray (EDX) analysis

The external surface and morphology of the eggshells was performed using Quanta 200 Environmental Scanning Electron Microscope (ESEM). GPC measurements of the hydosilylation products were done in chloroform on a GPC/SEC WGE 3010 (Brookhaven - Bures) after calibration with polystyrene standards. EDAX analysis was performed concurrently with SEM and performed at 5 points for eggshells and eggshells treated with citric acid.

Fourier transform infrared spectroscopy (FTIR) analysis

The functional groups present on the surface of eggshell were identified by Fourier transform infrared spectroscopy. FTIR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer equipped with a ZnSe crystal, in ATR (Attenuated Total Reflectance) mode in the range 600 - 4000 cm^{-1} at room temperature with a resolution of 4 cm^{-1} and accumulation of 32 scans.

Bread production process

To study the influence of ESM on the sensory and physico-chemical properties of bread, a control bread (without the addition of ESM) and bread with different additions of ESM were obtained according to the production recipe presented in Table 2.

The bread was prepared by the direct method using a Moulinex bread machine (kneading time: 18 min; fermentation and baking time: 75 min).

Table 2. *Recipe for bread obtaining*

Raw materials	Quantity [g]	Temperature [°C]
Wheat flour 650 type [g]	640	20
ESM [mL]	0 - 10 % *(% reported to flour)*	20
Water [mL]	400 - *x*	40
Salt [g]	10	20
Compressed yeast [g]	23	20
Sugar [g]	5	20
Sunflower oil [mL]	20	20

x - amount of ESM

Bread analysis

After baking, the bread was labeled and left for 3 h at room temperature for cooling, and then it was prepared for sensory and physico-chemical analysis. The sensory analysis was performed by the 20-points test [22].

Moisture (%), acidity (degrees of acidity), porosity (%), core elasticity (%) and ash content (%) were also determined notably following the Romanian STAS Standards.

Bread sensory analysis

The sensory analysis of bread (shape, external appearance, appearance of bread crust and crumb, consistency and behavior in mastication, bread smell and taste) met the requirements of the SR 91:2007 [23]. The samples were analyzed using the scoring scale to evaluate the organoleptic characteristics of bakery products of maximum 20 points [22]. The sensory evaluation was performed by a team of 5 tasters trained and coached beforehand.

Physico-chemical analysis of bread

Bread mass

This determination was made according to SR 878/1996 [23] using technical balance PS 3500.R2.M.

Determination of core porosity

The porosity of bread is given by the total volume of the pores in a certain volume expressed as a percentage but this property includes also the structure, uniformity, size, thickness of the membranes that delimit the pores. [22] The determination of the porosity was performed according to STAS 91/1983 [23] using a cylindrical metal with the height of 6 cm and diameter of 3 cm and a SHIMADZU Digital Balance for weighed the core cylinder taken out from the middle of the slice of bread.

Determination of core elasticity

This method is based on determining the compressibility and relaxation of the core, by pressing the bread under certain conditions and measuring the height at which it returns. This method is often used in bakery units and is realized by a cylindrical perforator [22]. The determination of elasticity was performed according to STAS 91/1983 [23] using a device for determining the elasticity of the bread core.

Determination of acidity

The acidity of bakery products is expressed in degrees of acidity and represents the volume in cm^3 of 1 N NaOH required to neutralize the acidity in 100 g of sample. The determination of acidity was performed according to STAS 91/1983 [23].

Determination of moisture

The moisture of the bread samples was determined according to SR 91:90 [23] using Laboratory oven 631 Nahita.

Determination of ash

The determination of the ash of the bread was determined according to SR 91:90 [23] using Laboratory oven L1003 CALORIS.

Microbiological analysis

The bread was also analyzed from a microbiological point of view, by determining the number of yeasts and molds according to the standard SR ISO 21527/ 1-2009 [23].

Nutritional analysis

The nutritional analysis, i.e. fat, protein, carbohydrate content and energy value was calculated for each sample. The energy analysis was calculated mathematically.

RESULTS AND DISCUSSION

Physico-chemical characterization of eggshells

Figure 2 shows the most significant peak of intensity of eggshell particle at 1427 cm^{-1} strongly associated with the presence of carbonate minerals within the eggshell matrix. There are also two observable peaks at about 713 cm^{-1} and 873 cm^{-1} which should be associated with the presence of calcium carbonate. Peak changes are observed between the sample with inorganic calcium in the form of carbonate and that with organic calcium in the form of citrate.

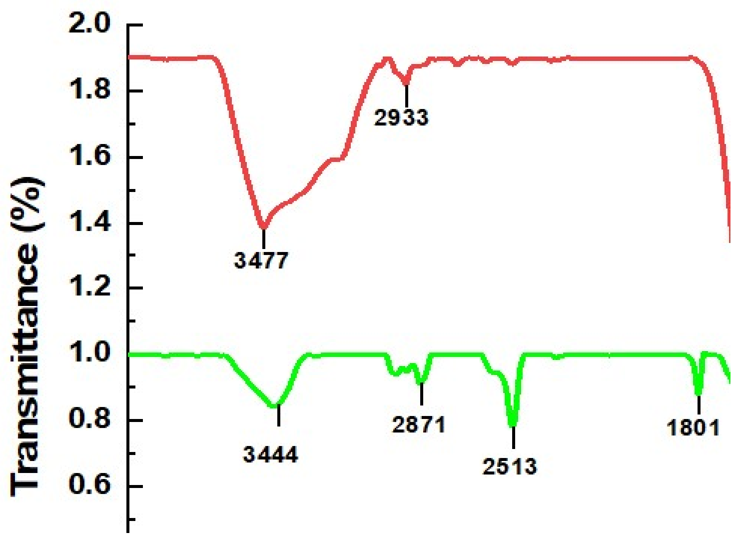
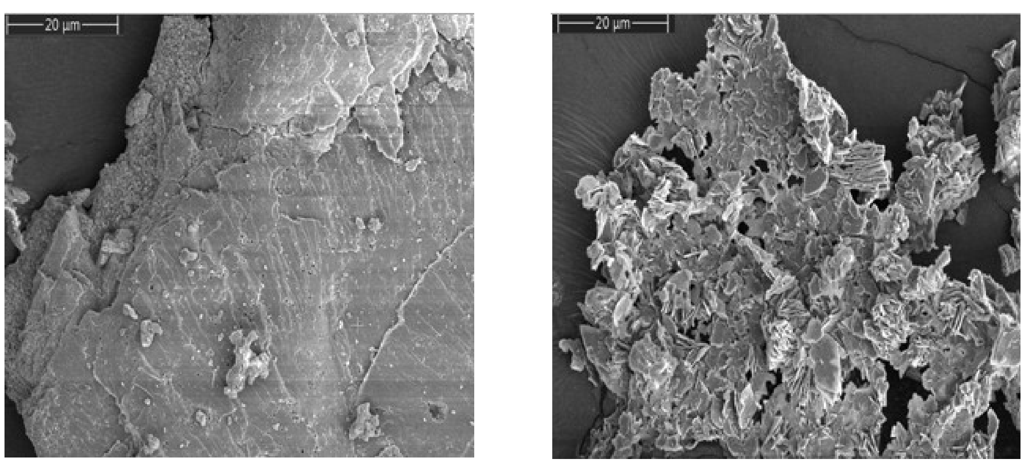


Figure 2. *FTIR spectra of eggshells samples*

The textural structure examination of eggshell can be observed from the SEM images in Figure 3.



a) *b)*

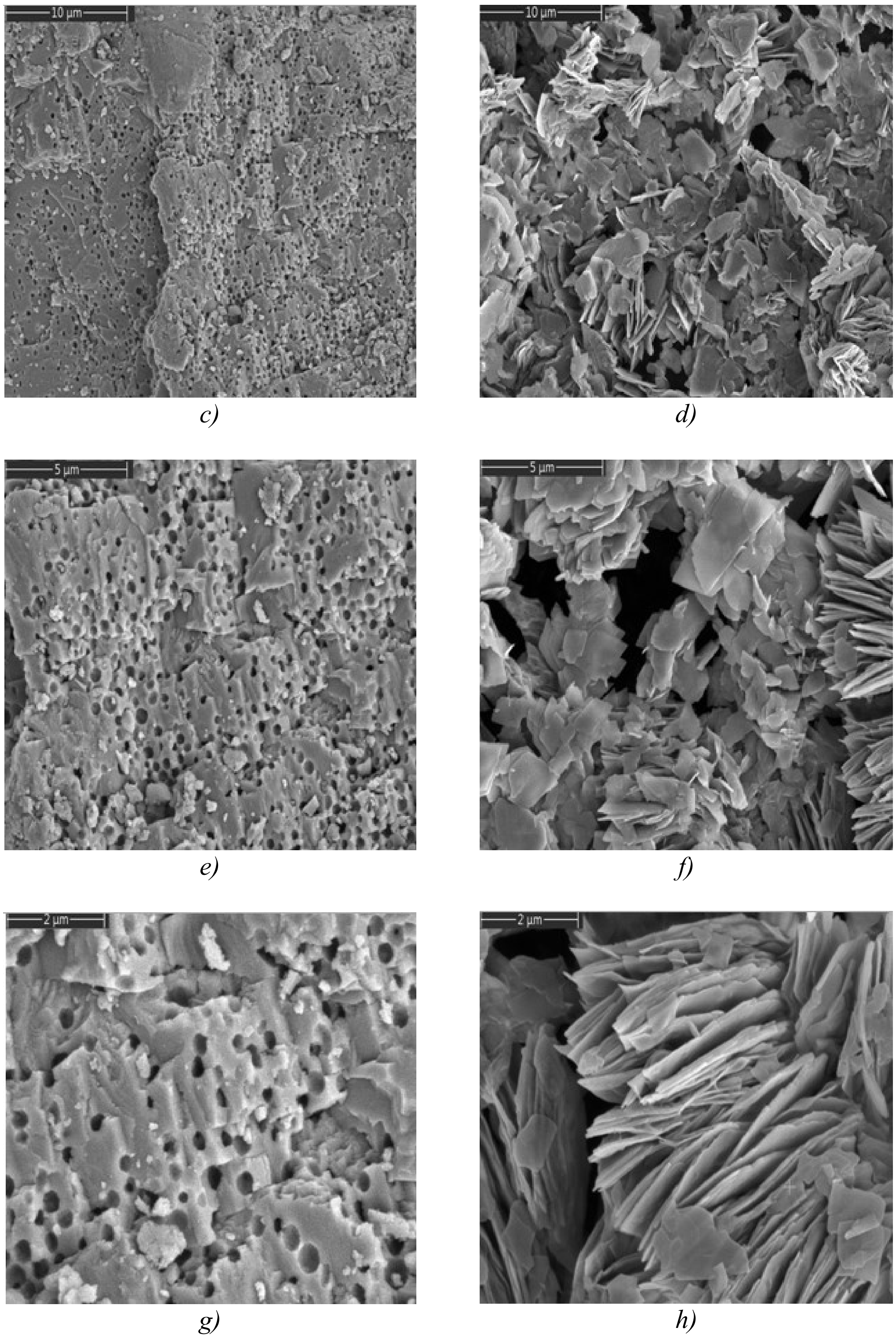


Figure 3. *SEM images: Samples of calcium eggshells in carbonate form (ES) at different scales (a, c, e, g); Samples of eggshells with calcium in citrate form (ESM) at different scales (b, d, f, h)*

From Figure 3, it can be clearly seen that the sample (hen eggshells) does not indicate well-defined pore structures but multilayered structures.
In Table 3 and Figure 4 are presented the results obtained by EDAX-SEM analysis in 5 distinct points, for the raw material, respectively for the chemically modified ES.
Elemental analysis by EDAX was performed for eggshells and eggshells modified with citric acid. The analysis showed that ES consisting of C, N, O, Mg, Ca and after the modification process, the amount of carbon increased, which confirms that the reaction to obtain calcium citrate took place (calcium has been transformed from an inorganic substance into an organic one).

Table 3. *Results for EDAX analysis for ES and ESM*

ES			ESM	
Element	**Weight [%]**	**Atomic [%]**	**Weight [%]**	**Atomic [%]**
C	10.38 ± 2.47	18.28 ± 3.06	21.62 ± 5.40	34.82 ± 5.15
N	1.46 ± 0.16	2.2 ± 0.12	0.82 ± 0.21	1.16 ± 0.27
O	41.8 ± 5.23	55.72 ± 2.91	35.68 ± 6.65	43.38 ± 3.55
Mg	0.54 ± 0.15	0.48 ± 0.10	0.28 ± 0.10	0.22 ± 0.08
Ca	**42.24 ± 7.50**	**22.9 ± 5.85**	**39.74 ± 12.50**	**20.18 ± 8.55**

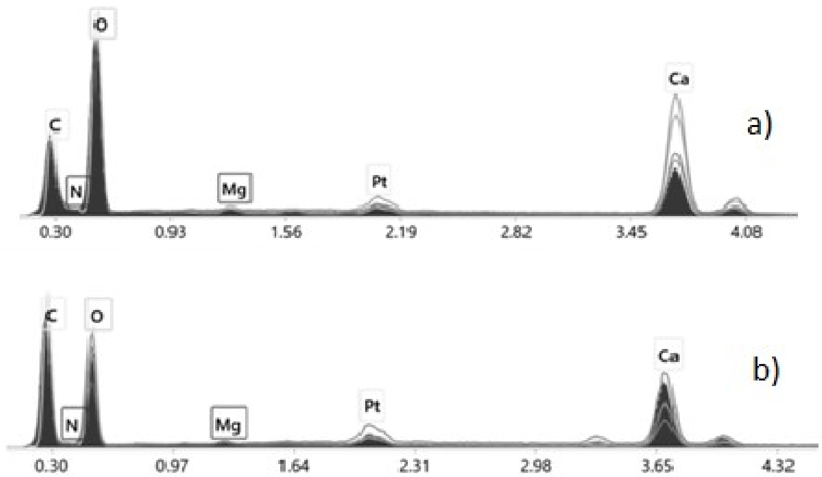


Figure 4. *EDAX analysis for the 5 distinct points*
a) Sample of calcium eggshells in carbonate form (ES); b) Sample of eggshells with calcium in citrate form (ESM)

Evaluation of bread quality with various additions of ESM

Figure 5 shows sectional images of the breads enriched with calcium from eggshells.

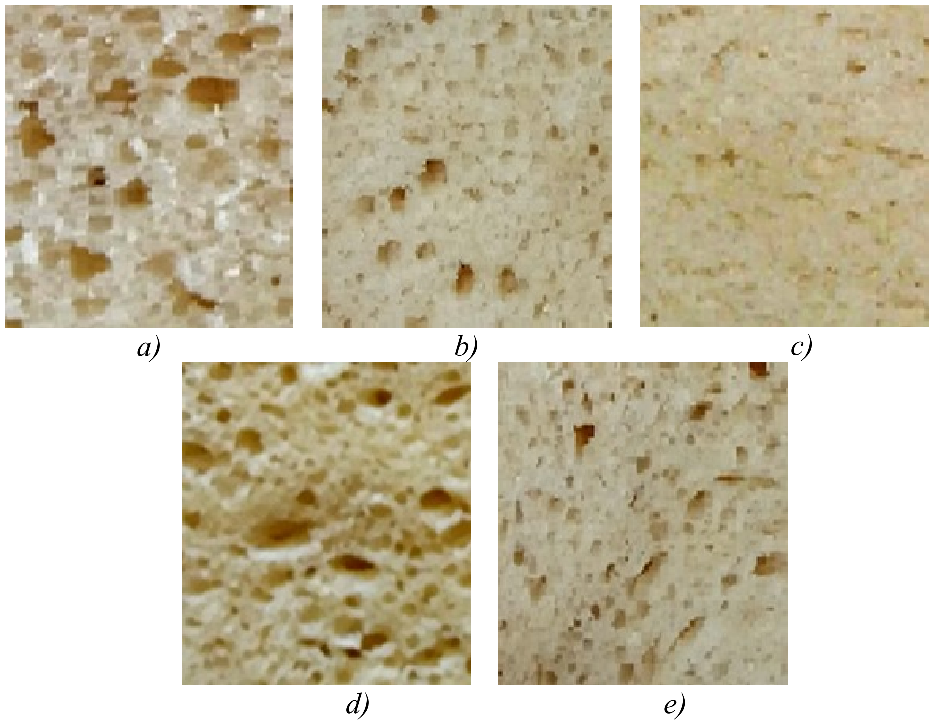


Figure 5. *Section images of bread with various ESM additions*
a) Bread control (B-ESM0); b) Bread with 2.5 % ESM (B-ESM2.5); c) Bread with 5 % ESM (B-ESM5); d) Bread with 7.5 % ESM (B-ESM7.5); e) Bread with 10 % ESM (B-ESM10)

From the images shown in Figure 5, it can be observed a color dependency on the dose of added acidified ES. The samples B-ESM2.5 and B-ESM10 according to the sensory analysis are not remarkable in comparison with the samples B-ESM5 and B-ESM7.5. According to the results presented in Table 4, it is observed that the samples B-ESM5 and B-ESM7.5 have the best sensory characteristics, obtaining the maximum score. In terms of consistency, the increase in the addition of ESM has led to an improvement in the quality of the core, which is not crumbly. The differences between the evaluations made by the tasters were not greater than 0.5 points.

Table 4. *Sensorial analysis properties of bread fortified with ESM*

Sensorial characteristics	***Samples***				
	B-ESM0	**B-ESM2.5**	**B-ESM5**	**B-ESM7.5**	**B-ESM10**
Shape, external appearance, volume	3	3	3	3	3
Appearance of bread crust	2.5	2.5	3	3	3
Appearance of bread crumb	3.5	4	4	4	4
Consistency and behavior in mastication	2	3	3	3	3
Bread smell	2.5	3	3	3	2.5
Bread taste	2.5	3	4	4	3
Total	**16**	**18.5**	**20**	**20**	**18.5**

The microstructure analysis shows that the bread core consists of pores with walls formed during the baking process from a compact mass of coagulated gluten. Inside the pores, starch granules are stretched on the walls, partially swollen and gelatinized. In fresh bread, the gelatinized starch granules are in contact with the mass of coagulated proteins, on their entire surface, the delimitation between them being not visible. In aged bread, the partially gelatinized starch granules are visibly separated from each other, due to the fact that a thin layer of air is formed around their surfaces, when the volume of the starch granules is reduced and the proteins on the pore walls do not change [22].
Eggshells macerated prevented the crushing of the core probably due to the adsorption of air by the ES, and this adsorption capacity is remarkable.
The influence of the addition of ESM on the physico-chemical properties of the bread is presented in Table 5.

Table 5. *Results of physico-chemical properties of bread with ESM*

Physico-chemical characteristics	Samples				
	B-ESM0	B-ESM2.5	B-ESM5	B-ESM7.5	B-ESM10
Mass [g]	921.0	936.0	964.0	984.0	995.0
Elasticity [%]	96.1	97.0	97.0	97.3	97.7
Porosity [% vol.]	66.6	68.4	68.6	82.8	68.8
Acidity [°A]	0.6	0.6	0.5	0.4	0.3
Ash [%]	1.8	1.9	2.4	2.7	2.8
Moisture [%]	45.9	41.4	39.8	39.6	40.8

From Table 5 it can be observed that ash percentage highlights an increase for samples that have 5.0 and 7.5 % addition of ESM. The increase of the addition of ESM led to a decrease in the acidity of the samples, according to the results presented in Table 5. Regarding the weight of final products, there is a slight increase, as a result of the increase in the addition of ESM (Table 4).
The microbiological analysis (Table 6) shows promising results for the bakery industry because a real problem is the molding of the products. ESM plays also a role of antiseptic in the preparation of bread, this being highlighted by the lack of yeasts and molds in the bread samples obtained.

Table 6. *Microbiological parameters*

Parameter	Samples					Limits according to Ord. ANSVSA 27/2011 [24]
	B-ESM0	B-ESM2.5	B-ESM5	B-ESM7.5	B-ESM10	
Yeast and molds [$CFU \cdot g^{-1}$]	2000	< 10	< 10	< 10	< 10	10 – 100 $CFU \cdot g^{-1}$

For the prototypes of bread with ESM, the microbiological results obtained fall within the limits provided in ANSVSA Order 27/2011.
The presence of calcium in the ESM and the low acidity values (Table 5) of the bread samples with different ESM inhibited the development of yeasts and molds. Another

explanation for the favorable results of the microbiological analysis after the addition of ES is the role of calcium in the intensification of the phagocytic activity of leukocytes in the human body, which can be further investigated on the dough [22].
The nutritional composition and the energy value of all samples are summarized in Table 7.

Table 7. *Nutritional composition*

Parameters	**Analytical method**	**B-ESM0**	**B-ESM2.5**	**B-ESM5**	**B-ESM7.5**	**B-ESM10**
Fats [%]	SR 91-90	0.7	0.9	0.9	0.9	1.1
Proteins [%]	SR 91-90	6.4	7.4	7.1	7.0	7.6
Carbohydrates [%]	Mathematical calculation	45.2	50.8	49.8	49.9	49.2
Energy value [kcal/100g]	Mathematical calculation	213.0	240.5	235.5	235.4	237.0

The results are similar for products that contain ESM. It can be observed higher percentage of fats, proteins and carbohydrates in comparison with the reference product (B-ESM0).

CONCLUSIONS

The recovery of waste from the food industry contributes to the sustainable development of the environment.
In Romania, the bakery industry occupies an important place in the production of consumer goods. Bread is a staple food in the diet customary daily because it can provide important compounds that are necessary for vital activity. Bread being a food consumed by a large part of the population, this research proved the feasibility of the production of good quality breads by valorizing the eggshell as a natural harmless additive.
This research is an answer to many problems that currently exist in the bakery industry.
Other than the enrichment of bread in calcium easily assimilated in citrate form, the final products with 5 and 7.5 % ESM does not crumble, had a superior taste and aroma. These products had resolved the increasing the shelf life of bread by inhibiting the development of molds and yeasts, a real problem encountered in the bakery industry. By using ESM, bread enriched in predominant calcium was obtained.
We consider the final products as innovative products obtained instantly at laboratory level, but easy to raise on an industrial scale.

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