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Preliminary studies on polyvinyl alcohol-based films modified with extracts of apple peel, aronia and rutin, respectively

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Abstract

The aim of this study was to obtain biodegradable packaging materials based on polyvinyl alcohol modified with bioactive compounds with antioxidants and antimicrobial properties to obtain a potential packaging material that extends the shelf life of the food and ensures the quality and safety of food. To impart these properties to the polyvinyl alcohol film, natural extracts of apple peel, aronia and rutin, respectively were used. The analysis of the polyphenolic compounds of the extracts was carried out by high performance liquid chromatography, the Folin-Ciocalteu method was used to calculate total polyphenols released from prepared films and the antioxidant activity was determined with 2,2-diphenyl-1-picrylhydrazyl method. The antimicrobial activity of extracts was tested against *Staphylococcus aureus* bacteria isolated from goat's milk. The results obtained indicated that aronia extract had the highest content of polyphenols with 462.3 mg/L, predominantly neochlorogenic acid. Also, the release of total polyphenols was higher for polyvinyl alcohol-based film modified with aronia extract. Consequently, the highest antioxidant activity was obtained by the modified film with aronia extract. The rutin-modified polyvinyl alcohol film showed the best antimicrobial activity. Polyvinyl alcohol films modified with aronia and rutin could represent potential packaging materials for foods with high risk of oxidation, but it requires more in-depth studies.

Key words: polyvinyl alcohol; polyphenols; aronia; apple peel; rutin; antioxidant activity; antimicrobial activity.

1. Introduction

The current trend is to use biodegradable packaging with functional properties suitable for food intended and as environmentally friendly as possible to reduce global pollution. The development of packaging materials that use bioactive compounds is constantly growing, and to reduce costs and increase material performance an innovative approach is to mix natural materials with biodegradable synthetic ones [1]. Biopolymers are widely used in the packaging industry as they are excellent means for incorporating various bioactive compounds, such as essential oils, fruit and plant extracts, fatty acids, agricultural waste, etc., possessing antioxidant and antimicrobial properties to preserve the quality and safety of food and extend shelf life [2].

Polyvinyl alcohol (PVA) is a synthetic semicrystalline polymer that has attracted the attention of researchers due to its non-toxicity and biodegradability, high film-forming ability, high optical transparency and good mechanical strength and high gas barrier properties [3]. PVA is a water-soluble polymer with high resistance to oil and chemicals and high stability to various organic solvents [4]. To improve the antioxidant and antimicrobial properties of PVA-based films, adding bioactive natural compounds is a promising strategy to impart multifunctional features to films [5]. Various natural compounds derived

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from plants, such as polyphenols [6, 7], lignin [8], anthocyanins [9], cellulose [10], carvacrol [11] etc., they have demonstrated their ability to improve the antioxidant and antimicrobial properties of PVA films.

Polyphenols are a large class of natural antioxidants that can be extracted from various sources and give the packaging material functional properties. Among berries and other plant sources, aronia (Aronia melanocarpa) has the highest content of phenolic compounds and has demonstrated the highest antioxidant activity. The phenolic content of aronia may differ depending on the environmental conditions, habitat, timing of harvest, degree of maturation. The main polyphenols present in aronia are phenolic acids, of which neochlorogenic acid predominates, followed by chlorogenic acid. Anthocyanins are another class of polyphenols present in aronia, the amount of which may differ depending on the species (grown or wild) and seasonal differences. In the composition of the aronia there are also flavonols, which are derivatives of quercitin, and procyanidins which give the bitter, astringent taste [12, 13].

Due to the presence of phenolic hydroxyl groups in their structure, polyphenols can easily interact with polymers by modifying their physical and chemical properties and giving them antioxidant and antimicrobial properties. The use of phenolic compounds extracted from apple peel would reduce food waste and the efficient use of huge quantities of waste from the food industry, having a positive impact on environmental pollution. Previous studies have indicated that polyphenols extracted from peel or apple seeds contain bioactive compounds, which are the secondary metabolites of plants, and exhibit strong antioxidant activity, as well as anti-cancer and anti-inflammatory activity. The main classes of phenolic compounds found in apples are flavan-3-ols, phenolic acids, flavonols, and dihydrochalcones [14-16].

Rutin, also called quercetin-3-rutinoside, vitamin P or rutoside is a glycosylated flavonoid that is found in a myriad of herbs, such as tea leaves, apples, onions, buckwheat, passion fruit, etc. Rutin is a secondary plant metabolite that exhibits pharmacological properties, such as antioxidant activity, which are exploited in medicine and nutrition. Rutin is a water-insoluble phenolic compound, but it has solubility in organic solvents such as ethanol. The introduction of rutin in the composition of biopolymers has led to the improvement of antioxidants, antimicrobial and antifungal properties [2, 17].

The purpose of this preliminary study was to obtain a PVA-based material modified with bioactive compounds that would give the film antioxidant and antimicrobial properties, to use it as a potential packaging material for fatty foods at high risk of oxidation with the aim of extending shelf life and preserving food quality and safety. In this paper was determined the individual polyphenolic compounds of extracts by high performance liquid chromatography (HPLC) method, the release of phenolic compounds from modified materials was determinated spectrophotometrically (Folin-Ciocalteu method) and their antioxidant capacity by method of the free radical scavenging capacity of 1,1-diphenyl-2-picrylhydrazyl (DPPH). It has also been studied the ability of the extracts to inhibit the development of *S. aureus* bacteria isolated from goat's milk.

2. Material and methods

2.1. Materials

Poly (vinyl alcohol) Mowiol® 28–99, Mw = 145,000 g·mol−1 was purchased from Sigma-Aldrich® (Munich, Germany). Glycerol for analysis (99,5%) (Gly) was purchased from Fagron Hrvatska (D. Zelina, Croatia). Citric acid monohydrate (assay 98%) (CA) was provided from Kemika (Zagreb, Croatia). Orto-phosphoric acid (85% HPLC-grade) was from Fluka (Buchs, Switzerland). Methanol (HPLC grade) was from J.T. Baker (Gliwice, Poland). Ethanol 96 % was purchase from Gram-Mol (Zagreb, Croatia). Rutin hydrate (95 % HPLC) was purchased from Sigma-Aldrich Chemie (Steinheim, Germany). Aronia fruits was harvested in Slavonia region (Croatia) at the commercial maturity stage. Apples were harvested from orchards in Croatia.

2.2 Preparation of extracts from aronia and apple peel

Apples were peeled, the peel was homogenized with a coffee grinder and stored in plastic bags in a refrigerator at -18 °C. The aronia beans were homogenized in a coffee grinder and kept in the same conditions. For the preparation of aqueous extracts from apple peel and aronia, 5 g of apple peel and aronia, respectively, such

preparations were dissolved in 100 mL of distilled water and the extraction was performed on an ultrasonic bath (Bandelin Sonorex RK 100, Berlin, Germany) for 30 minutes, and then they were left homogenized on an orbital shaker IKA® KS 130 Basic for 24 hours. The solutions thus obtained were initially filtered with filter paper, then were centrifuged for 5 minutes at 10,000 rpm using Eppendorf MiniSpin microcentrifuge (Hamburg, Germany) to remove impurities. Extracts were filtered through a 0.22 µm PTFE filters before injection into the HPLC system.

2.3. Films preparation

For obtaining all the films, the solution casting method was used. First, the PVA based film was prepared in the following mode and it was used as a reference film. The PVA granules (5 wt. %) were introduced into the Berzelius beaker with CA granules (0.57 wt. %) over which 100 ml distilled water was added. The solution was homogeneous for 2 hours into the water bath grant LSB Aqua Pro (Zagreb, Croatia) at 90 °C until the granules were completely dissolved, and a homogeneous mixture was formed. Then, Gly (1.5 wt. %) was added to the mixture and was allowed for homogenization for another 5 minutes. The solution thus obtained was introduced in glass Petri dish with a diameter of 90 mm and the dish allowed to dry for two days at room temperature. The film was labeled PVA.

PVA-based film modified with apple peel extract was obtained using the above-described procedure, only that the distilled water was replaced with the apple peel extract. The film was labeled PVA + Ap.

The PVA film modified with aronia extract was obtained in the same way, by replacing distilled water with aronia extract. The film was labeled PVA + A.

The PVA film modified with rutin was obtained by adding to the PVA film the rutin (0.06 wt. %) diluted in 5 ml ethanol. The film was labeled PVA + R. Three samples were prepared for each film.

2.4. *Film Thickness*

The thickness of the films was determined by manually measuring the film at 5 random points with a micrometer Mini digital thickness gauge (Sisak, Croatia), with the thickness being the arithmetic mean of the values.

2.5. Characterization of the films obtained and their extracts

2.5.1. Analysis of extracts by Reversed-Phase High-Performance Liquid Chromatography with Photo-Diode Array Detection (HPLC-PDA)

For the identification of individual polyphenols in apple peel extracts and aronia, 1 ml of each extract, filtered with PTFE membranes of 0.22 µm before injection, was taken. The samples were analyzed with an HPLC 1260 Infinity II system (Agilent technology, Santa Clara, CA, USA) with a quaternary pump, a PDA detector and a vial sampler. Phenolic compounds were separated using a Poroshell column 120 EC C – 18, 4.6 × 100 mm, 2.7 µm and a Poroshell protection column 120 EC C - 18 of 4.6 mm. The mobile phases were 0.1 % H_3PO_4 (mobile phase A) and 100 % HPLC grade methanol (mobile phase B). The flow was adjusted to 0.8 ml min^{-1} and the injection volume was 10 µL according to the developed and calibrated methods of Jakobek *et al*., [18]. The experiment was conducted three times for each test.

2.5.2. The determination of total polyphenols from films

For the determination of total polyphenols from the extracts and films obtained, the Folin-Ciocalteu method was used. In a 50 % ethanol solution, previously held for 30 minutes in the ultrasonic bath Bandelin Sonorex RK 100, were introduced 0.5 g of the obtained films cut into small pieces. A 30 µL aliquot from each sample was taken at time intervals of 5, 15, 30, 60, and 120 minutes and mixed with 2370 µL distilled water, 150 µL of Folin-Ciocalteu regent and 450 µL of Sodium Carbonate (200 g · L-1). The samples were incubated at 40 °C for 30 minutes, after that, the absorbance of the blank was measured at 765 nm with a UV-VIS Spectrophotometer Shimadzu UV-1280 (Zagreb, Croatia). Gallic acid solutions (0 to 500 mg L^{-1}) were measured with the same procedure. Calculation of total polyphenols was made according to the calibrating curve of gallic acid (absorbency vs concentration) created and were expressed as mg of gallic acid equivalents (GAE) per liter. Three samples were prepared for each time.

2.5.3. Antioxidant activity of films

The DPPH method was used to determine the antioxidant activity of films. For each film, 0.25 g film were dissolved in 4 ml of 50% ethanol and mixed for two hours at 320 rpm

with an orbital shaker IKA® KS 130 Basic and the extraction was performed on an ultrasonic bath (Bandelin Sonorex RK 100, Berlin, Germany) for 15 minutes. Five dilutions from each sample were analyzed. The reaction solution was prepared by mixing these dilutions with 300 µL DPPH methanolic solution (1 mM) and brought to 3 mL with methanol. The solutions thus obtained were kept in the dark for 15 minutes. The absorbance of sample (ASample) was read at 517 nm against prepared blank (sample dilution brought to 3000 mL with methanol). The DPPH control solution was prepared with 300 µL of 1mM DPPH solution and 2.7 mL methanol. Percent inhibition of DPPH radical was calculated for each dilution of sample according to formula:

$$\%\ inhibition = \frac{A_{DPPH} - A_{Sample}}{A_{DPPH}} \cdot 100$$

where: A_{DPPH} - blank absorbance.
A_{Sample} – sample absorbance.

2.6. Antimicrobial activity of extracts

The microbiological analysis of the extracts obtained was tested against Gram-positive bacteria, Staphylococcus aureus, isolated from goat milk in our microbiology department, on a Baird-Parker Agar Base (BPAB) culture medium. From the milk were made decimal dilutions in sterile saline 1:9 (mL), from the dilutions were made sowing on the culture medium and were identified typical colonies of black color, typical. The isolated stem was emulsified in physiological saline and sowing was carried out in cloth on the surface of the culture medium on which the extracts were applied. The culture medium was obtained by adding 3.15 g of BPAB to a 50 mL balloon of distilled water, which was inserted into autoclaves, together with three test tubes containing 4.5 mL of distilled water for 15 minutes. After autoclaving, the solution was cooled to 50°C, and in it was introduced 2.5 g/mL of egg emulsion Egg Yolk - Tellurite Emulsion. The resulting solution was inserted into sterilized 90 mm Petri dishes.

2.7. Statistical Analysis

All experiments were conducted in triplicates and the mean and standard deviation were determined, which did not exceed 5%. The degree of statistical significance was determined in Microsoft Excel, using One-Way Anova processing, the Tukey model.

3. Results and Discussion

3.1. Characterization of films obtained

The PVA-based film was modified with natural extracts of aronia, apple peel and rutin respectively to obtain a potential packaging material with antioxidants and antimicrobial properties that extend the shelf life of food and preserve the quality and food safety. In Table 1, macroscopic images of the films obtained can be seen.

PVA	PVA + R	PVA+ Ap	PVA + A
			

Table 1. The macroscopic images of PVA-based films. Where R – rutin, Ap – apple peel and A – aronia

First, the PVA film was prepared. It was used as a reference film and was compared to the other modified films. It had a homogeneous, transparent appearance and had a thickness of 0.11 ± 0.0055 mm.

The PVA film modified with rutin was translucent, homogeneous appearance with a very slight tinge of yellow and had the thickness of 0.10 ± 0.010 mm.

The PVA-based film modified with apple peel extract was homogeneous, transparent, with a slight tinge of yellow to pink and had the

thickness of 0.13 ± 0.0152 mm.
The PVA film modified with aronia extract was homogeneous, less transparent than other films, with a thickness of 0.11 ± 0.0148 mm.
Similar results were obtained by Gaikwad et al., [19] who prepared PVA-based films with the addition of apple pomace (AP) in various mass proportions and showed that the presence of AP in the film's matrix altered the film's coloration probably due to the presence of phenolic compounds in the composition of AP. Similary, Riaz et al., [20] obtained chitosan-based films with the addition of apple peel polyphenols (APP) in various mass proportions and indicated the change in the color of the films with the introduction of APP in the matrix of chitosan, the film acquiring a reddish color. The authors concluded that darker films improve the barrier against UV-Vis light by protecting food from nutrient loss and the formation of unpleasant odors.
Narasagoudr et al. [2] indicated the change in the color of the PVA and chitosan film with the introduction of the rutin into the film matrix, which has become darker with increasing rutin concentration. The authors indicated a high protection against UV-Vis light due to the aromatic group - OH present in the composition of the rutin that improved matrix absorption in the range of 200-400 nm.

3.2. Analysis of extracts by HPLC

Identification of phenolic compounds from the extracts obtained was carried out by HPLC analysis. Apple peel extract was 20.7 % dry matter and 79.3 % water, and aronia extract was 29.07 % dry matter and 70.93 % water. The phenols content of apple and aronia extracts can be observed in Table 2 and Table 3, respectively.

Table 2. The content of phenolic compounds of apple peel extract

Classes of polyphenols	Type of polyphenols	Percent of polyphenols (%)
Flavan-3-ols	Procyanidin B1	13.86 %
	(+)-Catechin	12.18 %
	Procyanidin B2	15.23 %
Dihydrochalcones	Phloretin-2-glucoside	4.78 %
Phenolic acids	Chlorogenic acid	7.23 %
Flavonols	Quercetin-3-galactoside	12.39 %
	Quercetin-3-rutinoside	3.46 %
	Quercetin-3-glucoside	7.89 %
	Quercetin-3-xiloside	13.18 %
	Quercetin-3-ramnoside	9.8 %

Table 3. The content of phenolic compounds of aronia extract

Classes of polyphenols	Type of polyphenols	Percent of polyphenols (%)
Phenolic acids	Neochlorogenic acid	46.68 %
	Chlorogenic Acid	30.87 %
Flavonols	Quercetin derivative	1.18 %
	Quercetin-3-galactoside	1.34 %
	Quercetin-3-glucoside	3.98 %
Anthocyanins	Cyanidin-3-galactoside	7.42 %
	Cyanidin-3-glucoside	1.24 %
	Cyanidin-3-arabinoside	6.1 %
	Cianydin-3-xiloside	1.19 %

The predominant class of phenolic compounds in the apple peel extract analyzed was the flavonols class with 46.72 % of the total polyphenols present into the extract. The type of polyphenol present in higher quantity was quercetin-3-xyloside with 13.18 %, followed

by quercetin-3-galactoside with 12.39 %. In this class were also present quercetin-3-ramnoside with 9.8 %, quercetin-3-glucoside with 7.89 % and in the small amount quercetin-3-rutinoside with 3.46 %. The flavonols class was followed by the flavan-3-ols class with a fairly close percentage, namely 41.27 % of the total phenolic compounds. Procyanidin B2 was present in the highest quantity with 15.23 %, followed by procyanidin B1 with 13.86 %, the difference between them was small and (+)-catechin with 12.18 %. The class of phenolic acids was presented by chlorogenic acid with 7.23 %, and the class of dihydrochalcones by phloretin-2-glucosides with 4.78 %, what is the polyphenol specific to apples. Similar results have been reported in literature, which may vary depending on the type of apple, method of extraction and geographical area [21, 22].

The predominant class of phenolic compounds identified in aronia extract was the class of phenolic acids which accounted for 77.55 % of the total phenolic compounds. In this class of poliphenols predominated neochlorogenic acid with 46.68 %, followed by chlorogenic acid with 30.87 %. The second class of phenolic compounds present in this extract was anthocyanins at a percentage of 15.95 %. Of these, cyanidin-3-galactoside was identified in a higher percentage, namely 7.42 %, followed by cyanidin-3-arabinoside with 6.1 % and lower percentages, cyanidin-3-glucoside with 1.24 % and cianydin-3-xyloside with 1.19 %. The third class of phenolic compounds identified in the composition of aronia extract was that of flavonols with a percentage of 6.5 %, in which quercetin-3-glucosides predominated by 3.98 %, followed by quercetin-3-galactosides by 1.34 % and quercetin derivative by the lowest percentage, namely 1.18 %. The percentage of phenolic compounds present in aronia was four times higher than that present in the apple peel. Similar results were obtained by Jakobek et al., [23] which studied four types of berries, namely red raspberries, blackberries, strawberries and aronia and they concluded that aronia contained the highest concentration of phenolic compounds. The authors identified the same types of anthocyanins in the studied aronia beans, and as flavonols they found quercetin as the main component of aronia and in a low percentage was found kaempferol, which in our study was not identified. Also, Long *et al.,* [24] identified phenolic acids as the predominant class present in the composition of aronia.

3.3. The determination of total polyphenols from films

The release of total polyphenols from obtained films was performed by Folin-Ciocalteu method. The highest value of the total polyphenol content was recorded by the PVA-based film modified with aronia extract, with an average of 717.06 mg GAE/L, among the values obtained by this film at all times measured there were no statistically significant differences. The total polyphenol content of the rutin-modified film averaged 372 mg GAE/L, with no statistically significant differences between the values obtained at all times measured. The lowest values of the total polyphenol content were obtained by the PVA-based film modified with apple peel extract, and did not record significant statistical differences between the measured times. Among the values obtained by the three modified films there were significant statistical differences.

The results obtained were in line with those indicated by the HPLC analysis showing that aronia extract recorded a higher percentage of polyphenols. These data are also confirmed by Sagandyk *et al*., [25] who studied black chokeberry (*Aronia melanocarpa*) and saskatoon berry (*Amelanchier ovalis*) grown in the Republic of Kazakhstan and the authors concluded that aronia had a higher total polyphenol content than saskatoon berry.

3.4. Antioxidant activity of films

The antioxidant capacity of a packaging material is an important feature because it can delay or prevent fat oxidation, thus preserving food quality and safety and extending the shelf life of food. Antioxidant activity is closely related to the content of phenolic compounds present in the film [6]. The antioxidant activity of the modified film was determined using DPPH radical scavenging method and the percentage of inhibition of DPPH radicals can be observed in Figure 1.

The PVA-based film did not show antioxidant activity. The highest percentage of inhibition of DPPH radicals was obtained by the modified film with aronia extract, namely 83.86 %, followed by the rutin-modified film with an inhibition rate of 34.34 %, and the lowest percentage was obtained by the modified apple peel extract film with 23.40 %.

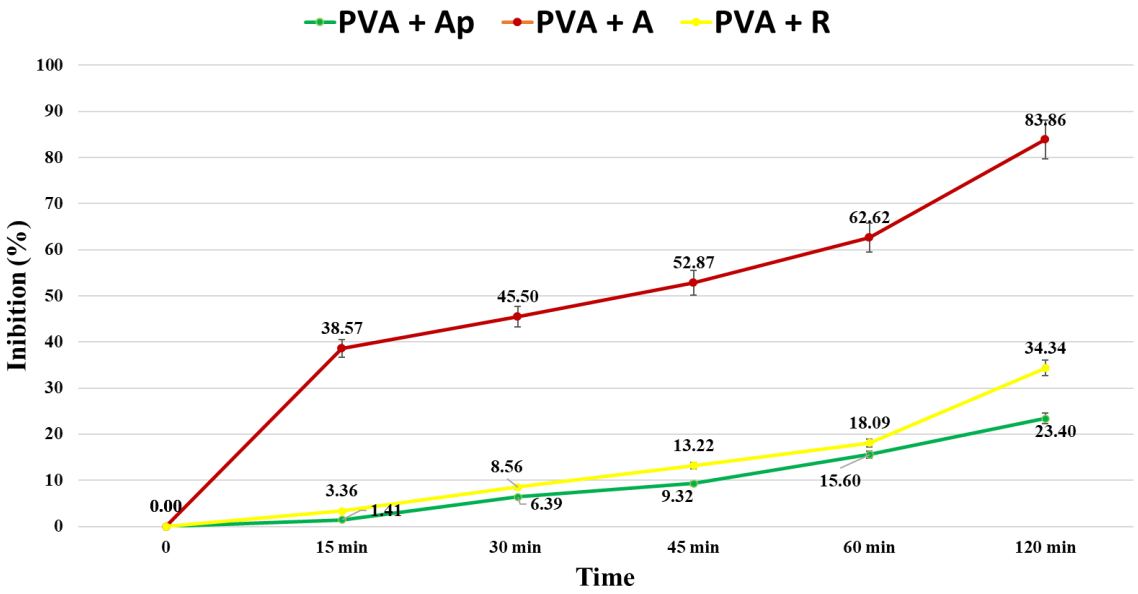

Figure 1. Antioxidant activity of the modified films using DPPH radical scavenging tests. Where: Ap – apple peel, A – aronia and R – rutin.

These results agree with those obtained from extracts analysis using HPLC and with the release of total polyphenols from obtained films. Similar results were obtained by Oun et al., [6] who prepared PVA-based and chitosan films modified with aronia, cellulose nanocrystals and grapefruit seeds extract, and the authors showed that the modified film recorded the highest antioxidant activity by the DPPH and ABTS methods with a 91 % and 95 % respectively inhibition rate. The authors also note that the film modified with aronia showed the highest percentage of inhibition against DPPH and ABTS radicals, namely 58 % and 69 %, respectively, probably due to the presence of anthocyanins, procyanidins and flavonols in the composition of aronia.

3.4. Antimicrobial activity of extracts

Antimicrobial activity of prepared extracts was tested against *S. aureus* gram-positive bacteria isolated from goat milk, and the assessment of antibacterial activity was done by measuring inhibition areas. Antimicrobial activity of the extracts obtained can be seen in Figure 2.

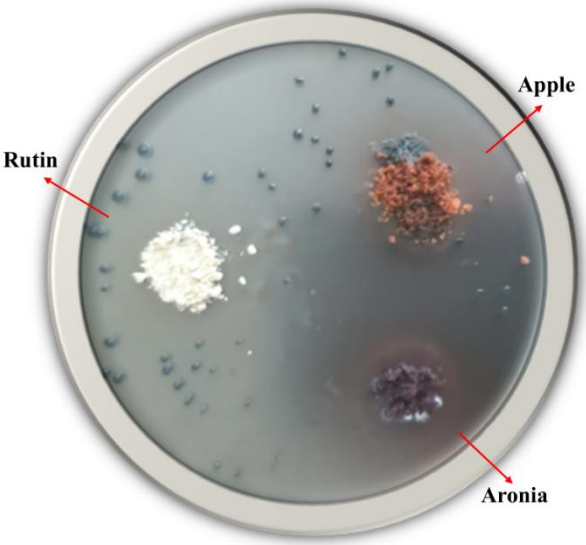

Figure 2. Antimicrobial activity of the apple peel and aronia extracts and rutin, respectively

All extracts have shown antibacterial activity against *S. aureus* bacteria. In the inhibition zone of aronia extract and apple peel extract, molds have developed. Aronia extract inhibited the development of *S. aureus* bacteria, achieving the highest inhibition zone, namely, between 15 and 22 mm. The rutin showed an inhibition area between 7 and 12 mm, and the apple peel extract showed similar results, with an inhibition area between 6 and 12 mm.

Similar results were obtained by Long si colab., [5] who prepared films based on PVA and chitosan with the addition of aronia extract and demonstrated the ability to inhibit films obtained against three food-borne pathogens, *S. aureus*, *E. coli* and *P. aeruginosa*. The authors attribute this antimicrobial activity to anthocyanins and phenolic acids present in the composition of aronia capable of destroying the cell membrane and inhibiting the extracellular secretion of enzymes.

Sun *et al*., [26] prepared chitosan-based films with the addition of apple polyphenols and tested antimicrobial activity against three bacteria *(Escherichia coli*, *Listeria monocytogenes* and *Staphylococcus aureus*), three moulds (*Colletotrichum fructicola*, *Botryosphaerial dothidea* and *Alternaria tenuissima*) and three yeasts (*Saccharomyces cerevisia*, baker's yeast and *Tropical candida*). The films obtained proved their activity against bacteria and molds, but not against yeasts, the authors attributing this to the presence of amino groups in chitosan and the presence of phenolic compounds that cause physiological changes in the cell membrane leading to cell death.

Narasagoudr *et al.*, [2] prepared PVA-based and chitosan films and tested the films obtained against two pathogenic bacteria, *S. aureus* and *E. Coli*. The modified films inhibited the development of the tested bacteria but had higher activity against *E. Coli*. Authors attributed this to the diverse structure of the cell membrane.

4. Conclusion

The purpose of this study was to prepare modified PVA-based films with extracts from apple peel, aronia and rutin, respectively, with the intention of obtaining a potential packaging material with antioxidant and antimicrobial properties, in order to exploit its potential for preserving food quality and safety, as well as extending its shelf life. The composition of the extracts by HPLC, the total content of polyphenols in the modified films, the antioxidant activity of the obtained films, as well as the antimicrobial activity of the active polyphenolic compounds used were studied.

Aronia extract has the highest concentration of phenolic compounds. Consequently, the PVA-based film modified with aronia extract had the highest total polyphenol content. The modified film with aronia extract also showed the highest antioxidant activity. All modified bioactive compound films inhibited the growth of *S. aureus*.

The modification of the PVA-based film with phenolic compounds gave it antioxidant properties, probably due to the presence in the phenolic composition of highly reactive hydroxyl groups, which showed high capacity of inhibition of DPPH radicals.

PVA-based films modified with phenolic compounds could represent potential packaging materials for high-oxidation foods, but require several studies.

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