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THE IMPACT OF A PICKERING EMULSION SYSTEM STABILIZED BY ZINC OXIDE AND STARCH ON THE PHYSIOCHEMICAL AND FUNCTIONAL GROUPS PROPERTIES OF YOGHURT

Marouane Chemek[1], Ammar Kadi[2], Ahmed Adnan AL-Khafagi[3], Mourad Chemek[4,5], Artem Malinin[2], Irina Potoroko[2]

[1] *Departement of Biomedical Sciences, University of Cagliari Cittadella Universitaria di Monserrato, Monserrato, Cagliari 09042, Italy marouane.chemek@unica.it and chemekm@ yahoo.com (M.C.)*

[2] *Department of Food and Biotechnology, South Ural State University Chelyabinsk 454080, Russia, chemekm@yahoo.com (M.C.); ammarka89@gmail.com (A.K.) artemmalinin3@gmail.com (A.M.); irina_potoroko@mail.ru (I.P.)*

[3] *Anesthesia Techniques Department, College of Health and Medical Techniques Al-Mustaqbal University, 51001, Babylon Iraq, ahmed.adnan.abdalameer@uomus.edu.iq (A.A.A.)*

[4] *Laboratoire de recherche:Synthèse asymétrique et ingénierie moléculaire de matériaux organiques pour l'électronique organique (LR18ES19) Faculté des Sciences de Monastir, 5000 Monastir Tunisie, chmek_mourad@yahoo.fr (M.Cd.)*

[5] *Institut Supérieur des Sciences Appliquées et de Technologie de Sousse (ISSAT-Sousse) Université de Sousse-Tunisie, Tunisia, chmek_mourad@yahoo.fr (M.Cd.)*

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ABSTRACT

The dataset extensively examines the effect of Pickering emulsion (stabilized by starch/zinc oxide) incorporation on the physicochemical and functional groups properties of set-type yogurt. The Pickering emulsion was formed with helping of ultrasonic treatment. The application of Pickering emulsions to the yoghurt structure did not significantly change the values of important textural features on the 1st, seventh and fourteenth days of storage, and the results of viscosity, pH, acidity, and antioxidant all made sense and were consistent with earlier research. Similarly, an identic FT-IR pattern with a slight change due to the ultrasonic treatment during the addition of the Pickering emulsion was noticed in the fortified yoghurt when comparing to control samples. This study therefore suggests the development of functional yoghurt using the Pickering emulsion system as a bioactive compounds delivery system.

Keywords: Pickering emulsion, yoghurt, zinc oxide, starch, fortification.

INTRODUCTION

Functional foods enhanced with bioactive compounds (BAC) have gained appeal in global markets due to their multiple health advantages and improved popularity among consumers [1]. It has been shown that BAC, such as polyphenols, polyunsaturated fatty acids, and carotenoids, reduce the risk of heart disease, cancer, and other diseases [2]. However, most of BAC are unstable during processing, storage, and digestion, and have limited bioavailability [3]. Encapsulation methods can be an effective means of addressing these issues in the development of BAC-fortified foods and beverages, since they enhance the beneficial compounds' stability, bioavailability, and activity [4, 5]. Among encapsulation and delivery system created by scientist figure the Pickering emulsion (PE) approach. The effective delivery of bioactive chemicals using PE has garnered significant interest in the past couple of years [6]. PE systems unlike conventional emulsions, are stabilized by small solid particles without the need of surfactants. The surfactant-free nature of PE makes them attractive in food systems as they address the need for safe and environmentally-friendly encapsulation [6, 7]. Research has indicated that a wide range of naturally occurring solid particles, classified as food-grade substances (such as flavonoids, protein-based particles, and polysaccharide particles like starch and chitosan), can be utilized to stabilize PE [8]. However, the stability of PE prepared with these materials is not very high [6]. Therefore, the search for other compounds is necessary to increase the stability of PE in food system. Zinc oxide (ZnO), the well-known food supplement and generally recognized as safe (GRAS) element, may be a potential, but little-studied emulsifier for a variety of uses [1, 9]. A few studies published in the last year suggested that ZnO may be used as a reliable stabilizer in a range of PE systems [10, 11] . However, studies about the incorporation of PE based on ZnO in food system is lacking.

The aim of this data is to prepare a high stable PE based in food grade materials (starch) and GRASS element (ZnO), to study some of its characteristics, and to investigate their effect on the physicochemical and functional groups proprieties of a food product after its addition with the help of non-thermal technology (Ultrasonication). The chosen food system in our study is a yoghurt, which is one of the secondary dairy products that is most extensively accepted by customers and is thought to be one of the most useful and highly nutritious food items.

EXPERIMENTAL

Preparation and characterization of Pickering emulsion

Starch/ZnO-based solution was first prepared by mixing an amount of 5.0 g of resistant potato starch and 0.02, 0.03 and 0.05 g of ZnO powder respectively, with 85 mL of distilled water in a beaker per 100 cm^3. Then 40 mL of the mixed solution was taken into a 100 cm^3 beaker and 5 mL of sunflower oil was added progressively during ultrasound process. Ultrasound procedure was carried out using an ultrasonic homogenizer, Sonicator Q700, Qsonica (tech. choir. device power: 700 W, frequency 20 kHz, and amplitude from 1 - 100 %). The amplitude during processing was 100 % for a duration of 4 min (three times) with interruptions (three times) at a temperature from 32°C to 60°C.

The long-term stability of emulsions was examined by detecting the relative volumes of the three phases (oil, water, emulsion) as a function of time. The shear viscosity of emulsions was measured as a function of the shear rate with a cone-and-plate geometry in a stress rheometer (SR-200, Rheometrics) at 25°C, and the results were fitted with a modified power law model.

The Pickering emulsion (1 mL) was mixed with DPPH ethanol solution (0.12 mM) and incubated in the dark for 30 min at 25°C. The absorbance of the sample was then measured at 517 nm. The DPPH radical scavenging activities (%) were calculated using Eq. (1):

$$DPPH(\%) = \left(1 - \frac{A_s - A_c}{A_b}\right) \times 100\% \qquad (1)$$

where As, Ab, and Ac are the absorbance of the Pickering emulsion, blank, and control, respectively.

Yogurt manufacture and fortification

1 % PE based on starch/ ZnO with different ZnO concentration (0.02/ 0.03/ 0.05) in an amount of 1 mL were added to 200 mL of milk (fat content of 2.5 %). An ultrasound treatment for 30 seconds was performed during the addition of PE to the milk volume. Then, milks samples were subjected to a fermentation step to obtain yogurt using the LYOBAC-D starter culture YOYO 35. Fermentation was carried out at a temperature of 37°C for 20 h.

After fermentation, the following parameters: active and titrated acidity, viscosity, and antioxidant activity in the different obtained yogurt samples were determined on the 1st, seventh and fourteenth days of storage as described below.

Description of the studied yoghurt groups

4 different yogurt groups (n = 3 for each group), with fat concentration of 2.5 % and manufactured with the application of ultrasonication during the addition of PE system based on starch and different ZnO concentration, have been used. The following Table 1 describe the content and manufacture way used for each yogurt groups.

Physico-chemical analysis of yogurt

Determination of pH and titratable acidity

The approximate pH measurements were performed by using a strip of universal indicator paper. The titratable acidity was determined by alkali titrating sample with

Table 1. Description of samples/groups used in the study.

Groups	Samples manufactured way
Group 1 (n = 3)	Yoghurt made with milk which contains 2.5 % fat (control sample)
Group 2 (n = 3)	Yoghurt made with milk which contains 2.5 % fat and treated with ultrasound treatment for 30 sec during the addition of PE system based on starch/ZnO (ZnO concentration: 0.05 %)
Group 3 (n = 3)	Yoghurt made with milk which contains 2.5 % fat and treated with ultrasound treatment for 30 second during the addition of PE system based on starch/ZnO (ZnO concentration: 0.02 %)
Group 4 (n = 3)	Yoghurt made with milk which contains 2.5 % fat and treated with ultrasound treatment for 30 sec during the addition of PE system based on starch/ZnO (ZnO concentration: 0.03 %)

0.1 N NaOH solution and using phenolphthalein as an indicator [12].

Determination of the degree of viscosity in yogurt

The viscosity of yogurt is determined using a vibration meter sv-10 as described by Kadi et al. [7, 12]. The data were collected using Wingather software (Brookfield DV-III Ultra), and 100 data points were averaged.

Determination of antioxidant activities in yoghurt

Total antioxidant activity of AOA, DPPH, %, estimated by determining the absorption capacity of the free radical 1,1-diphenyl-2-picrylhydrazyl spectrophotometrically at 515 nm using a methanolic solution of DPPH.

Fourier-transform infrared spectroscopy (FT-IR) analysis

FT-IR analysis was performed according to the method described by Saberi et al. [13]. Yogurt samples were freeze-dried and the lyophilized powder mixed thoroughly with potassium bromide (KBr), then pressed enough to transform into small, transparent disks. The infrared spectra of samples were collected at a resolution of 4 cm^{-1} in the range of 4000 - 400 cm^{-1}.

Statistical analysis

The results are described as means ± standard deviations. Data were collected and using ANOVA software calculated the mean deviation difference of significant ($P < 0.05$).

RESULTS AND DISCUSSION

Characterization of the Pickering emulsion with the addition of zinc oxide at different concentrations

Results related to the study of the PE proprieties are presented in Fig. 1. Our results showed that PE system stabilized by starch/ZnO at different concentration of ZnO presented good and similar value for the unbroken emulsion (stability) and antioxidant activity percentage. However, concerning viscosity parameter, PE stabilized by starch/ZnO at a concentration of 0.05 mg of ZnO presented much higher significant values (19.8) than those of the other two PE system stabilized by starch/ZnO at a concentration of 0.02 mg and 0.03 mg of ZnO, respectively.

Physicochemical determinations of the fortified yogurts with Pickering emulsion

Results related to the physico-chemical parameters (pH, titrable acidity, viscosity, and antioxidant activity) of yogurt samples are presented in Fig. 2, 3 and 4.

pH and acidity of yoghurt samples

A decrease in pH in an acidic meal, such as yoghurt, signifies the release of lactic acid into the medium by lactic acid bacteria (LAB). Food acidity is a measure of the number of free acids and other chemical compounds present in the food. The norm of active and titratable acidity of classic yogurt without added sugar is respectively from 4.5 to 5 (pH) and 75°T to 140°T (titratable acidity).

Results for determinations of pH and titratable acidity on the first, seventh and fourteenth days of

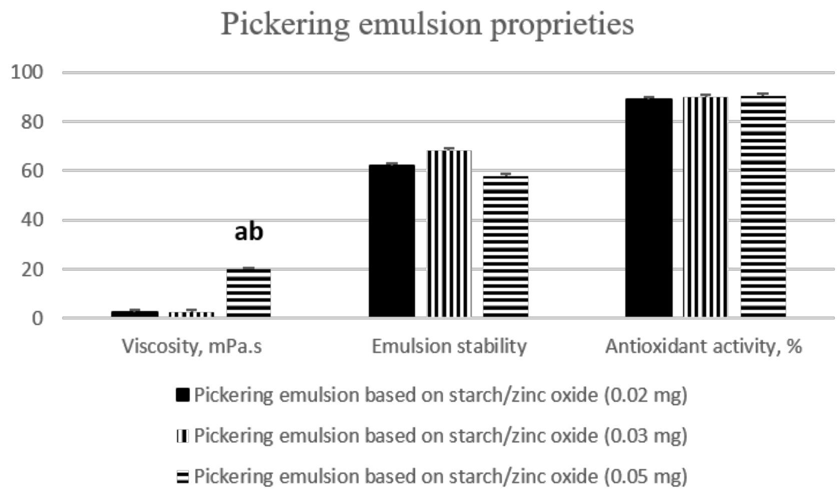


Fig. 1. Study of different proprieties (viscosity, stability and antioxidant activity) of Pickering emulsion stabilized by starch/zinc oxide at different concentration (0.02, 0.03 and 0.05 mg). a: $p < 0.05$ significance from 0.02 mg group; b: $p < 0.05$ significance from 0.03 mg group.

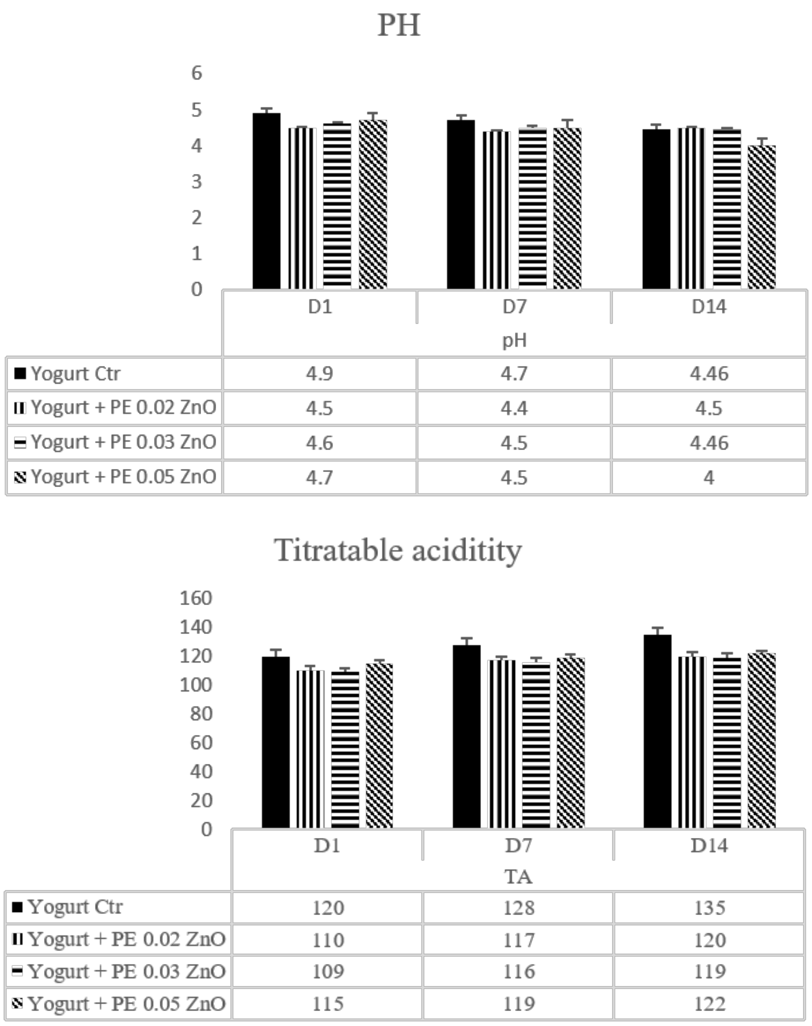
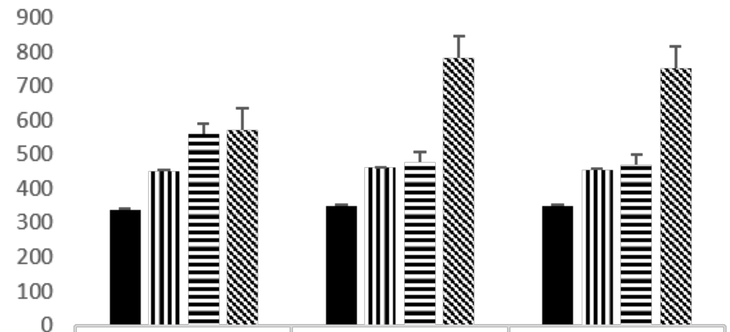


Fig. 2. pH and titratable acidity measurement in control and treated yoghurt samples.



	D1	D7	D14
	Viscosity		
Yogurt Ctr	338	348	350
Yogurt + PE 0.02 ZnO	450	460	455
Yogurt + PE 0.03 ZnO	560	478	470
Yogurt + PE 0.05 ZnO	570	780	750

Fig. 3. Viscosity measurement in control and treated yoghurt samples.

storage, showed that the average values of yogurts samples from different fortification groups are in the norm and no significant differences were shown between the values of fortified and control yogurt (Fig. 2).

Remarkably, on the first day, yoghurt samples containing Pickering emulsions had lower pH levels and increased titrated acidity, indicating active lactic acid generation. On the seventh and fourteenth days, pH levels dropped but titrated acidity increased, indicating that fermentation was still taking place. The finding that yogurt storage led to a decrease in pH due to lactic acid production by yogurt bacteria, consistent with previous studies indicating a decrease in pH in yogurt fortified with zinc nanoparticles [14, 15]. Interestingly, fortified samples were usually less acidic, which might indicate that PE influence on lactic acid bacteria activity (Fig. 2). This finding is consisting with the results of El-Sayed et al. who showed that adding 40 and 60 mg of bio-synthesized zinc oxide nanoparticles to yoghurt milk inhibited the growth of the starting culture leading to a considerable reduction in the acidity level of yoghurt fortified samples [16].

Viscosity of yoghurt samples

Viscosity is an important factor in determining the yogurt quality indicators that are related to both product stability and oral taste of fermented milk. Stability of product viscosity is very important for its quality characteristics.

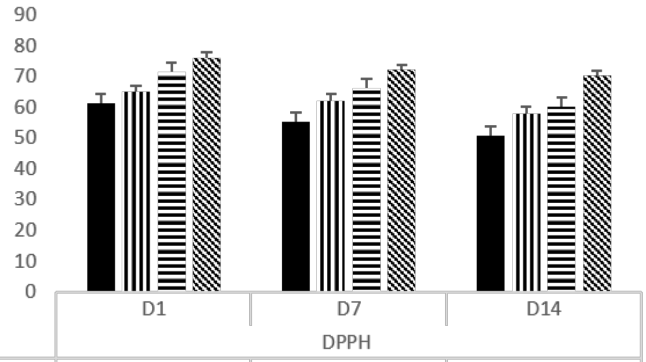
Studies of the viscosity of yogurt samples were carried out using a vibro-viscosimeter, model SV-10. The viscosity of the fortified yoghurt samples was notably greater on the first day than that of the control. In particular, the PE system with 0.03 mg ZnO (560 mPa s) and 0.05 mg ZnO (570 mPa s) samples had greater viscosities. When compared to the control samples, the fortified samples' viscosity increased even more on the seventh day, the PE system with 0.05 mg ZnO having the highest viscosity (780 mPa s). Viscosity in the fortified samples barely decreased on day fourteen, although it was still greater than in the control group (Fig. 3). The PE system with 0.05 mg ZnO maintained its greatest viscosity of 750 mPa s. These finding is consistent with the study of El-Sabie et al. [17] who indicated a significant increase in the values of zinc-fortified yogurt viscosity in comparison to control samples.

Antioxidant activity of yoghurt samples

Antioxidant activity in the fortified samples was greater on day one of storage than in the control group. The yoghurt sample fortified with the PE system with 0.05 mg ZnO showed the greatest activity (75.9 %). Antioxidant activity dropped in all samples on day seven, although it was still greater in the fortified samples relative to the control. The reduction in antioxidant activity persisted on day fourteen, but it was still greater in the fortified samples (Fig. 4).

Functional groups study of the fortified yoghurt samples using FT-IR

The following Table 2 describe the main vibration band indicated in Fig. 5 obtained for control and fortified yogurt samples. The results showed that all yogurt samples contain approximately the same 6 observed functional groups which had different transmittance patterns. Similar patterns of structures were recorded for control and fortified yogurt samples. However, we can notice the appearance of many smalls pics around the



DPPH	D1	D7	D14
Yogurt Ctr	61.26	55.1	50.5
Yogurt + PE 0.02 ZnO	65	62	58
Yogurt + PE 0.03 ZnO	71.2	66	60
Yogurt + PE 0.05 ZnO	75.9	72	70.1

Fig. 4. Antioxidant activity measurement in control and fortified yoghurt samples.

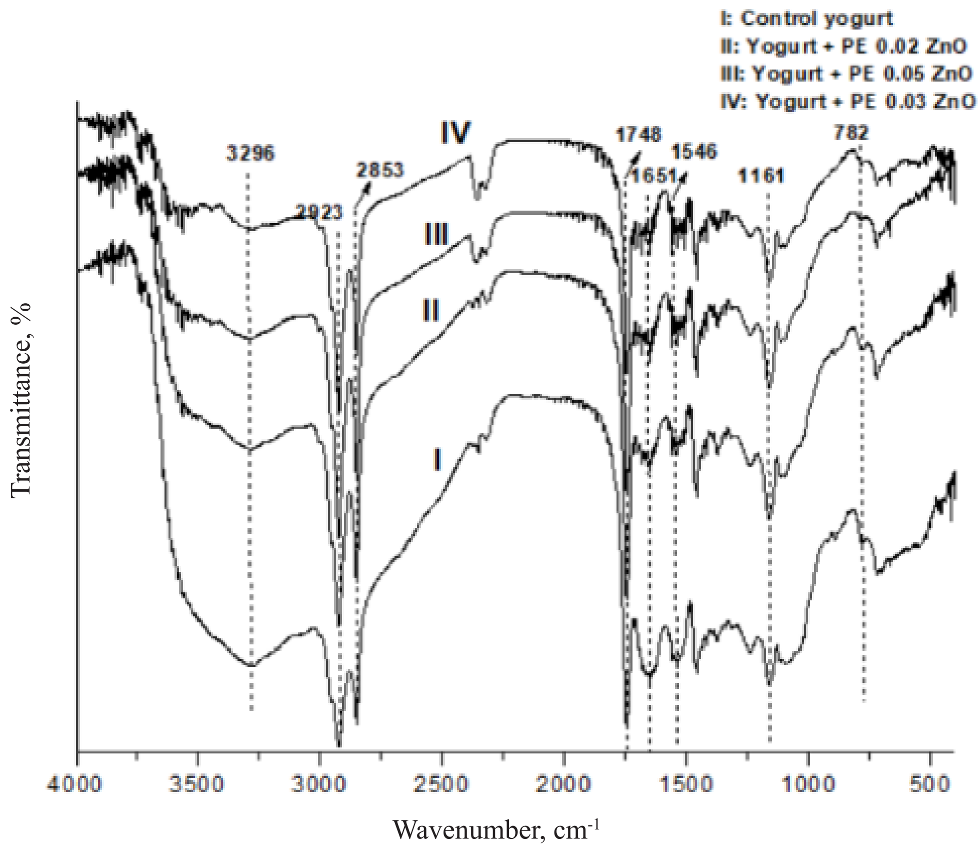


Fig. 5. FT-IR spectroscopy of yogurt samples (fat concentration 2.5 %) fortified with Pickering emulsion based on starch/zinc oxide (ZnO) at different concentration: 0.05, 0.03 and 0.02 %).

Table 2. Functional groups identified by FT-IR spectrum observed in control and fortified/ultrasonicated yogurt samples (fat concentration 2.5 %).

Band region, cm^{-1}	Functional group
782	α-glycosidic bond
1161	Carbohydrate (C-O stretch or carbohydrates C-O stretch)
1651, 1546	Amide I, and II
1748	fatty acids and fatty acid esters (C=O stretch)
2923, 2853	structure of polysaccharide compounds and long fatty acids (CH_2 stretching)
3296	hydroxyl groups

band related to the vibration of amide I and II in proteins, present in yoghurt samples fortified with PE based on starch/ZnO (at different concentration of ZnO: 0.05, 0.03 and 0.02 %). These effects could be related to the asymmetrical stretching vibration of amide I and II due to the treatment processes (ultrasound) utilized during the addition of PE system and could further influence the structural integrity and overall quality, which coincide with the investigation of Sarker & Ali Siddiqui, [18].

CONCLUSIONS

Pickering emulsion system stabilized by starch/ZnO presented good stability and high viscosity was seen where ZnO was used at a concentration of 0.05 mg. Key textural features of yogurt were not changed significantly, on the 1st, seventh and fourteenth days of storage, after the addition of PE system. Thus, the results of the study suggest the possibility of obtaining a functional yogurt (fortified with BAC) using as BAC delivery system, PE, which can be stabilized by a combination of GRAS element (ZnO) and food grade materials (starch). This technology and formulation are promising for the formation of a new yogurt to ensure the health of the population.

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***Authors' contributions**: M.C, A.M.: Experimental work, Writing; A.K, A.A.A, M.Cd: Experimental work, Review, Editing; I.P: Conceptualization, Design of the research, and Editing of the manuscript.*

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