نشریه علمی - پژوهشی

پژوهشهای علوم و صنایع غذایی ایران

جلد ۱۱ شماره ۶

سال ۱۳۹۴

شاپا: ۱۷۳۵-۴۱۶۱

عنوان مقالات

نشریه پژوهش های علوم و صنایع غذایی ایران

با شماره پروانه ۱۲۴/۸۴۷ و درجه علمی – پژوهشی شماره ۳/۱۱/۸۱۰ از وزارت علوم، تحقیقات و فناوری ۸۸/۵/۱۰

جلد ۱۱ شماره ۶ بهمن- اسفند ۱۳۹۴

درجه علمی- پژوهشی این نشریه طی نامه ۳/۱۱/۴۷۶۷۳ از وزارت علوم، تحقیقات و فناوری تا سال ۱۳۹۳ تمدید شده است.
۹۰/۴/۱۴

ناشر:گروه علوم و صنایع غذایی دانشکده کشاورزی، دانشگاه فردوسی مشهد **چاپ:** مؤسسه چاپ و انتشارات دانشگاه فردوسی مشهد

شمارگان: ۲۵۰ نسخه **قیمت:** ۵۰۰۰ ریال (دانشجویان ۲۵۰۰ ریال)

نشانی: مشهد- کد پستی ۹۱۷۷۵ صندوق پستی ۱۱۶۳

دانشگاه فردوسی مشهد، دانشکده کشاورزی - گروه علوم وصنایع غذایی- دفتر نشریه پژوهش های علوم وصنایع غذایی ایران.

تلفن: ۲۰-۸۷۹۵۶۱۸ داخلی ۳۲۱ نمابر: ۸۷۸۷۴۳۰

این نشریه درپایگاههای زیر نمایه شده است:

پایگاه استنادی علوم ایران(ISC)، پایگاه اطلاعات علمی جهاد دانشگاهی(SID)، بانک اطلاعات نشریات کشور (MAGIRAN)

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این نشریه در سایت http://jm.um.ac.ir/index.php/food_tech/index به صورت مقاله کامل نمایه شده است.

بسم الله الرحمن الرحیم

مندرجات

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 719-728

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۲۸-۷۱۹

Textural characteristics of pasta enriched with full fat soy flour; An optimization study using Response Surface Methodology

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Received: 2013.11.24
Accepted: 2014.03.05

Abstract

The influence of 0-27 g/100g of full-fat soy flour (FFSF), 31-35g/100g of water content and extrusion conditions on the textural characteristics of spaghetti were evaluated. Process was performed with screw speed of 10-40 rpm and water circulating temperature of 35-70$^{\circ C}$. This enrichment resulted in significant differences in mechanical strength and cutting parameter. Based on the mixture surface and contour plots, it was found that the optimum textural characteristic of spaghetti could be obtained by addition of 20.6 g/100g FFSF and 35.0 g/100g water and process in screw speed of 40 rpm and temperature of 35^{oC}.

Keywords: Spaghetti; Mixture design; Rheology.

Introduction

Durum wheat flour is the main ingredient in the formulation of pasta products; however, it is deficient in lysine. Therefore, many researchers have focused on improving of pasta quality by addition of ingredients such as lupine (Rayas et al., 1996; Morad et al., 1980), cowpea (Bergman *et al*., 1994), gluten (Cubadda, *et al*. 2007), quinoa, broad bean, chick pea and buck wheat (Chillo, *et al*., 2008), corn (Taha *et al*., 1992), wheat bran (Manthey *et al*., 2002), barley bran (Marconi *et al*., 2000) and dietary fiber of pea (Edwards *et al*., 1995).

Dough rheology effects by substitution of gluten by proteins such as legume seeds proteins. This substitution causes dilution of gluten, and consequently, it weakens dough. Therefore, the gluten network has a great influence on the rheological parameters of the dough. Furthermore, the quantity of added water is very important, and it affects dough material distribution, dough hydration and subsequently gluten system development. The conversion of dough rheology may be due to the physicochemical changes of flour. This supported by the work of Kordonowy *et al*. (1985), who showed that as bran content in mixture of flour was increased, dough development time and water absorption was also increased. In addition, Morad *et al*. (1980) indicated that adding lupin and defatted soybean to wheat flour increased water absorption and dough stability and decreased dough development time. Moreover, Sroan *et al*. (2004) confirmed that soy lecithin (natural antioxidant) even at the minimum concentrations improves rheological properties of the dough.

Soybean has many valuable components and consumption of soybean products is useful for bone's health, healthy brain, immune function, controls the heart attack and some cancers. In our previous research, sensory and nutritional characteristic (Nasehi *et al*. 2009a) and cooking quality (Nasehi *et al*. 2009b) of spaghetti enriched with full fat soy flour were evaluated. Thus, the objective of this paper was to study the textural properties of this kind of enriched spaghetti.

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Materials and methods

Flour's analysis

The hard wheat flour (HWF) that produced from spring hard wheat (Golestan variety) was purchased from the main company (Razavi Corporation, Mashhad, Iran), whereas the full fat soy flour (FFSF) was obtained from the industrial unit (Toos Soya Corporation, Mashhad, Iran).

The standard methods of AACC (1995) were employed for the assessment of chemical composition of HWF and FFSF. All samples and their mixtures were analyzed for crude protein, crude fat, crude fiber, moisture, and ash.

Farinograph characteristics of flours were determined according to the approved method of AACC (54-21) using farinograph equipment (Brabender OHG, Duisburg, Germany). Farinograph characteristics of mixed flours such as water absorption, dough development time, mixing time, dough stability, mixing tolerance index and valurimitry index were extracted from farinograph curve.

Spaghetti formulations and production

The amount of the basic ingredient used for making spaghetti was calculated based on the standard methods of AACC (66-41). The range of concentration used in the formulation was as follows: HWF (42.0-69.0 g/100g), FFSF (0-27.0 g/100g) and distilled water (31.0- 35.0 g/100g).

In order to spaghetti production, all the ingredients were mixed prior to extrusion for 10 minutes at 70 rpm in a laboratory pasta maker (designed by Research & Development Center of Modern Food Technology, Ferdowsi University of Mashhad, Iran). The extruder parameters were as follows: screw length of 400 mm; barrel diameter of 35 mm; die diameter of 200 mm, includes 40 Orifice with a diameter 1.8 mm; flow rate of 6-26 kg/h. Two extrusion variables studied were screw speed (10-40 rpm) and temperature of circulating water (35-70$^{\circ C}$).

From the mixture design used in this study, four different extrusion conditions (based on the temperature of circulating water and screw speed of extruder) were employed. These conditions were 40 rpm and 70$^{\circ C}$; 40 rpm and 35$^{\circ C}$; 10rpm and 70$^{\circ C}$; 10rpm and 35$^{\circ C}$. The mixing and extrusion processes were operated under partial vacuum (0.7-0.8 atm). Pressure in extruder was in the range of 200-1000 lbf/in^2 for different samples. Spaghetti samples were dried in a dryer at a local factory (Adish Corporation, Mashhad, Iran). Temperature of a dryer was fixed at 50$^{\circ C}$, but the relative humidity was reduced gradually from 95.0% to 65.0% during the 20 h of drying period. The average diameter of spaghetti was 1.90±0.03mm.

Textural measurements

Mechanical strength

Mechanical strength of dehydrated spaghetti was measured using a texture analyzer (QTS, CNS Farnell, UK) for breaking of spaghetti strand. Mechanical strength was expressed as the force (gf) required breaking one strand of dry spaghetti. The conditions used throughout the experiment included a cross head speed of 10 mm/minutes and a load cell of 5kg. The textural properties of samples, including rupture force (g), hardness (g) and toughness (g.mm) were determined using the computer software provided by a texture analyzer.

Cooking time

Duration needed for optimum cooking of spaghetti based on the standard AACC method (16-50), is the time that white core was not observed after compressed the cooked spaghetti, and overcooking was obtained by adding 10 minutes to the best time needed for perfect cooking the spaghetti.

Cutting test

Surface stickiness of the sample was determined according to Dexter et al. (1983) with some modifications according to Grant *et al.* (1993). To measure of spaghetti stickiness, a texture analyzer (QTS, CNS Farnell, UK) with a shiny aluminum plate (100mm× 100mm× 6mm) as base plate, an aluminum

plate (100x100x6 mm) as a sample holder with a rectangular opening (44mm×44mm) for plunger-to-sample access, and a polished aluminum plunger (43mm× 43mm) for contact surface was used.

Stickiness test was started 13 minutes after the end of cooking. One minute before testing, sample holder plate was placed over the spaghetti strands, and excess water was blotted using tissue. The plunger was moved vertically with a computer software program. Throughout the testing, a cross-head speed of 40mm/minutes was applied and afterward; adhesiveness work (g.mm) and stickiness (N/mm2) values were measured.

Statistical analysis

The design of experiments with mixtures and the applied response surface analysis was used. The main purpose of using this design was to verify how the rheological properties of spaghetti were affected by the variation of the proportions of the mixture components, i.e. the ingredients used in the spaghetti formulation.

A mixture design via the 36-point-extreme-vertices was constructed to enable the study of the effect of varying ratios of HWF, FFSF, and water content, and process conditions. The software (V14.2, 2005; Minitab Inc. Pennsylvania, State Collage, USA) was used to build the empirical design, the Scheffe's canonical special cubic equation for three components and two process variables was fitted to data collected at each experimental point using forward selection stepwise multiple regression analysis as described by Cornell (2002).

Result and discussion

Farinograph experiment

Results of farinograph experiment of flours samples are shown in Table 1. The results indicated that mixtures with the maximum amount of FFSF had the highest value for absorption of water, dough development time, valurimitry index, mixing time and mixing tolerance index. These results are supported by the work of Paraskevopoulou *et al*. (2010), which showed that adding lupin protein isolate to wheat flour increase the dough development time and dough stability plus the resistance to deformation and the extensibility of the dough. These enhancing effects might be the result entrapment of lupin protein particles within the gluten network system. It found that the vegetable proteins in the dough are in the form of hydrated but not fully in dispersed particles form. Similar results were reported by Roccia *et al*. (2009) who found that the substitution of wheat protein by soy protein decreased mixture elasticity, indicating dough network weakening. Gluten network formation was interfered with soy proteins probably due to both non-covalent and covalent wheat–soy protein interactions.

Furthermore, the proximate analysis of flours showed that the amount of protein, fiber, fat, moisture and ash in FFSF were 37.7, 14.0, 18.0, 5.0 and 5.0g/100g based on complete weight, relatively. The protein, fiber, fat, moisture and ash in HWF were 8.3, 0.3, 0.9, 13.0 and 0.5g/100g based on total weight, respectively. All the nutrient compositions in FFSF were higher than the HWF, except for moisture content

Table 1. Farinograph characteristics of flours [a]

Substitution (%)	Water absorption (%)	Mixing time (min)	Dough development time (min)	Dough stability (min)	Mixing tolerance index (BU)	Valurimitry Index
0[b]	61.5	1	2.5	9.5	47	50
9.2	64.9	1.4	3.5	9.15	50	52
9.5	65	1.5	4.6	9.5	65	57
18.7	68.7	2.4	4.9	10.4	70	55
26.9	71.5	3.5	5.4	10.25	70	58

[a] Mean belong to three replications.

[b] Hard wheat flour

Table 2. Mean values of the mechanical strength of spaghetti from different formulations [a]

Mixture	Toughness (g.mm)	Hardness (g)	Rupture force (g)
1	75.62	151.2	37.40
2	213.53	255.60	26.80
3	239.23	351.75	41.20
4	114.17	205.05	34.60
5	73.25	153.4	32.60
6	76.57	145.84	36.84
7	45.63	133.17	29.83
8	33.12	90.20	30.60
9	44.63	106.00	24.60
10	425.25	452.60	47.00
11	348.35	403.34	50.34
12	245.71	273.84	48.00
13	207.47	231.50	43.00
14	198.22	236.00	45.00
15	60.27	157.50	40.17
16	43.13	129.34	38.17
17	53.96	140.50	31.00
18	42.32	121.34	33.34
19	335.92	376.00	40.17
20	405.21	446.00	49.17
21	177.99	283.67	45.50
22	163.06	263.00	45.00
23	109.16	205.34	40.83
24	53.75	137.84	38.34
25	54.64	133.00	33.50
26	42.23	119.67	34.67
27	33.27	103.17	36.84
28	457.99	373.33	50.17
29	453.19	439.67	48.40
30	253.19	323.17	48.83
31	146.68	161.50	38.00
32	107.17	189.17	43.84
33	34.73	141.34	40.00
34	45.89	114.34	38.50
35	21.38	81.67	38.34
36	32.29	195.34	40.50
LSD[b]	95.72	93.36	5.512

[a] Mean belong to three replications.
[b] The smallest difference in column ($P \leq 0.05$)

Textural characteristics

Mechanical strength

Table 2 shows the mechanical strength of spaghetti, which includes rupture force, hardness and toughness. Predicted equations obtained from the regression analysis are listed in Table 3. Mixture of contour plots which are related to these equations are shown in Fig. 1(a-c).

When hardness values of enriched spaghetti were taken into consideration, it was noted that the fortified spaghetti samples had lower hardness compared to the control (Fig.1b). The hardness decreased ($P \leq 0.05$) from 452 grams in spaghetti made from HWF to 80 grams in the sample enriched with 27 g/100g FFSF (Table 2). The regression analyses indicated that the interactions between water, HWF and temperature of circulating water decreased hardness via linear ($P \leq 0.05$) term (Table 3).

This is not supported by the work of Sozer *et al*. (2008) which showed that spaghetti enriched with bran had higher hardness and lower adhesiveness than other spaghetti samples.

Cutting parameters

Table 4 shows the cutting test characteristics of spaghetti, which includes firmness, cutting force, work to cut (cutting energy) and maximum cutting stress. Predicted

equations obtained from the regression analysis are listed in Table 5. Mixture of contour plots which are related to these equations are shown in Fig. 2 (a-f).

In general, the firmness of spaghetti after optimum cooking time was higher for the spaghetti contains FFSF (Fig.2a). The firmness increased (P≤0.05) from 3.97g.cm in spaghetti made from HWF to 8.43g.cm in the sample enriched with FFSF (Table 4). The interactions between ingredient and temperature of circulating water had positive significant effects on this character via linear (P≤0.01) term (Table 5). When spaghetti samples were overcooked (Fig.2b), the firmness was not changed significantly (P≤0.05).

Several factors are believed to be important in the firmness estimation, flour composition (particularly type of protein and its composition), cooked pasta diameter and water absorption are the main ones. Our study also revealed that protein composition had an impressive effect on pasta firmness. This finding was in agreement with that of Grant et al. (1993) who reported that firmness of spaghetti made from weak wheat was lower than control. They discovered that cutting parameter of spaghetti in relation to damaged starch was due to shortage gluten content. Furthermore, Edwards et al. (1995) showed spaghetti enriched with bran after optimum and over cooking, time was softer than control, due to disrupter gluten-starch network.

Stickiness parameters

Table 4 shows the stickiness parameters of spaghetti which includes adhesiveness work and stickiness. Predicted equations obtained from the regression analysis are listed in Table 5. Mixtures of contour plots which are related to these equations are shown in Fig. 3(a-d).

In general, the adhesiveness work after optimum cooking time of enriched samples was lower than control (Fig. 3a). This parameter decreased (P≤0.05) from 308 g.mm in spaghetti made from HWF to 213g.mm in a sample enriched with FFSF (Table 4). When spaghetti samples were overcooked, this parameter decreased significantly (P≤0.05) in enriched spaghetti (Fig. 3b). The regression analyses indicated that the ingredients used in the formulation had a significant effect on this parameter for optimum and over cooking time via linear (P≤0.001) term (Table 5). When a stickiness value of enriched spaghetti was taken into consideration, it was found that this parameter was not changed significantly (P≤0.05) after optimal and over cooking time (Fig. 3 c & d). This finding was supported by Rho et al. (1989), who concluded that fatty acids produced in a storage period restrict inflation of starch and therefore, affect the viscosity of starch and decrease stickiness of a noodle. On the other hand, Matsuo et al. (1986) confirmed that unipolar lipids prevent surface stickiness in spaghetti.

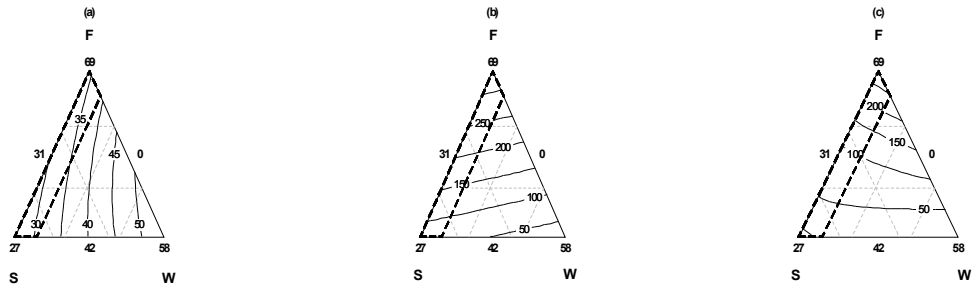

Fig. 1. Mixture contour plots of the predicted surface for cooking and color quality of pasta enriched with full fat soy flour (FFSF) dependent on components in the conditions optimized; (a), Rupture force (b) Hardness, (c) Toughness

Table 3. Predicted model for experimental data of Mechanical strength of the spaghetti [a, b]

Parameter	Predicted model	R^2 value	R^2 Adjust
Rupture force	$= 0.514\ F + 0.1009\ S + 0.309\ W - 0.0665\ WR^{***} - 0.7269FT^{**} + 0.0211\ FWT^{**} - 0.0540FRT^{***}$	0.80	0.759
Hardness	$= 7.1878\ F - 2.8195S - 4.3138\ W - 0.0122\ FWT^{*}$	0.769	0.748
Toughness	$= 6.704\ F + 16.2931\ S - 3.436\ W - 0.5109\ FS^{**} + 0.0519\ FSRT^{*} - 0.0309\ FWRT^{***}$	0.845	0.817

a F: Hard wheat flour, S: Full fat soy flour, W: Water content, R: Screw speed of extruder. T: Temperature of circulating water.
b ***: P≤0.001, **: P≤0.01, *: P≤0.05, without *: Significance was not calculated because of it was a forced term.

Table 4. Mean values of the cutting and stickiness parameters of spaghetti from different formulations [a]

Mixture	Stickiness (N/m2)		Adhesiveness work (g.mm)		Maximum cutting stress (g/mm^2)		Work to cut (g/mm)		Cutting force (g)		Firmness (g.cm)	
	Over	Opt	Over	Opt	Over	Opt	Over	Opt	Over	Opt	Over	Opt
1	265.28	305.1	344.4	281.0	9.76	11.59	43.37	52.22	95.34	107.0	4.36	4.82
2	334.25	342.4	294.4	258.1	10.00	11.23	44.03	43.75	99.00	102.0	4.22	3.97
3	509.3	448.3	282.9	266.3	10.48	11.49	44.21	46.86	100.0	110.3	4.92	4.50
4	353.6	382.0	300.9	265.9	11.22	13,20	50.21	57.41	110.3	122.0	4.78	5.30
5	329.0	326.3	294.2	269.8	11.74	14.22	50.27	58.86	111.7	130.7	4.52	5.41
6	350.2	344.9	266.1	264.4	11.50	14.66	49.28	61.38	105.7	127.0	5.88	5.32
7	376.7	331.6	271.2	251.4	13.00	17.51	61.67	76.55	124.0	148.7	5.10	6.50
8	448.3	313.0	282.1	245.6	12.32	14.09	54.65	60.42	114.0	124.0	5.42	5.32
9	419.1	435.1	235.6	228.0	13.35	18.40	59.27	71.31	122.0	152.7	4.60	5.92
10	300.6	307.7	329.7	284.0	9.65	13.08	44.47	56.99	100.0	124.7	3.52	5.43
11	373.1	280.0	314.3	274.5	7.39	16.36	33.62	68.69	73.34	151.0	4.70	6.34
12	385.5	360.8	314.0	239.0	11.08	13.44	48.07	58.38	108.3	124.3	5.06	5.40
13	295.3	260.0	314.6	260.9	10.20	14.07	49.64	63.51	104.0	103.3	4.41	5.88
14	389.1	321.0	282.6	251.6	10.00	14.19	43.71	59.3	101.0	131.7	4.44	5.50
15	369.6	362.5	275.0	234.7	9.93	20.36	44.60	93.84	99.00	183.0	4.81	8.43
16	482.8	565.0	265.6	228.8	10.84	16.90	48.34	74.15	108.0	154.0	4.72	6.76
17	314.8	442.1	276.0	213.7	11.79	18.40	49.90	86.5	111.7	164.0	4.67	7.70
18	422.6	341.4	260.8	237.4	11.36	19.27	49.08	91.46	108.0	170.0	4.10	8.10
19	318.3	323.6	338.2	290.6	8.62	12.65	39.44	51.74	66.89	112.4	4.50	4.59
20	369.6	364.3	328.8	285.8	10.53	12.01	45.47	51.56	104.3	113.0	5.08	4.85
21	431.5	397.9	311.8	183.2	10.18	15.69	50.03	70.42	105.7	148.3	5.2	6.66
22	341.4	341.4	312.7	278.2	10.63	13.41	49.92	55.76	108.3	127.0	4.56	5.28
23	410.3	329.0	301.8	280.0	10.35	15.52	46.10	67.06	102.3	139.7	4.25	6.04
24	463.4	387.3	285.5	232.7	10.34	17.63	45.00	75.64	97.67	155.7	4.00	6.68
25	509.3	413.8	287.4	241.5	9.60	17.13	42.67	79.93	90.00	148.0	4.67	6.90
26	521.7	311.3	242.6	245.0	11.90	18.87	51.43	78.82	108.3	161.3	4.67	6.74
27	481.1	334.3	259.6	241.6	11.53	14.98	50.28	69.74	107.0	139.3	4.17	6.49
28	373.1	273.2	354.6	271.1	8.77	11.40	41.09	49.71	89.00	110.0	3.71	4.79
29	328.9	443.9	371.6	308.4	8.24	11.51	36.60	46.20	83.66	107.5	3.77	4.45
30	491.7	562.4	315.0	270.8	8.67	13.60	37.85	61.18	86.33	128.3	4.32	5.70
31	535.9	408.5	311.6	278.0	9.86	13.35	42.76	49.92	99.67	125.5	3.88	4.81
32	527.9	295.2	284.0	257.2	8.90	12.70	39.35	54.41	87.66	114.3	4.01	4.93
33	410.3	326.3	267.24	218.0	10.10	15.03	43.20	62.83	93.75	128.7	3.87	5.37
34	631.4	554.4	233.8	234.3	9.50	14.21	40.96	61.36	89.75	124.3	3.87	5.37
35	382.0	228.1	280.5	231.6	9.76	15.67	41.87	69.37	95.25	131.7	3.86	5.83
36	527.9	299.8	237.1	238.3	10.70	16.30	42.00	71.11	98.3	134.7	4.00	5.87
Lsd[b]	110.5	-	27.96	32.01	1.201	2.222	6.126	11.68	11.84	17.49	0.6197	1.016

a Optimum cooking (opt), over cooking (over).
bThe smallest difference in column ($P \leq 0.05$)

Table 5. Predicted model for experimental data of the cutting and stickiness parameters of the spaghetti [a, b]

Parameter		*Predicted model*	R^2 *value*	R^2 *Adjust*
Firmness	Optimum cooking	$=0.0416\ F + 0.1096\ S + 0.0654\ W - 0.0157\ WT^{***}$	0.670	0.639
	Overcooking	$= 0.0394F + 0.0530\ S + 0.0496\ W + 0.1185 \times 10^{-4}\ FSWR^{***} + 0.0004\ SWRT^{**}$	0.531	0.471
Cutting force	Optimum cooking	$= 1.3358\ F + 2.650S + 0.8363\ W + 4.909\ SR^{*} - 0.1423\ SWR^{*} - 0.2933\ WT^{***}$	0.750	0.709
	Overcooking	$= 0.9217\ F + 1.3565\ S + 1.0139\ W + 0.0002\ FSWR^{***} + 0.0759\ FRT^{**}$	0.601	0.549
Work to cut	Optimum cooking	$=0.3533\ F + 1.3325\ S + 0.8615\ W - 0.1734\ WT^{***}$	0.727	0.701
	Overcooking	$= 0.3159\ F + 0.5998\ S + 0.6405\ W + 0.0001\ FSWR^{***} + 0.0824\ WRT^{***}$	0.651	0.606
Maximum cutting stress	Optimum cooking	$= 0.129\ F + 0.3297\ S + 0.1123\ W - 0.0280\ WT^{**}$	0.735	0.710
	Overcooking	$= 0.0937\ F + 0.1791\ S + 0.0917\ W + 0.2357 \times 10^{4}\ FSWR^{***} + 0.0170\ WRT^{***}$	0.739	0.705
Adhesiveness work	Optimum cooking	$= 3.4583\ F + 1.6806\ S + 1.3399\ W$	0.450	0.418
	Overcooking	$= 2.7616\ F - 0.2601\ S + 4.4\ W$	0.760	0.745
Stickiness	Optimum cooking	$=5.5619F+6.6271S\ 0.03366W$	0.025	0.000
	Overcooking	$= 5.7881F + 9.8154S - 0.8403W - 0.0528\ FSR^{**}$	0.434	0.381

a F: Hard wheat flour, S: Full fat soy flour, W: Water content, R: Screw speed of extruder. T: Temperature of circulating water.
b ***: P≤0.001, **: P≤0.01, *: P≤0.05, without *: Significance was not calculated because of it was a forced term.

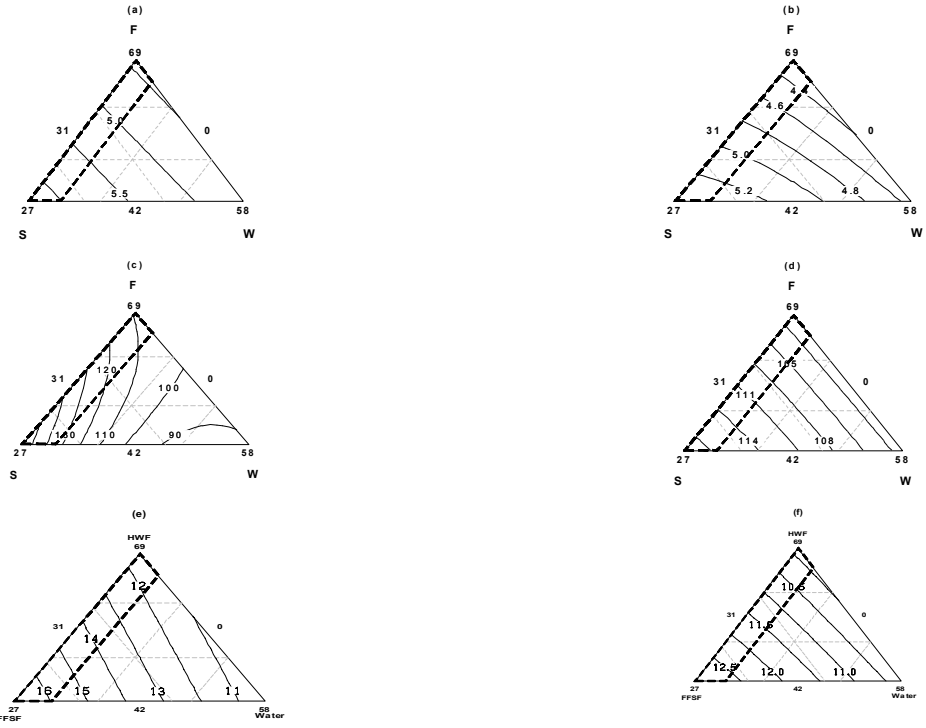

Fig. 2. Mixture contour plots of the predicted surface for cooking and color quality of pasta enriched with full fat soy flour (FFSF) dependent on components in the conditions optimized; (a) Firmness for optimum cooking, (b) Firmness for overcooking, (c) Cutting force for optimum cooking, (d) Cutting force for overcooking, (e) Maximum cutting stress for optimum cooking, (f) Maximum cutting stress for overcookin

Fig. 3. Mixture contour plots of the predicted surface for cooking and color quality of pasta enriched with full fat soy flour (FFSF) dependent on components in the conditions optimized; (a) Adhesiveness work for optimum cooking, (b) Adhesiveness work for overcooking, (c) Stickiness for optimum cooking, (d) Stickiness for overcooking

Conclusions

Addition of FFSF and extrusion processing conditions influenced the texture of spaghetti. This enrichment resulted in significant differences ($P \leq 0.05$) in mechanical strength and cutting parameters, but when FFSF was increased, no significant difference was observed in the stickiness characteristics after optimum and over cooking time. All predicted models for mechanical strength showed high regression ($R^2 \geq 75.0$), while for cutting and stickiness parameters, the value was low ($R^2 \leq 75.0$). Our results revealed that temperature of circulating water and screw speed of extruder had no significant effect independently on the textural characteristic of FFSF-fortified spaghetti. Of course, the interaction between them and components after optimum cooking time had a positive on the cutting parameters. On the other hand, interaction between components and process variable after over cooking time had a negative mechanical strength and cutting parameter. Based on the mixture surface and contour plots, the ideal textural characteristic of spaghetti was produced when 44.4 g/100g HWF, 20.6 g/100g FFSF and 35.0 g/100g water content were added and processed at screw speed of 40 rpm and temperature of 35oC. The textural characteristics of spaghetti measured at these perfect conditions were as: toughness, 69.9 (g.mm); firmness after optimum cooking, 6.95 (g.cm); firmness after over cooking, 4.67 (g.cm); stickiness after optimum cooking, 371.7 (N/m^2); and stickiness after over cooking, 381.6 (N/m^2).

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نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۲۸-۷۱۹

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 719-728

بهینه‌سازی ویژگی‌های بافتی فرآورده‌های خمیری حاوی آرد کامل سویا با استفاده از روش سطح پاسخ

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تاریخ دریافت:۱۳۹۲/۰۹/۰۳
تاریخ پذیرش:۱۳۹۲/۱۲/۱۴

چکیده

تاثیر افزودن آرد کامل سویا در دامنه ۰ تا ۲۷ درصد و آب از ۳۱ تا ۳۵ درصد در فرمول و همچنین شرایط مختلف اکستروژن بـر روی ویژگـی هـای بافتی اسپاگتی به منظور تولید فرآورده سلامتی بخش، مورد بررسی قرار گرفت. فرآیند در اکسترودری با سرعت چرخش مارپیچ در دامنه ۱۰ تا ۴۰ دور بر دقیقه و آب سیرکولاسیون با دمای ۳۵ تا ۷۰ درجه سانتی‌گراد، انجام شد. نتایج نشان داد که افزودن آرد کامل سویا سبب اختلاف معنی‌داری در استحکام مکانیکی و شاخص های برشی شد. بررسی آماری نتایج با استفاده از طرح مخلوط نشان داد که بهترین اسپاگتی زمانی تولید می شود که فرمول حـاوی ۲۰/۶ درصد آرد کامل سویا، ۴۴/۷ گرم بر صد گرم آرد نول و ۳۵ گرم بر صد گرم آب در اکسترودر با سرعت چرخش مارپیچ ۴۰ دور بـر دقیقـه و دمـای آب سیرکولاسیون ۳۵ درجه سانتی گراد، فرآوری شود.

واژه‌های کلیدی: اسپاگتی، رئولوژی، طرح مخلوط.

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Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 729-737

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۳۷-۷۲۹

Evaluation of antioxidant activities of *Mentha piperita* essential oils obtained by different extraction methods

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Received: 2014.08.01
Accepted: 2015.02.07

Abstract

As traditional extraction methods like Hydrodistillation (HD) and steamdistillation (SD) have long extraction times, some novel extraction methods like microwave-assisted hydrodistillation (MAHD) and ohmic-assisted hydrodistillation (OAHD) are recently introduced. In this study, essential oils of *Mentha piperita* were extracted by OAHD and MAHD and the results were compared with those of the SD and HD to clarify if these novel procedures have significant effect on antioxidant activities of extracted essential oils. The results showed that OAHD and MAHD are able to reduce extraction time (up to 72%) and also required electrical energy. Furthermore, all extracted essential oils were shown to have approximately same physical properties (relative density and visual color) and antioxidant activity using DPPH and β-carotene bleaching methods. The findings of this study revealed the applicability of using mint essential oil obtained by MAHD and OAHD as a natural antioxidant in food and pharmaceutical products.

Keywords: Essential oils, Hydrodistillaion, *Mentha piperita*, Microwave-assisted hydrodistillation, Ohmic-assisted hydrodistillation, Steamdistillation.

Introduction

The genus *Mentha* (family Lamiaceae), including more than 25 species, grows widely throughout the temperate regions of the world (Gulluce *et al*, 2007). *Mentha piperita* commonly known as peppermint frequently cultivated in many countries of East Asia, Europe, America and Australia for the production of essential oils (Gulluce *et al*., 2007 and Pandey *et al*., 2003). The essential oils and extracts from peppermint have been in use since ancient times for the treatment of many digestive tract diseases and in cuisines (Iscan *et al*., 2002).

Essential oils of mint aerial parts contain a large number of aromatic chemicals like menthol, menthone, isomenthone and menthofuran. These compounds are commercially important for the pharmaceutical, food, cosmetic and beverages industries (Carmines, 2002; Bakkali *et al*., 2008).

The peppermint oil is reported to have anti-oxidant properties, antibacterial activity and is one of the most important constituents of some over-the-counter remedies in Europe for irritable bowel syndrome (Pittler and Ernst, 1998; Singh *et al*., 2011).

As the living tissues are under the threat of damage by reactive oxygen derivatives which resulted from aerobic metabolism, it is therefore important to prevent oxidation. Such free radicals are usually short-lived species but they possess a single unpaired electron, rendering them highly reactive against biologically important macromolecules including DNA, proteins and membrane lipids. To counteract this threat to their integrity, cells have evolved a variety of defense systems based on both water-soluble and lipid-soluble antioxidant species, and on antioxidant enzymes. A high proportion of the antioxidant systems of the human body are dependent on dietary constituents.

The most widely used synthetic

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antioxidants in food (butylated hydroxytoluene BHT, butylated hydroxyanisole BHA, propyl galate PG and tertiary butyl hydroquinone TBHQ) have been suspected to cause or promote negative health effects including mutagenic and carcinogenic consequence (Branen, 1975; Barlow, 1990; Namiki, 1990). Consequently, there is a growing interest in studies of natural additives as potential antioxidants. The search for natural antioxidants, especially of plant origin, has notably increased in recent years (Ebrahimzadeh *et al*., 2010).

There are a number of conventional methods for extracting essential oils, e.g. hydrodistillation (HD), steam distillation (SD) and organic solvent extraction (Presti *et al*., 2005). However, SD and HD methods suffer from some disadvantages including losses of volatile compounds and long extraction times and are known to be energy intensive methods. Furthermore, elevated temperatures can cause partial or full degradation of natural constituents especially monoterpenes which are vulnerable to structural changes under steam distillation conditions (Presti *et al*., 2005). Conventional solvent extraction method has introduced to involve losses of more volatile compounds during removal of the solvent (Moyler, 1991; Presti *et al*., 2005).

Because of disadvantages of traditional methods of extraction, researchers introduce and evaluate some alternative extraction methods such as microwave-assisted hydrodistillation (MAHD) and ohmic-assisted hydrodistillation (OAHD). MAHD was compared with HD in the extraction of essential oils from *Thymus vulgaris* L. (Golmakani and Rezaei, 2008). Gavahian *et al*. (2011) used a combination of ohmic heating and distillation for separation of essentials oils from *Zataria multiflora* Boiss (Shirazi Thyme) and found significant reductions in extraction time and consumed energy for ohmic-assisted hydrodistillation (OAHD) compare to conventional hydrodistillation method. This research team also reported similar result on OAHD for *Thymus vulgaris* and *Myrtus communis* (Gavahian *et al*., 2012; Gavahian *et al*., 2013).

Despite many studies reported on novel methods of extraction and also mint essential oils, there is no report which can clarify if different methods of extraction have significant effect on antioxidant activities of extracted essential oils from this medicinal herb. Therefore, the aim of this work was to use different techniques (including HD, SD, MAHD and OAHD) for the extraction of essential oils from dried peppermint areal parts and to compare the antioxidant activity of extracted essential oils.

Materials and methods

Plant materials

Fresh aerial parts of peppermint before flowering stage were collected from an indigenous crop in Noor-Abad (Mamasani, Sothern Iran), in July 2013. The herbs were then dried in a dark room under ambient conditions (30-40 °C) for four days on a large screened tray, packed in high density poly ethylene (HDPE) bags, put in a cardboard box and kept in a dark and cool place for further experiments. The moisture content of the plants was measured in triplicate using a laboratory oven by drying until reaching constant weight and was about 12.4±0.2%.

Steam distillation

SD was performed using a laboratory heater (MAG-K; Gerhardt Ltd., Germany; and 500 W) as the heating source (Presti *et al*., 2005). In SD procedures, 15 g of dried peppermint aerial parts placed in the junction of flask and Clevenger device. The bottom of the junction was perforated to let steam easily travel. 0.5 L distilled water were heated in the apparatus flask for up to 2 h from initial temperature of 27±1°C (similar to initial temperature of material in other studied extraction methods). The extraction process continued until no more essential oils were obtained and also required time to collect all extractable oil was recorded as total needed extraction time (i.e. the period of time between start of process and the time afterward no more essential oil collected). To remove water, the extracted essential oils were

then dried over anhydrous sodium sulfate and stored in amber vials at 4 °C for further experiments.

Hydrodistillation

HD is an approved method that is used as a reference for the quantification of essential oils (Stahl-Biskup, 2002). HD was carried out in a similar way as dicribed by Gavahian *et al*., 2012. Briefly, Fifteen grams of dried peppermint aerial parts with 0.5 L distilled water were put into HD with a Clevenger-type apparatus and essential oils were extracted until the time that no more essential oils were obtained. Removal of water from essential oils was performed as described for SD samples. The extracted essential oils were then stored in a cool (4 °C) and dry place for further experiments.

Ohmic assisted hydrodistillation

OAHD was performed using modified version of an ohmic distillator device with platinum electrodes as designed and developed by Farahnaky *et al*., 2010, in the Department of Food Science and Technology of Shiraz University. OAHD was performed at 220 V, 50 Hz and similar to that described by Gavahian *et al*., 2012.

In OAHD procedures, 30 g of dried peppermint aerial parts and 0.5 L salted water (1 NaCl%, w/v) were heated in the apparatus flask for up to 2 h from initial temperature of 27±1°C (similar to initial temperature of material in HD method). The extraction process continued until no more essential oils were obtained. Anhydrous sodium sulfate was used to remove water from the extracted essential oils and the dried essential oils were stored in amber vials at 4 °C for further experiments.

Microwave assisted hydro distillation

A domestic microwave oven (NN-S674MF, Panasonic, Japan, 32 l, 1100 W; variable in 110 W increments, 2.45 GHz) was modified for MAHD operation and the extractor performed similar to that described by Golmakani and Rezaei, 2008. Thirty grams of mint samples were placed in a 1 L flask containing salted water (500 ml, 1% v/v). The flask was setup within the microwave oven cavity and a Clevenger was used on the top (outside the oven) to collect the extracted essential oils. In addition, the volume and dimensions of the utilized container and condenser were exactly similar to that used for other studied extraction processes. The microwave oven was operated at 500 W power level for a period which was was sufficient to extract all the essential oils from the sample.

Removing of water from MAHD samples were conducted similar to the method described for OAHD samples. These dried essential oils were stored in amber vials at 4°C until they were used for analysis.

Energy Consumption during extraction

In all extraction methods, the amounts of energy consumption during extraction were monitored using the designed software. In addition, the input power consumption was monitored using a separate Wattmeter at the entrance of electrical heater power supply (i.e. at the entrance of ohmic apparatus power supply, microwave apparatus power supply and laboratory heaters of HD and SD power supplies). Afterward, the amount of required energy (kW) for extraction of one milliliter of mint essential oil in each extraction method (OAHD, MAHD, HD and SD) was calculated. These calculations were conducted similar to that was reported by Gavahian *et al*., 2011. Moreover, the equivalent amount of emitted carbon dioxide (as a green house gas) of consumed energy was calculated according to the literature: to obtain 1 kWh from coal or fuel, i.e. 800 g of CO_2 will be emitted to the atmosphere during combustion of fossil fuels (Ferhat *et al*., 2006).

Physical properties

Specific gravity of the essential oils from the mint samples were measured according to Food Chemical Codex (FCC) (FCC, 1996) at 25 °C. In addition, the color of the oils was determined visually as directed in FCC (FCC, 1996).

Antioxidant activity

Free radical scavenging activity

The antioxidant activity of the extracted peppermint essential oils were assessed by their ability to scavenging 2,2-diphenyl-1-picrylhydrazyl stable radicals (DPPH) by using the method described by Burits and Bucar, 2000. Briefly, 50 microlitres of different concentrations of the essential oils samples in methanol (10–60 mg/mL) were added to 5 mL of a 0.004% methanol solution of DPPH. After incubating for 30 min at room temperature and under dark condition, the absorbance of the samples was read against a blank at 517 nm using a spectrophotometer (Reyleigh UV9200, China). Inhibition of free radical DPPH in percent (I%) was calculated using Equation 1:

$$I\% = (A_{blank}-A_{sample}/A_{blank})\times 100 \quad (1)$$

Where A_{blank} is the absorbance of the blank (containing all reagents except the test compound) and A_{sample} is the absorbance of the test essential oil or BHT. IC_{50} is defined as the concentration sufficient to obtain 50% of a maximum scavenging capacity, which was calculated from the plot of inhibition percentage against concentration. All tests and analysis were run in triplicate and averaged.

β-carotene-linoleic acid test

Antioxidant activities of extracted essential oils were also determined using β-Carotene bleaching assay. In this test, antioxidant capacity is determined by measuring the inhibition of the volatile organic compounds and the conjugated diene hydroperoxides arising from linoleic acid oxidation. A stock solution of β -carotene-linoleic acid mixture was prepared as follows: 0.2 mg of β -carotene was dissolved in 10 mL of chloroform and 1 mL was added to 20 mg linoleic acid and 200 mg of Tween 40. Chloroform was gently removed under a stream of nitrogen gas. Then, 50 mL of distilled water, saturated with oxygen (30 minutes, 100 mL min^{-1}), was added with vigorous shaking. 200 µl of ethanolic stock solution of sample and BHT were separately mixed with 5 mL emulsion. Readings of all samples were taken immediately by spectrophotometer at t= 0 minute at 470 nm. The cuvettes were incubated in a water bath at 50ºC for 30 minutes. Then, absorbances of samples at 470 nm were determined by spectrophotometer (Zhang *et al*., 2006). All determinations were performed in triplicate and the results were averaged. The percentage inhibition was calculated using the equation 2:

$$\%Inhibition = (A_{sample(t)}-A_{control(t)})/(A_{control(0)}-A_{control(t)}) \times 100 \quad (2)$$

Where $A_{sample(t)}$ and $A_{control(t)}$ are the absorbance of the sample and control at t, respectively, and $A_{control(0)}$ is absorbance of the control at t= 0 minute.

Statistical analysis

All extraction processes were performed in triplicates. An independent samples t-test was performed to determine significant differences between the means using SPSS (version 19.0.0; IBM Institute Inc., USA).

Results and discussions

Comparison of extraction duration and yield

The required time for extraction essential oils from peppermint using different methods are presented in Table 1. As the data shows, both traditional methods (HD and SD) require approximately same time to perform the extraction process but more time than OAHD and MAHD methods. Before extraction time of 20 min, the novel studied methods (OAHD and MAHD) resulted in oil recovery to that obtained by HD after more than 55 minutes. In the other word, OAHD and MAHD require less than 32% time of that needed in SD and HD. Therefore, saving time is an obvious advantage of these new methods of extraction in comparison to traditional methods. This is due to higher extraction rate in OAHD and MAHD. In OAHD heating is applied through ohmic heating, which causes heat generation within the materials. Due to internal heat generation, the heating is faster than traditional

systems used for heating foods where heat must travel gradually from the outside surface of container (i.e. the surface of heater) to the inside material (Singh and Heldman, 2009). In contrast to conventional heating systems, microwave heating (which is employed in MAHD) penetrate materials, and heating extends within the entire food material. The rate of heating is therefore more rapid (Singh and Heldman, 2009). Although the mechanism of heating in OAHD and MAHD is completely different, in this study both of them resulted in similar extraction duration.

There are a number of parameters that can influence the essential oil content of aromatic herbs including harvest time, ecological and climatic conditions (i.e. Clark *et al*., 1980; Baranauskiene, 2003; Tabatabaie and Nazari, 2007). It was previously reported that the oil content of peppermint can vary by harvest time from 0.72% to more than 3% and oil yield of peppermint depends on growing stage (White *et al*., 1987). In this study the resulted yields in all methods were in the range of the previous reports on peppermint. As presented in Table 1, SD yields lower amount of essential oils than other studied methods. The lower yield in SD process can be related to packing of mint leaves in junction of steam distillatory device (i.e. the part of device where mint areal parts were placed) which can prevent leaves from perfect extraction.

Comparison of energy consumption

In terms of time and energy, the reduced cost of extraction is clearly an advantage for the studied novel extraction methods (OAHD and MAHD) (Tables 1 and 2). The traditional methods (HD and SD) require long extraction times (about one hour) while OAHD and MAHD need approximately third amount of this time. The energy requirement to perform the extraction, based on the power consumptions of the electromantle for 1 ml of extracted oils, was 0.7 kWh and 0.8 kWh for HD and SD while this value was 0.1 kWh for OAHD and 0.2 kWh for MAHD, respectively. This indicates a substantial saving in the extraction cost by novel studied extraction methods (especially OAHD) compared to the conventional extraction techniques (HD and SD). Regarding environmental impacts, the calculated quantity of carbon dioxide (the primary greenhouse gas) emitted to the atmosphere is higher in the case of HD (551 g CO_2/ml of essential oils) and SD (668 g CO_2/ml of essential oils) than for OAHD (108 g CO_2/ml of essential oils) and MAHD (170 g CO_2/ml of essential oils). In other words, the emitted CO_2 for extraction of equal volume of essential oils by studied novel extraction methods are far less than that of emitted by studied tradition extraction methods.

Based on the findings of this research and the previously reported data on OAHD and MAHD, OAHD and MAHD are therefore suggested as "environmentally friendly" extraction methods (from energy consumption view point). However, unlike MAHD, OAHD lacks the risk of radiation leakage and its hazards to the operators.

Physical properties evaluation

The physical properties (specific gravity and color) of mint essential oils extracted by SD, HD, OAHD and MAHD are shown in Table 1. There is no significant difference between both traditional and novel studied methods for the specific gravity. Every essential oil has a typical range of densities at specified temperatures. Generally, the densities of essential oils range from 0.780 to 0.970 $g.cm^{-3}$ (Bowles, 2003). Similarly, sensory color perceptions of all samples were similar and within the range indicated by Food Chemical Codex (FCC).

From the physical tests of the extracted essential oils, it can be concluded that OAHD and MAHD, as possible substitutions techniques for traditional methods, did not introduce any considerable changes to the studied physical properties of the extracted essential oils from mint aerial parts.

Antioxidant activity

The extracted essential oils of peppermint by studied methods were explored for antioxidant activity by evaluating their IC_{50}

(from DPPH assay) and Inhibition of linoleic acid peroxidation (from β-carotene bleaching assay), and the results are given in Table 3.

Table 1. Effect of extraction methods on total needed extraction time, yield and physical properties of mint essential oils.

	SD	HD	OAHD	MAHD
Total extraction time (min)	$58.75^{a} \pm 2.85$	$55.88^{a} \pm 3.30$	$18.54^{b} \pm 2.23$	$16.50^{b} \pm 1.01$
Yield (%V/W)	$2.00^{b} \pm 0.27$	$2.29^{a} \pm 0.16$	$2.25^{a} \pm 0.10$	$2.17^{a} \pm 0.14$
Relative density	$0.91^{a} \pm 0.01$	$0.91^{a} \pm 0.01$	$0.91^{a} \pm 0.01$	$0.91^{a} \pm 0.01$
Visual color	Pale yellow	Pale yellow	Pale yellow	Pale yellow

* The same letters in each row indicate that the means are not significantly different (p <0.05).

Table 2. Effect of extraction method on energy consumption.

	SD	HD	OAHD	MAHD
Total electrical energy consumption (kWh)	0.50^{a}±0.02	0.47^{a}±0.03	0.09^{c}±0.01	0.14^{b}±0.01
Electric consumption (kWh/ml essential oils)	0.835^{a}±0.095	0.689^{a}±0.081	0.135^{c}±0.011	0.212^{b}±0.020
emitted CO_2 (g/ ml essential oils)	668.3^{a}±76.1	551.2^{a}±64.8	108.3^{c}±8.7	169.8^{b}±16.4

* Values are Mean ± SD (n-=3) of each *Mentha peppireta*, analyzed individually in triplicate. The same letters in each row indicate that the means are not significantly different (p <0.05).

Table 3. Effect of extraction methods on the antioxidant activity of *Mentha piperita* essential oils

	SD	HD	OAHD	MAHD	BHT
DPPH, IC_{50}, (μg mL^{-1})	10.4^{a}±0.6	9.8^{a}±0.9	9.9^{a}±0.9	9.6^{a}±0.7	5.2^{b}±0.4
Inhibition of linoleic acid peroxidation (%)	40.34^{b}±2.9	40.8^{b}±3.1	41.0^{b}±3.0	41.0^{b}±3.7	91.8^{a}±1.2

* Values are Mean ± SD (n-=3) of each *Mentha peppireta*, analyzed individually in triplicate. The same letters in each row indicate that the means are not significantly different (p <0.05).

Totally, lower IC_{50} value reflects a better protective action. IC_{50} values of the extracted essential oils (using SD, NHD, OAHD and MAHD) have been compared with BHT. The free radical-scavenging activities of all extracted essential oils were approximately similar (9.6±0.7 μg.mL^{-1} for MAHD *vs.* 9.8±0.9, 9.9±0.9 μg.mL^{-1} and 10.4±0.6 for HD, OAHD and SD, respectively). In addition, antioxidant activity of BHT as positive control was compared in a parallel experiment that showed lower IC_{50} value (i.e. higher antioxidant activity) with IC_{50} of 5.2±0.4 μg.mL^{-1}.The similarity in antioxidant activity of extracted essential oils by studied methods revealed that new proposed extraction methods which have been studied in this study did not considerably affect the IC_{50} value of extracted essential oils. The IC_{50} of mint essential oils are approximately two times greater than IC_{50} of BHT. Similar results have been reported before. For example Singh *et al*., 2011 reported an IC_{50} for *M. pepperita* essential oil to be twice of that of BHT (15.2±0.9 vs 6.1 ±0.3, respectively). The most powerful scavenging compounds were reported to be monoterpene ketones (menthone and isomenthone) and 1,8-cineole (Mimica-Dukic *et al*., 2003).

The rate of β-carotene bleaching can be slowed down in the presence of antioxidants (Tepe *et al*., 2005; Kulisic *et al*., 2004). Therefore, antioxidant activities of the extracted essential oils in comparison with synthetic antioxidants (BHT) were evaluated (Table 2). As can be seen in Table 2, there are no significant differences between the antioxidant activities of all extracted essential

oils (41.0±3.0 for OAHD *vs.* 40.34±2.9, 40.8±3.1 and 41.0±3.7 for SD, HD and MAHD, respectively). Moreover, antioxidant activity of BHT was approximately two times greater than *M. piperita* oil. This theme has also been reported by other researchers. For instance, Yadegarinia *et al*. (2006) reported that the percent of inhibition in β -carotene bleaching test of mint oil was 50.17 while this value was 86.75 for BHT. The results were almost consistent with the data obtained from the DPPH test. Generally the essential oils rich in phenolic compounds exhibited significant antioxidant activity (Lu and Foo, 2000).

These properties are in high demand by the food industry in order to find possible alternatives to synthetic chemicals (namely BHT, phenolics). Oxidative stress is involved in the pathogenesis of numerous diseases. These results suggest that the mint essential oils have a potent antioxidant activity. In addition using OAHD and MAHD as alternative methods for extraction of mint essential oil will not significantly vary its antioxidant properties.

Conclusion

In this study, novel extraction methods (OAHD and MAHD) resulted in a reduced extraction time and extraction energy compared to the conventional techniques. After 16 min of MAHD extraction, it was possible to collect almost all the existing essential oils of the mint (2.2%, indeed), whereas in SD process, after 59 min, less amount of essential oils was extractable (2.0%, indeed). Essential oils obtained by all studied novel and traditional methods were almost similar in their antioxidant activities. MAHD and OAHD can be considered as applicable alternative methods of extraction since they require significantly less amounts of time and energy to operate. In comparison to traditional SD, not only could they increase oil yield but also resulted in the oils with similar antioxidant activities.

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نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۳۷-۷۲۹

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 729-737

ارزیابی فعالیت آنتی‌اکسیدانی روغن‌های اساسی نعناع فلفلی (*Menthapiperita*) با روش‌های متفاوت استخراج

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تاریخ دریافت:۱۳۹۳/۰۵/۱۰
تاریخ پذیرش:۱۳۹۳/۱۱/۱۸

چکیده

به دلیل طولانی بودن زمان استخراج روش‌های سنتی از جمله تقطیر با آب (HD) و تقطیر با بخار آب (SD)، اخیراً روش‌های جدیدی مانند تقطیر با آب در حضور امواج مایکرو (MAHD) و تقطیر مقاومتی (OAHD) معرفی شده‌اند. در پژوهش حاضر، روغنهای اسانسی نعناع فلفلی (*Menthapiperita*) به روش‌های OAHD و MAHD استخراج و فعالیت آنتی‌اکسیدانی آنها با روغن‌های اسانسی حاصل از روش‌های SD و HD مقایسه شد. نتایج حاکی از آن بود که روش‌های OAHD و MAHD سبب کاهش زمان استخراج (تا ۷۲ درصد) و نیز انرژی الکتریکی لازم می‌شوند. علاوه بر این، تمام روغن‌های اسانسی استخراج شده دارای خواص فیزیکی (دانسیته نسبی و رنگ) و فعالیت آنتی‌اکسیدانی (روشهای DPPH و رنگبری بتا-کاروتن) تقریباً یکسانی بودند. یافته‌های این تحقیق نشان داد روغن اسانسی نعناع فلفلی حاصل از روش‌های OAHD و MAHD را می‌توان به عنوان فراورده‌ای آنتی‌اکسیدانی در مواد غذایی و دارویی مورد استفاده قرار داد.

واژه‌های کلیدی: روغن‌های اسانسی، تقطیر با آب، نعناع فلفلی، امواج مایکرو، تقطیر مقاومتی، تقطیر با بخار آب.

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Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 738-746

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۴۶-۷۳۸

Effect of Whey Protein- Rice Bran Oil Incorporated *Zataria multiflora* Extract Edible Coating on Chemical, Physical and Microbial Quality of Chicken Egg

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Received: 2015.09.19
Accepted: 2016.04.09

Abstract

In this study, the effects of coating with whey protein concentrate (7.5% w/v) alone and/or in combination with rice bran oil and *Zataria multiflora* extract on the quality attributes and egg shelf life were observed and analyzed during 4 weeks. Weight loss, Haugh index, yolk index, pH, air cell depth, shell strength and the impact of this coating on the microbial load of the eggs surface were studied at the end of each week. After 4 weeks of storage, the weight loss in all of the treated eggs with whey protein concentrate and 0.2 gr of rice bran oil was significantly lower than that of the control group($P<0/05$). Regards to Haugh index and yolk index, egg shelf life increased about 4 weeks compared with the control samples. Haugh Index changes revealed that the coated samples remained at grade A after 3 weeks of storage, while the control samples were relegated from grade AA to B after one week. pH values of the control group were higher than those of the coated groups. The shell strength of the coated group was more than that of the control group (uncoated) and in coated samples, whey protein concentrate and 0.2 gr of rice bran oil coated samples had high shell strength. The depth of the air cell of the coated groups was determined to be less than that of the control group during the storage period. The minimum inhibitory concentration was 1 µL of *Zataria multiflora* extract. In sensory evaluation, the coated eggs had more overall acceptance than the uncoated group. In conclusion, coating as a practical and cost effective method can maintain the quality parameters of eggs and lead to durability of supply conditions in addition to the product marketability

Keywords: Edible coating, chicken egg, whey protein concentrate, rice bran oil, *Zataria multiflora* extract, Shelf life.

Introduction

Nowadays, edible films have revolutionized food packing industry. There have been quite number of studies on the importance of such packing.

The aim of food packaging is to preserve the quality and safety of the food. The concern about packaging waste has led the world to establish a directive to reducing the impact of packaging waste on the environment. Edible films and coatings offer an efficient alternative for packaging which provides barriers to moisture, gas or solute, improve mechanical integrity of foods, transports food ingredients and is completely biodegradable, reducing thus environment pollution (Yoshida et al., 2004). The film-forming properties of several proteins have been utilized in developing edible, protective films and coatings (Gennadios et al., 1994). Edible films and coatings derived from whey protein have been investigated for their application as new packaging (Javanmard and Golestan, 2007, Javanmard 2007, 2008).

Many applications for protein-based edible films have been proposed but little attention has been paid to the feasibility of using these films in real food systems. Edible film wraps may be able to partially replace some conventional synthetic packaging materials used to preserve and protect foods (O'Riordan *et al.* 2005).

There is a growing consumer preference for natural agents which have been isolated from microbiological, plant, and animal sources.

Active substances of biological origin have a powerful wide-spectrum activity with low toxicity, and are expected to be used for food

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preservation as a means of antimicrobial packaging. *Zataria multiflora* Boiss belonging to Laminaceae family is a local plant in Iran.

Traditionally it is used as flavor especially for yoghurt.The main oil essence compound of it is carvacrol and thymol (Aligiannis *et al*., 2001).

Eggs are a good source of high quality protein and provide a unique and well-balanced source of nutrients for persons of all ages. Maintaining fresh egg quality from producer to consumer is one of the major problems facing those engaged in marketing eggs. While a considerable amount of research has been conducted with films made from milk proteins on fruits and vegetables and other dairy foods, there are limited studies addressing the application of these films on eggs. Mpieri and Obanu (1984) investigated the efficiency of peanut oil, cottonseed oil and coconut oil in maintaining egg quality under tropical conditions. Hettiarachy *et al*. (2002) studied effects of edible coatings containing serum proteins, carboxymethyl cellulose, gluten and soy protein isolates on the egg with the mechanical and antibacterial properties. Alleonil and Aloisio (2004) used a milk serum protein concentrate coating on the internal quality of eggs.

Biladeau and Keener (2009) determined effects of four coatings on eggs may extend shelf-life under refrigerated storage. Four food-grade coatings, paraffin wax, mineral oil, soy protein isolate, and whey protein isolate (WPI) were selected. Suppakul *et al*. (2010) were examined the effect of coating with methylcellulose and hydroxypropyl methylcellulose on the strength and permeability of water vapor in eggs. Wardy et al. (2010) evaluated the ecacy of soybean oil compared to chitosan, whey protein concentrate (WPC) and mineral oil as coating materials for extending the she lf life of chicken eggs.

The objective of this study was to coat eggs with whey protein-rice bran oil and Zataria multiflora extract and observe the changes of chemical, physical and microbiological properties of the whole coated egg.

Materials and methods

Whey protein Concentrate (WPC 85% protein) supplied by Arla Foods (Videbaek Denmark), rice bran oil obtained from Etka Company (Manjil-Iran), and Glycerol (Gly) (Merk) was added as a plasticizer to all film-forming solutions. Chicken egg was supplied from Tehran Super star mall. *Zataria multiflora* was purchased from local market in Shiraz-Iran.

Film formation

Heat-denatured WPC films were prepared using the Shaw N.B. *et.al*. Method (2002). Aqueous solution of 7.5% (w/w) WPC was prepared and was stirred continuously on a magnetic stirrer at room temperature for 2h. To prepare heat-denatured coating, WPC solutions were heated at 90°C for 30 min in a water bath. Heated solutions were cooled to room temperature and adjusted to pH 7.0 with drop-wise addition of 1N NaOH. Gly was added to film-forming solutions to give glycerol: protein (Gly: Pr) ratios (w/w) of 1/2 and this ratio was kept constant throughout the study. The rice bran oil was added in the amounts of 0.2, 0.4, and 0.6 g in 100 ml coating solution to the heat denatured WPC solution containing glycerol. Zataria multiflora extract (1 and 2 µL in 100 ml coating solution) was added to the solutions. Whole eggs dipped in coating solutions and were allowed to dry at room temperature over 1h and then all samples stored for 28 days at room environment temperature and humidity (table 1).

Determination of weight loss

Before and after preservation, the samples were weighed in cold storage with a digital scale BA 310S model (Sartorius, Germany) with the precision of 0.01 gram Quauz GT 2100 and their weight loss because of dehydration was determined and reported in percentages.

Determination of air cell depth

The air cell depth of eggs was measured by a digital clipper using a bright light source

behind the egg to show egg air cell through the shell (candling). A very simple candling device was made in our Lab using (Kekeocha method, 1985), that is, placing a lamp in a dark chamber (paper box) and positioning an egg on top of the chamber in a hole and looking at the interior quality.

pH Measurements

The albumen and yolk were separated and pH was measured using a model 220 Denver Instrument pH meter (Denver Instrument, Denver, CO).

Shell strength measurement

Shell strength was analyzed on an egg shell force Gauge –Model-2 texture analyzer (Japan). The eggs were placed in a 1.3- cm diameter polyvinyl chloride cap with the blunt and round tips of the eggs being horizontal and 90 º from the 70-cm diameter cylinder probe when contact was made with the sides of the egg.

Haugh unit

Haugh unit was calculated by the following formula:

Haugh unit=100 log (H - 1.7 $G^{0.37}$+ 7.6)

Where H is the height of the thick albumen in millimeters and G is the mass of the whole egg in grams. The parameter H was estimated by averaging three measurements carried out in different points of thick albumen at the distance of 10 mm from the yolk using a digital caliper.

Yolk index

Yolk index was calculated as yolk height /yolk width. Yolk width was measured by a digital caliper.

Microbial analysis

Microbial analysis of aerobic mesophilic bacteria was carried out on the day of arrival and a month after the storage for each sample using the procedure by AOAC. For mesophilic aerobic plate counts, the whole egg samples were washed with sterile peptone water (diluted 1:10) and the subsequent dilutions were prepared by mixing a 1-ml sample with 9 ml of sterile peptone water. For bacterial counts, 0.1 ml of selected dilutions was spread on plates containing solid nutrient agar (Merck) and incubated for 24–48 h at 35 °C. Microbial counts were expressed as the number of viable bacterial colonies per egg (log CFU/egg). Minimum inhibition concentration was determined using the research results by Ramazan and Javanmard (2011).

Sensory analysis

To investigate the sensory characteristics of the eggs, 5-Point Hedonic Scale was used. 10 trained panelists (IROST staffs and postgraduate students) evaluated the egg surface transparency and shell gloss, shell smell and odor, broken eggs smell and odor and finally the overall acceptability. In this test, scores were of 1 to 5 for excellent and the least characteristic, respectively.

Statistical analysis

Data from microbial properties, weight loss, pH , Haugh unit, egg air cell height, egg shell strength and sensory properties were subjected to an analysis of different coating formulations and coated eggs compared with uncoated and storage time (0.0, 1,2, 3, 4 weeks) by simple and interaction effects using ANOVA. The comparison of means was according to Post Hoc multiple test .

Results and discussions

Table 2 shows weight loss changes of control and coated eggs during storage. The greatest water loss occurred in control uncoated eggs (6.122±0.380 %) after 4 weeks of storage. Coated eggs led to minimum weight loss. Increasing the rice bran oil content had a significant effect on the weight loss of the eggs. The results agree with the findings of Wardy *et al*. (2010) which shows that coating of eggs can be effective in minimizing the weight loss during 5 weeks storage but coating formulation with WPC and rice bran oil in this research revealed less weight loss (table 2).

Whey protein films may exhibit poor misture barrier properties because of their

hydrophilicity. But WPC and rice bran oil coatings obviously rendered excellent sealing properties , and their hydrophobicity confers good moisture barrier properties for eggs destined for extended storage at room temperature.

The shell strength of a chicken egg is an important economic consideration. (Wang *et al.* 1996). The results from this study found significant ($P<0.05$) change in shell strength during storage. The strongest shell strength belonged to coating containing whey protein concentrate and 2 grams of rice bran oil. The other coated eggs and the uncoated eggs had less strength and there was no significant difference between them. Increasing concentrations of rice bran oil in coating formulations decreased egg shell strength. Wang *et al.* (1996) showed that protein based edible coating exhibit the least moisture loss, the strongest shell strength and coated eggs maintained a higher Haugh unit.

Air cell depth increased depending on the storage time and the size of eggs, and even it reached 16 mm. The depth of the air cell is a rough indication of the age of the egg and there is often a relation between this depth and the internal quality. Results showed that the depth of the air cell for the coated eggs were significantly ($P <0/05$) lower than that of the control group (Table 3). The mean air cell depth in the control uncoated eggs were found to be 13.167±1.041 mm after 4 weeks of storage. Coating containing whey protein concentrate and 2 grams of rice bran oil showed the least depth of the air cell.

Haugh unit between 20 and 100 for albumin is estimated to be inappropriate (unsuitable) and excellent quality respectively for human consumption. More haugh unit represents a better quality of albumin. The results of the changes in the haugh units are shown in table 4. There was downward trend of Haugh unit over the 4-week storage period in control and treated samples. This result agree with the findings of Wardy *et al*. (2010) that found the Haugh unit significantly decreased by increasing storage periods at both 25^{oC} and 4^{oC}.

The albumen height decrease during storage is attributed to the proteolysis of ovomucin and cleavage of disulphide bonds and interactions with lysozyme (Stevens, 1996). The lowest haugh unit was in the control group (44.827±14.726) after 4 weeks of storage. Coated eggs with WPC+0.2 Rice bran oil+ 1µL Z. multiflora extract showed the highest haugh unit (63/948±5.257). Haugh unit >72, 60 to 72 and 31 to 60 demonstrated AA, A and B, respectively. Eggs coated with WPC-Rice bran oil incorporated with Zataria multiflora had significantly higher Haugh units than those of uncoated samples. Compared with coated eggs, uncoated eggs gained B grade at the end of the first week, while all coated eggs maintained A grade quality up to the end of the 2 weeks of storage. The incorporation of rice bran oil in coating formulation significantly increased Haugh units in the eggs (Table 4).

The primary yolk index of eggs was 0.37± 0.02 on the first day of study. The yolk index decreased from 0.310±0.010 to 0.240±0.010 for the control uncoated eggs after 4 weeks of storage. All coated eggs after 4 weeks of storage showed significantly ($P<0.05$) higher yolk index than the control uncoated eggs. Among coated eggs, only those coated with 0.2 rice bran oil showed significantly higher yolk index (Table 5). The yolk index decrease due to weakening of the membranes and liquefaction of the yolk was caused mainly by water diffusion from the albumen (Obanu and Mpieri, 1984).

Nutrient Broth was used to determine the minimum inhibition concentration of the extract. 1 µL of Zataria multiflora extract was selected to be the effective dose. Initial total mesophilic counts on the whole egg surface were 2.32±0.18 log10 CFU. After 4 weeks of storage the mean bacterial loads on the surface of uncoated eggs (control) was 2.76±0.23 log10 CFU. The coated samples W, W+0.2 R, W+0.4 R, W+0.6 R, W+0.2 R+Z1, W+0.2 R+Z2, W+0.4 R+Z1, W+0.4 R+Z2, W+0.6 R+Z1 and W+0.6 R+Z2 showed 1.47, 1, 0.49, 0.5, 0.51, 0.0, 0.21, 0.0,0.0 and 0.0 log10 CFU total mesophilic counts, respectively.

Eggs albumen pH is an important value of

egg quality and freshness. In this research (Table 6), changes in pH of coated and uncoated eggs were significant (interactions between coating treatment s *storage time, $P < 0.05$).

Table 7 shows the sensory evaluations of the control uncoated and coated eggs in different WPC, rice bran oil and Zataria multiflora extract. After 21 days of storage, concentrations of rice bran oil in coating formulations gave no significant difference in the surface shell smoothness of the eggs (Table 7). Adding 0.4 and 0.6 rice bran oil showed significant effect on in shell gloss (opacity). The broken egg smell and overall acceptability of the coated eggs with 0.6 rice bran oil and 2µL Zataria multiflora extract had significantly ($P < 0.05$) lower points than those of the control and other treatments. There was no significant difference in the shell smell of the coated eggs and the uncoated ones (control).

Table 1. Sample preparation and treatment

Sample	Treatment
Control	Uncoated eggs
W	Coated with WPC
W+0.2 R	WPC+0.2 Rice bran oil
W+0.4 R	WPC+0.4 Rice bran oil
W+0.6 R	WPC+0.6 Rice bran oil
W+0.2 R+Z1	WPC+0.2 Rice bran oil+ *Z. multiflora* extract 1µL
W+0.2 R+Z2	WPC+0.2 Rice bran oil+ *Z. multiflora* extract 2µL
W+0.4 R+Z1	WPC+0.4 Rice bran oil+ *Z. multiflora* extract 1µL
W+0.4 R+Z2	WPC+0.4 Rice bran oil+ *Z. multiflora* extract 2µL
W+0.6 R+Z1	WPC+0.6 Rice bran oil+ *Z. multiflora* extract 1µL
W+0.6 R+Z2	WPC+0.6 Rice bran oil+ *Z. multiflora* extract 2µL

Table 2. Weight loss (%)* changes in eggs coated and uncoated within 4 weeks of storage at ambient conditions

	Storage time (week)			
	1	2	3	4
Control	0.724 ± 0.210^{ax}	1.538 ± 0.177^{bz}	3.935 ± 0.684^{cn}	6.122 ± 0.380^{dk}
W	0.487 ± 0.156^{ay}	1.096 ± 0.122^{bw}	2.426 ± 0.104^{ep}	3.697 ± 0.513^{cn}
W+0.2 R	0.420 ± 0.199^{ay}	1.036 ± 0.124^{bw}	2.171 ± 0.828^{ep}	3.249 ± 1.266^{cm}
W+0.4 R	0.677 ± 0.260^{ax}	1.329 ± 0.188^{bw}	2.407 ± 0.343^{ep}	3.220 ± 0.442^{cm}
W+0.6 R	0.729 ± 0.055^{ax}	1.490 ± 0.191^{bw}	2.696 ± 0.347^{eq}	3.338 ± 0.248^{cm}
W+0.2 R+Z1	0.468 ± 0.183^{ay}	1.010 ± 0.095^{bw}	2.173 ± 0.339^{ep}	3.358 ± 0.382^{cm}
W+0.2 R+Z2	0.700 ± 0.131^{ay}	1.148 ± 0.087^{bw}	2.155 ± 0.168^{ep}	3.402 ± 0.722^{cm}
W+0.4 R+Z1	0.469 ± 0.148^{ay}	1.042 ± 0.071^{bw}	2.146 ± 0.711^{ep}	3.412 ± 0.288^{cm}
W+0.4 R+Z2	0.514 ± 0.097^{ay}	1.047 ± 0.057^{bw}	2.183 ± 0.174^{ep}	3.250 ± 0.255^{cm}
W+0.6 R+Z1	0.481 ± 0.207^{ay}	1.254 ± 0.267^{bw}	2.290 ± 0.425^{ep}	3.492 ± 0.552^{cm}
W+0.6 R+Z2	0.518 ± 0.084^{ay}	1.145 ± 0.162^{bw}	2.365 ± 0.405^{ep}	3.321 ± 0.567^{cm}

*Means ± SD of 3 measurements

Table 3. Air cell depth (mm) changes in coated and uncoated eggs within 4 weeks of storage at ambient conditions

Treatments	Storage time (week)				
	0	1	2	3	4
Control	2.750 ± 0.354^{bs}	5.533 ± 0.503^{ev}	7.000 ± 1.000^{gx}	8.500 ± 0.500^{hy}	13.167 ± 1.041^{jo}
W	2.500 ± 0.000^{bs}	$3.167\pm.289^{ct}$	4.000 ± 0.000^{du}	6.000 ± 0.000^{fw}	$9.000\pm.000^{iz}$
W+0.2 R	2.500 ± 0.000^{ar}	2.833 ± 0.289^{bs}	3.500 ± 0.500^{ct}	4.333 ± 0.764^{du}	5.000 ± 1.000^{ev}
W+0.4 R	2.500 ± 0.000^{bs}	3.667 ± 0.764^{ct}	5.167 ± 0.764^{ev}	5.667 ± 0.764^{ev}	7.167 ± 0.764^{gx}
W+0.6 R	2.750 ± 0.354^{bs}	4.000 ± 1.000^{du}	6.167 ± 0.289^{fw}	6.167 ± 1.258^{fw}	7.500 ± 0.500^{gx}
W+0.2 R+Z1	3.250 ± 1.061^{ct}	4.000 ± 0.500^{du}	5.000 ± 0.500^{ev}	6.500 ± 0.500^{fw}	7.833 ± 1.607^{gx}
W+0.2 R+Z2	3.250 ± 0.354^{ct}	3.667 ± 0.764^{ct}	5.750 ± 0.354^{ev}	5.333 ± 0.764^{ev}	8.500 ± 0.866^{hy}
W+0.4 R+Z1	2.750 ± 0.354^{bs}	4.500 ± 0.500^{du}	6.000 ± 1.000^{fw}	6.833 ± 1.041^{fw}	9.333 ± 1.528^{iz}
W+0.4 R+Z2	2.833 ± 0.764^{bs}	3.750 ± 1.061^{ct}	4.833 ± 1.041^{du}	6.500 ± 0.500^{fw}	8.833 ± 0.764^{hy}
W+0.6 R+Z1	2.500 ± 0.707^{bs}	3.833 ± 0.764^{ct}	5.167 ± 0.289^{ev}	7.000 ± 0.500^{gx}	9.167 ± 1.041^{iz}
W+0.6 R+Z2	3.167 ± 0.764^{bs}	4.000 ± 0.500^{du}	5.667 ± 1.155^{ev}	6.667 ± 0.764^{fw}	8.667 ± 0.289^{hy}

Means with same superscript are not significantly different ($P > 0.05$).

Table 4. Haugh units (±SD) and grades changes in eggs coated and uncoated within 4 weeks of storage at ambient conditions

Treatments	Storage time (week)				
	0	1	2	3	4
Control	74.6 ± 6.834	67.421±6.940 ^{ax*} A**	59.206±7.225 ^{bz} B	53.088±15.129 ^{a} B	44.827±14.726^{bz} B
W		68.210±7.180 ^{cy} A	64.355±4.370 ^{ax} A	54.635±9.908 ^{bz} B	50.820±5.227 ^{bz} B
W+0.2 R		76.988±7.979 ^{cy} AA	76.502±8.901 ^{cy} AA	70.309±4.721 ^{ax} A	51.645±6.690 ^{bz} B
W+0.4 R		80.217±2.992^{cy} AA	65.990±3.854 ^{ax} A	60.640±2.606^{axz} A	53.939±12.137^{bz} B
W+0.6 R		73.593±2.984 ^{cy} AA	66.223±7.773 ^{ax} A	65.539±7.070 ^{ax} A	51.767±5.930 ^{bz} B
W+0.2 R+Z1		74.940±13.169 ^{ax} AA	60.377±12.854^{ax} A	66.812±12.196 ^{ax} A	63.948±5.257 ^{ax} A
W+0.2 R+Z2		75.652±3.099 ^{cy} AA	72.467±10.741^{cy} AA	65.792±8.156 ^{ax} A	52.170±0.700 ^{bz} B
W+0.4 R+Z1		77.844±9.794 ^{cy} AA	65.236±2.037 ^{ax} A	63.531±4.269 ^{ax} A	50.622±17.283^{bz} B
W+0.4 R+Z2		73.546±9.173 ^{cy} AA	65.057±5.622 ^{ax} A	62.914±10.766^{ax} A	52.210±4.450 ^{bz} B
W+0.6 R+Z1		72.374±5.164 ^{cy} AA	64.970±2.900 ^{ax} A	60.972±2.187^{axz} A	53.888±10.462^{bz} B
W+0.6 R+Z2		73.077±4.849 ^{cy} AA	60.861±8.85^{ax} A	60.034±21.791^{axz} A	48.591±14.717^{bz} B

* Means with same superscript are not significantly different ($P > 0.05$).

**A and B indicate degree of the eggs depend of Hu

Table 5. Yolk index (±SD) changes in coated and uncoated eggs within 4 weeks of storage at ambient conditions

Treatments	Storage time (week)				
	0	1	2	3	4
Control	0.37± 0.02	0.310±0.010^{ax}	0.280±0.010^{cy}	0.267±0.006^{dz}	0.240±0.010^{dz}
W		0.347±0.006^{bw}	0.320±0.010^{ax}	0.303±0.006^{ax}	0.283±0.006^{cy}
W+0.2 R		0.360±0.010^{bw}	0.350±0.010^{bw}	0.313±0.006^{ax}	0.307±0.006^{ax}
W+0.4 R		0.350±0.010^{bw}	0.330±0.000^{bx}	0.317±0.006^{ax}	0.287±0.006^{cy}
W+0.6 R		0.340±0.010^{bw}	0.320±0.010^{ax}	0.297±0.006^{cy}	0.280±0.010^{cy}
W+0.2 R+Z1		0.357±0.006^{bw}	0.343±0.006^{bw}	0.317±0.006^{ax}	0.303±0.006^{ax}
W+0.2 R+Z2		0.347±0.006^{bw}	0.330±0.010^{bx}	0.303±0.006^{ax}	0.297±0.006^{cy}
W+0.4 R+Z1		0.340±0.010^{bw}	0.320±0.010^{ax}	0.307±0.006^{ax}	0.280±0.000^{cy}
W+0.4 R+Z2		0.338±0.013^{bw}	0.320±0.010^{ax}	0.303±0.006^{ax}	0.293±0.006^{cy}
W+0.6 R+Z1		0.320±0.010^{ax}	0.297±0.015^{cy}	0.290±0.010^{cy}	0.277±0.006^{cy}
W+0.6 R+Z2		0.323±0.006^{ax}	0.303±0.006^{ax}	0.293±0.006^{cy}	0.267±0.006^{dz}

Means with same superscript are not significantly different ($P > 0.05$).

Table 6. Albumen pH (±SD) changes in coated and uncoated eggs within 4 weeks of storage at ambient conditions

Treatments	Storage time (week)			
	1	2	3	4
Control	9.031±0.217^{va}	9.117±0.147^{wd}	9.243±0.112^{wd}	9.557±0.120^{z}
W	7.977±0.232^{va}	8.983±0.310^{yc}	8.280±0.602^{xc}	9.197±0.164^{w}
W+0.2 R	7.840±0.227^{va}	8.500±0.066^{xyc}	8.933±0.100^{yc}	9.143±0.130^{w}
W+0.4 R	8.270±0.132^{xb}	9.010±0.272^{wd}	9.060±0.066^{wd}	9.157±0.064^{w}
W+0.6 R	8.897±0.175^{yc}	8.877±0.404^{yc}	9.207±0.078^{wd}	9.237±0.085^{w}
W+0.2 R+Z1	8.213±0.040^{xb}	9.177±0.196^{wd}	9.033±0.131^{wd}	9.333±0.187^{w}
W+0.2 R+Z2	8.307±0.119^{xb}	8.987±0.364^{yc}	9.163±0.070^{wd}	9.267±0.156^{wd}
W+0.4 R+Z1	8.520±0.391^{yc}	8.683±0.115^{yc}	9.153±0.242^{wd}	9.187±0.059^{wd}
W+0.4 R+Z2	8.527±0.460^{yc}	8.703±0.169^{yc}	9.083±0.263^{wd}	9.323±0.206^{wd}
W+0.6 R+Z1	8.973±0.194^{yc}	8.797±0.306^{yc}	9.073±0.150^{wd}	9.390±0.135^{wd}
W+0.6 R+Z2	8.583±0.452^{yc}	8.957±0.224^{yc}	9.200±0.202^{wd}	9.403±0.127^{wd}

Means with same superscript are not significantly different ($P > 0.05$).

Table 7. Sensory properties of coated and uncoated eggs within 4 weeks of storage at ambient conditions

Traits \ Treatments	Control	W	W+0.2 R	W+0.4 R	W+0.6 R	W+0.2 R+Z1	W+0.2 R+Z2	W+0.4 R+Z1	W+0.4 R+Z2	W+0.6 R+Z1	W+0.6 R+Z2
Shell smoothness	3.2^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3.2^{a}	3.2^{a}	3^{a}	3.2^{a}	3.2^{a}	3^{a}
Shell gloss	3.2^{a}	3^{a}	3.2^{a}	2.6^{b}	2.6^{b}	3^{a}	3.2^{a}	3.6^{a}	3^{a}	2.8^{b}	2.8^{b}
Shell smell	3.2^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3.2^{a}	3.2^{a}	3^{a}	3^{a}	3.2^{a}	3^{a}
Broken egg smell	3^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3^{a}	2.8^{b}
Overall acceptability	3.4^{a}	3^{a}	3^{a}	3^{a}	3^{a}	3.2^{a}	3.2^{a}	3.2^{a}	3.2^{a}	3.6^{a}	2.8^{b}

Conclusion

Edible WPC-rice bran oil containing Zataria multiflora essential oils were tested for their application as an antimicrobial edible coating on eggs. The results indicate that adding rice bran oil to WPC films makes them more perceptible in a food system while maintaining moisture and oxygen barrier, certain tensile properties as well as the improvement of the shelf life of the eggs. Adding the essential oils of Zataria multiflora as active substances of biological origin have also a powerful wide-spectrum activity against microbial load on egg surface. This edible coating can fulfill a packaging function in real food applications.

Acknowledgment

We would like to thank IROST for the equipment support, and we would also wish to express our sincere thanks to Asre- Enghelab Research Center for their cooperation in the completion of this study.

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نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۴۶-۷۳۸

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 738-746

تأثیر پوشش خوراکی پروتئین آب پنیر حاوی عصاره آویشن شیرازی و روغن سبوس برنج بر کیفیت شیمیایی، فیزیکی و میکروبی تخم‌مرغ

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تاریخ دریافت:۱۳۹۴/۰۶/۲۸
تاریخ پذیرش:۱۳۹۵/۰۱/۲۱

چکیده

هدف از این تحقیق، استفاده از پوشش خوراکی فعال بر پایه پروتئین آب پنیر حاوی روغن سبوس برنج و ترکیب ضدمیکروبی عصاره آویشن شیرازی، به منظور بهبود خواص فیزیکی و شیمیایی، میکروبی و استحکام ساختاری تخم‌مرغ در برابر شکستگی و بطور کلی افزایش کیفیت و ماندگاری تخم‌مرغ می‌باشد. در این پژوهش، تأثیر پوشش‌دهی با کنسانتره پروتئین آب پنیر به تنهایی و در ترکیب با روغن سبوس برنج و ترکیب ضدمیکروبی عصاره آویشن شیرازی بر روی ویژگی‌های کیفی و ماندگاری تخم‌مرغ بررسی شد .نتایج نشان داد که میزان درصد کاهش وزن در همه گروه‌های پوشش داده شده به طور معنی‌داری ($P< ۰/۰۵$) کمتر از گروه شاهد (فاقد پوشش) است. ماندگاری تخم‌مرغ نیز با توجه به میزان اندیس Haugh و اندیس زرده حدود ۴ هفته نسبت به نمونه‌های شاهد افزایش یافت . استحکام پوسته گروه‌های پوشش‌دار بیشتر از گروه کنترل بود . .حداقل غلظت ممانعت کنندگی عصاره آویشن شیرازی در محیط کشت ۱میکرولیتر بود. غلظت ۱ میکرولیتر عصاره آویشن شیرازی باعث کاهش بار میکروبی کل سطح پوسته تخم‌مرغ تا ۸۷ ٪ گردیده و غلظت ۲ میکرولیتر، بار میکروبی کل را به صفر کاهش داد. در ارزیابی‌های حسی، از نظر گروه ارزیاب، تخم‌مرغ‌های پوشش دیده نسبت به گروه پوشش ندیده (شاهد) پذیرش نهایی بیشتری داشته و در میان تیمارها نیز تخم مرغ های پوشش دیده حاوی درصد پائین روغن سبوس برنج، پذیرش نهایی بیشتری از نظر مصرف‌کنندگان داشته است. بطور کلی استفاده از روش پوشش دهی به عنوان یک روش کاربردی و مقرون به صرفه، می‌تواند باعث حفظ پارامترهای کیفی در تخم‌مرغ شده و علاوه بر حفظ بازارپسندی محصول، منجر به افزایش ماندگاری در شرایط عرضه آن گردد.

واژه‌های کلیدی: پوشش خوراکی، تخم‌مرغ، کنسانتره پروتئین آب پنیر، عصاره آویشن شیرازی، ماندگاری

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Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 747-757

نشریه پژوهشهای علوم و صنایع غذایی ایران
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Prediction of Papaya fruit moisture content using hybrid GMDH - neural network modeling during thin layer drying process

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Received: 2015.11.23
Accepted: 2013.03.05

Abstract

In this work, a hybrid GMDH–neural network model was developed in order to predict the moisture content of papaya slices during hot air drying in a cabinet dryer. For this purpose, parameters including drying time, slices thickness and drying temperature were considered as the inputs and the amount of moisture ratio (MR) was estimated as the output. Exactly 50% of the data points were used for training and 50% for testing. In addition, four different mathematical models were fitted to the experimental data and compared with the GMDH model. The determination coefficient (R^2) and root mean square error (RMSE) computed for the GMDH model were 0.9960 and 0.0220,and for the best mathematical model (Newton model) were 0.9954 and 0.0230, respectively. Thus, it was deduced that the estimation of moisture content of thin layer papaya fruit slices could be better modeled by a GMDH model than by the mathematical models.

Keywords: Drying process; GMDH; Mathematical Modeling; Papaya fruit; Neural Network

Introduction

Papaya (*Carica papaya* L.) also called papaw is a tropical fruit that is widely cultivated and consumed, both for its agreeable flavor as well as its many pharmacological properties (De Oliveira and Vitória, 2011). Papaya is rich in vitamin C, K+, carotenoid and fiber content and has been considered as a top-ranking fruit (Liebman, 1992). FAO reported that papaya has been ranked third with 11.2 million tons or 15.36 percent of the total tropical fruit production in 2010.

Water is one of the major food components which affects on many physico-chemical and biological attributes. The amount of moisture content has a decisive effect on the quality of foodstuffs. Drying due to reducing the moisture content or making water hard to access, is of the most effective operations to reduce the spoilage of agricultural products (Izadifar and Mowla, 2003).

In characterizing the drying parameters, the thin-layer drying procedure was found to be the most feasible tool (Aghdam *et al.*, 2015). Different types of models have been used by several researchers to predict the moisture content/drying rate of food materials which finally led to different expression for the prediction (Dinani *et al.*, 2014; Kingsly and Singh, 2007; Koukouch *et al.*, 2015; Wang *et al.*, 2007; Yousefi *et al.*, 2013a; Yousefi *et al.*, 2013b). Most of these models are mathematical ones which classified to theoretical, semi-theoretical and empirical models (Demirtas *et al.*, 1998; Midilli *et al.*, 2002). Lately, a new predictive method based on artificial neural networks systems (ANNs) has been used to model the drying process of different food and agricultural products like potato and green pea (Kamiński *et al.*, 1998), Echinacea angustifolia (Erenturk *et al.*, 2004), grain (Liu *et al.*, 2007), tomato (Movagharnejad and Nikzad, 2007), shelled corn (Momenzadeh *et al.*, 2011) and pomegranate arils (Nikbakht *et al.*, 2014). The ANNs are mostly considered as nonlinear and highly flexible universal approximators (Park and Sandberg, 1991; Powell, 1987). Nonetheless, its main drawback is that the detected dependencies are concealed behind neural network structure (Nariman-Zadeh and Jamali, 2007). Contrarily, the group method of

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data handling (GMDH) is applied to develop a model which is hidden in the empirical data (Ivakhnenko, 1971). The GMDH method was originated by Ivakhneko in 1966 and it has been improved and evolved over the past 40 years. The GMDH algorithm connects the inputs to outputs with high order polynomial networks which are mainly feed-forward and multi-layered neural networks (Onwubolu, 2009). In this approach, the nodes are hidden units and the activation polynomial coefficients are weights which are estimated by ordinary least square regression (Ghanadzadeh *et al.*, 2012; Onwubolu, 2009). In recent years, however, the use of such self-organized networks has led to successful application of the GMDH-type algorithm in a wide range of areas in engineering and science (Abdolrahimi *et al.*, 2014; Ahmadi *et al.*, 2007; Atashrouz *et al.*, 2015; Najafzadeh, 2015; Pazuki and Kakhki, 2013).

Based on the literature review, no specific study was found to be associated with the estimation of moisture content of papaya fruit using GMDH. Therefore, the purpose of this work was to undertake a study to investigate the thin-layer drying process of papaya slices in a cabinet drier and modeling of the experimental data using group method of data handling (GMDH) to estimate the moisture content of papaya fruit. In addition to GMDH, four well-known thin-layer empirical models were employed for the estimation, and finally the estimation quality of both types of models was evaluated and compared.

Materials and methods

Experimental Study

Papaya fruits used in this research were purchased from a local market in the Bahookalat region (Sistan & Baluchestan province, Iran) and stored in a refrigerator at 4 ± 1 °C before they were subjected to the drying process. The fruits were washed, peeled and cut into three thicknesses of 3, 5 and 7 mm. A cabinet dryer (Model JE10 TECH, F-02G, South Korea) with controllable airflow, temperature and air humidity monitoring systems was applied for the hot air drying process. The absolute humidity and the hot-air velocity for all drying temperatures were 0.6±0.02 g/kg dry air and 1±0.1 m/s, respectively. The schematic figure of the drying system used is shown in Fig. 1. The initial moisture content of papaya slices was measured using a laboratory oven dryer (Galenkamp, UK) operated at 105 °C. The initial moisture content obtained for the slices was 84.48%±0.05% (w. b.). During the drying period, the weight of the samples was recorded by programmable balance software at intervals of 5 min. The moisture content in the final product was 15±0.02% (w. b.). Drying was performed at three temperature levels of 40, 50 and 60 °C. Moisture ratio (MR) variations with time were plotted for various conditions. MR is defined by the equation:

$$MR = \frac{M - M_e}{M_0 - M_e} \quad (1)$$

Where M is the moisture content of the samples at any drying time and M0 is the initial moisture content. The moisture ratio equation was simplified to M/M0 as value of Me (equilibrium moisture content) is relatively small compared with that of M or M0 (Akgun and Doymaz, 2005).

Group Method of Data handling (GMDH):The Group method of data handling (GMDH) is a polynomial based model. According to the GMDH approach, each layer can be obtained from a quadratic polynomial function. Thus the input variables are projected to the output variable. The main goal in this method is finding of function, f, that project the input variables to the output variable.

Therefore, the output variable (Y_i) can be written from the input variables as the following form:

$$Y_i = f(X_{i1}, X_{i2}, X_{i3}, ..., X_{in}) \; i = (1, 2, 3, ..., M) \quad (2)$$

Where, X s are input variables. The structure of the GMDH can be obtained using the minimization of an objective function. The objective function can be written as:

$$\omega = \sum_{i=1}^{M} [Y(X_{i1}, X_{i2}, ..., X_i) - y_i]^2 \quad (3)$$

Where, in the above equation y_i is actual data.

The general function between the inputs and the output variables was proposed by Ivakhnekoin the following form (Ivakhnenko, 1968):

$$Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1}^{n}\sum_{j=1}^{n} a_{ij} X_i X_j + \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} a_{ijk} X_i X_j X_k + \ldots \quad (4)$$

In this work, a quadratic polynomials function with only two variables (neurons) is considered

$$Y = G(X_i, X_j) = a_0 + a_1 X_i + a_2 X_j + a_3 X_{ij} + a_4 X_i^2 + a_5 X_j^2 \quad (5)$$

Where, parameters ą can be calculated from the minimization of Eq. (3). The least squares technique from multiple regression analysis is applied to calculate these parameters which obtained from solution of the following matrix:

$$Aa = Y \quad (6)$$

Where, a is the vector of unknown parameters of the quadratic polynomial (Eq. (6)):

$$A = \{a_0, a_1, a_2, a_3, a_4, a_5\} \quad (7)$$

and

$$y = \{ y_1, y_2, y_3, \ldots, y_M \}^T \quad (8)$$

Where, y is the vector of the actual data.

$$A = \begin{bmatrix} 1 & X_{1p} & X_{1q} & X_{1p}X_{1q} & X_{1p}^2 & X_{1q}^2 \\ 1 & X_{2p} & X_{2q} & X_{2p}X_{2q} & X_{2p}^2 & X_{2q}^2 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & X_{Mp} & X_{Mq} & X_{Mp}X_{Mq} & X_{Mp}^2 & X_{Mq}^2 \end{bmatrix} \quad (9)$$

Therefore, the vector of unknown parameter is given as below:

$$a = (A^T A)^{-1} A^T Y \quad (10)$$

Results and discussions

The influence of drying factors (Time, Thickness and Temperature) and their interactions on MR is shown in Table 1. It can be observed that the influence of all factors and their interactions was statistically significant ($p<0.05$). In this work, hybrid GMDH-type neural network was developed for estimation of papaya fruit MR during drying in a cabinet dryer. The experimental data contained 390 points while 50% of these data points were randomly used for training and 50% for testing. To further check for any possibility of over-fitting, different ratios in a range from 1 to 9 with increment of 0.5 are consecutively tested to find the optimum value. No over-fitting and considerably lesser error were observed that can be justified by rough linearity of data set.

Fig 2 shows the optimal structure of GMDH–Neural Network model developed with one hidden layer. As it can be seen from Fig 2, the proposed model has one input layer, one middle layer and one output layer.

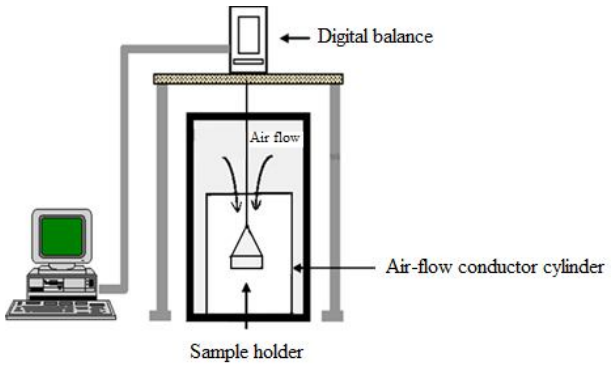

Fig. 1. Schematic figure of the drying system used.

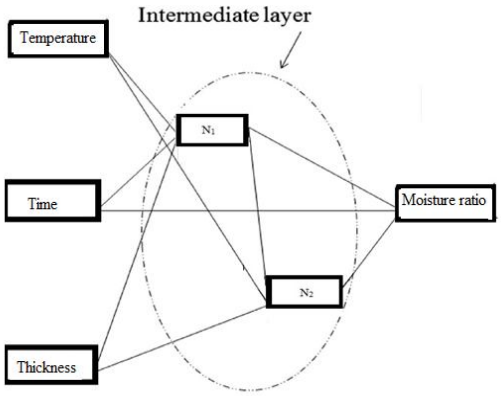

Fig.2. A schematic diagram of the GMDH model

Table 1. Effect of drying factors (Time, Thickness and Temperature) and their interactions on MR

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Temperature	.043	2	.021	350.386	.000
Thickness	.113	2	.056	922.568	.000
Time	4.937	3	1.646	26931.061	.000
Temperature* Thickness	.002	4	.000	7.023	.000
Temperature * Time	.005	6	.001	13.174	.000
Thickness * Time	.005	6	.001	13.447	.000
Temperature * Thickness * Time	.002	12	.000	2.629	.012
Error	.002	36	6.111E-005		
Total	18.785	72			
Corrected Total	5.109	71			

Generated functions corresponding to each node with total correlation function are reported in Table 2. It is worth meaning that all input variables were accepted by the model. In other words, the GMDH model provided an automated selection of essential input variables and built polynomial equations to model. These polynomial equations showed the quantitative relationship between input and output variables (Table 2). It should be noted that, the GMDH was modeled with three inputs (temperature (°C), thickness (mm) and time (min)) and three neurons in the hidden layer and one in the output layer (moisture ratio). The performance of the training and testing by the network were estimated by *AAD %* (Average Absolute Deviations) as bellow:

$$\% \ AAD = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{Y_i^{model} - Y_i^{actual}}{Y_i^{actual}} \right| \qquad (11)$$

Where, the superscripts of "model" and "actual" refer to the model and actual results, respectively. The actual and predicted results together with related Average Absolute Deviations Percent (AAD %) are reported in Table 3. This table demonstrated the differences between experimental data and GMDH model that clearly shows the reliability and accuracy of the proposed GMDH model in estimation of moisture ratio.

Moreover, the experimental and predicted values were compared in Fig. 3 and 4. As it can be observed, the results of the GMDH model were in very good agreement with the experimental data (R^2= 0.9960).

Some statistical tests can be used for determining the models accuracy and reliability of the GMDH model. These statistical values can be defined as shown in Table 4 and their values were calculated based on the output of the network. The high value of R^2 (0.9960) in addition with the low values of RMSE (0.022), MSE (0.00048) and MAD (0.0099) for GMDH model indicated the high performance of that for estimation of MR.

Fig 5 shows the sensitivity of moisture ratio to input variables. It is found that the sensitivity to the temperature was more than other inputs so that sensitivity of this parameter was near 40%. It can be concluded that the temperature has the most important role in this system.

In agreement with this result, the high sensitivity of many agricultural crops to drying temperature is reported using activation energy parameter (Kaleemullah and Kailappan, 2005; Park *et al*., 2002). Variation of MR with respect to drying time for the three temperatures and three thicknesses (experimental data) are shown in Fig 6 (a) and (b), respectively.

In addition with the GMDH modelling, the moisture ratio values obtained under various experimental conditions were subjected to four empirical mathematical models. Calculated R^2 and RMSE indicated that the Newton model was the best among the mathematical models considered for fitting the experimental data (Table 5).

The comparison between R^2 (0.9954) and RMSE (0.0230) of Newton and GMDH network models (R^2 = 0.9960, RMSE = 0.022)

demonstrated that GMDH predicted the closest data to the experimental ones.

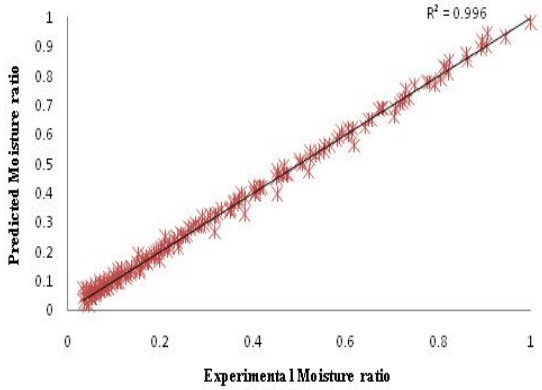

Fig. 3. Comparison of actual and predicted data by group method of data handling (GMDH).

Table 2. Polynomial equations for prediction of moisture ratio (MR) with GMDH model*

Nod 1	N_1 = 0.923027–Time×0.0071617–Time×Thickness×1.76534e-05+Time^2×1.43249e05+ Tem.×0.00609525+ Tem.×Thickness×0.00043174-Tem.^{2}×0.000178618
Node 2	N_2 = 0.059891+Tem.×8.72889e-05+Tem.×Thickness×4.42286e-05+Tem.×N_1×0.0058998-Tem.^{2}×2.32451e-05-Thickness×N_1*0.00692694+N_1×0.549558+N_1^2×0.260731
Output	Moisture ratio= -0.869111+Time×0.00743856+Time×N_1×0.0290015-Time×N_2×0.0415924-Time^2×1.2391e-05+N_2×3.34531–N_2^2×1.46832

*Variables' units (Tim (min), Thickness (mm), Temperature (°C)).

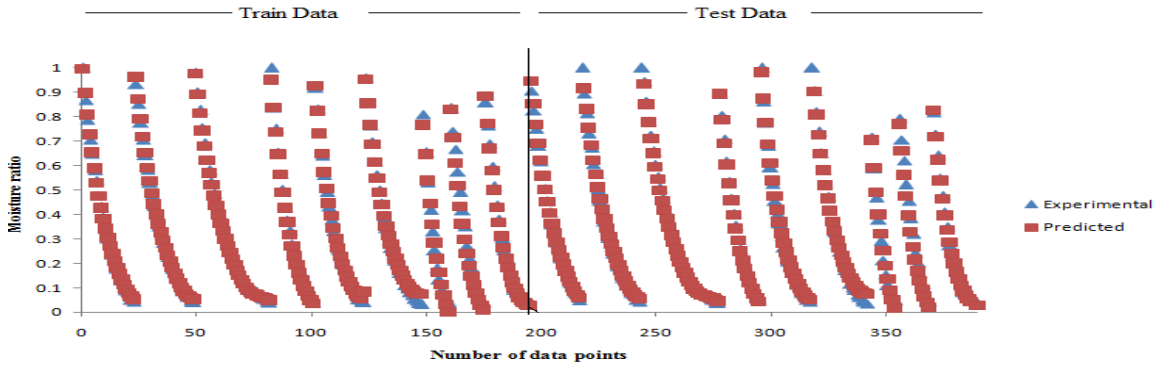

Fig. 4. Predicted moisture ratio plotted against data number

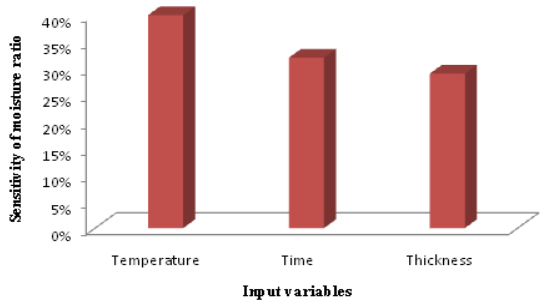

Fig. 5. Comparison of moisture ratio sensitivity with input variables.

Table 3. Comparison between GMDH model and experimental data based on computed average absolute deviation (AAD %) for summary of results

No.	Actual	Predicted(GMDH)	AAD%(GMDH)
1	1	0.995202	0.479838
2	0.868176	0.896439	3.255500
3	0.785821	0.807018	2.697410
4	0.704622	0.726257	3.070438
5	0.646416	0.653413	1.082482
6	0.579872	0.587718	1.353096
7	0.539785	0.528405	2.108246
8	0.477067	0.474735	0.488791
9	0.429248	0.426016	0.752928
10	0.388898	0.381618	1.871908
11	0.338726	0.340986	0.667144
12	0.301440	0.303642	0.730385
13	0.270976	0.269198	0.656167
14	0.235537	0.237348	0.769148
15	0.206465	0.207872	0.681891
16	0.176211	0.180628	2.506822
17	0.155078	0.155544	0.300634
18	0.12841	0.132612	3.272015
19	0.103101	0.111870	8.505066
20	0.088343	0.093395	5.719329
21	0.070668	0.077284	9.361598
22	0.050300	0.063633	26.50629
23	0.041000	0.052526	28.11122
24	0.932317	0.961745	3.156424
25	0.850333	0.871819	2.526847
26	0.774874	0.790389	2.002309
27	0.705421	0.716780	1.610281
28	0.641496	0.650269	1.367593
29	0.582659	0.590116	1.279865
30	0.528505	0.535594	1.34126
31	0.478662	0.486007	1.53462
32	0.432785	0.440714	1.832069
33	0.390561	0.399138	2.196197
34	0.351697	0.360777	2.581923
35	0.315926	0.325212	2.939219
36	0.283002	0.292106	3.216859
37	0.252699	0.261209	3.367482
38	0.224808	0.232349	3.354326
39	0.199137	0.20543	3.160208
40	0.175509	0.180423	2.799591
Total			03.63211

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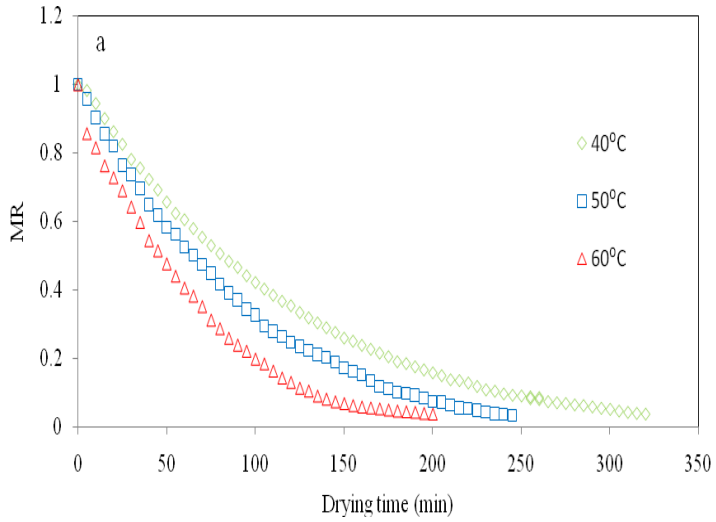
Table 4. Model statistics GMDH model for predicting moisture ratio

Statistics		Training	Testing
Absolute Fraction of variance (R^2)	$R^2 = 1 - \left[\sum_{i=1}^{N} (Y_i^{model} - Y_i^{actual})^2 / \sum_{i=1}^{N} (Y_i^{actual})^2 \right]$	0.9989	0.9960
Root Mean Square Error (RMSE)	$RMSE = \left[\sum_{i=1}^{N} (Y_i^{model} - Y_i^{actual})^2 / N \right]^{1/2}$	0. 017	0.022
Mean Square Error (MSE)	$MSE = \sum_{i=1}^{N} (Y_i^{model} - Y_i^{actual})^2 / N$	0.00029	0.00048
Mean Absolute Deviation (MAD)	$MAD = \sum_{i=1}^{N} \left\| Y_i^{model} - Y_i^{actual} \right\| / N$	0. 0081	0.0099



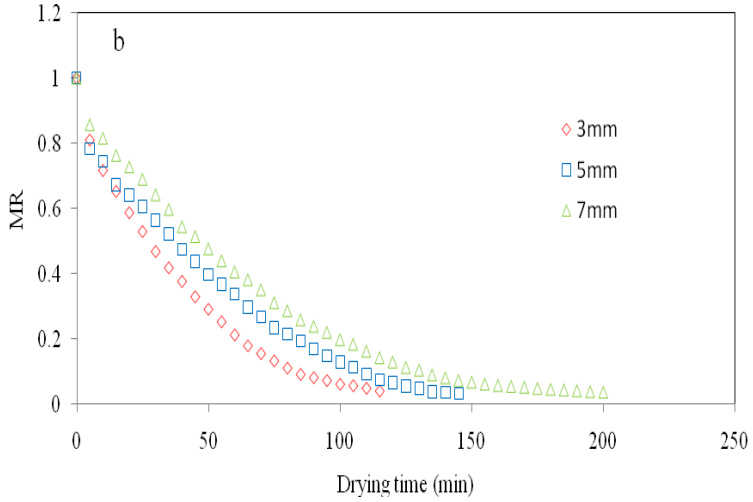


Fig. 6. (a) Effect of drying temperature on moisture ratio (MR) (for thickness of 7 mm), (b) effect of thickness on moisture ratio (MR) (for drying temperature of 60 °C).

Table 5. Statistical analyses for the mathematical models

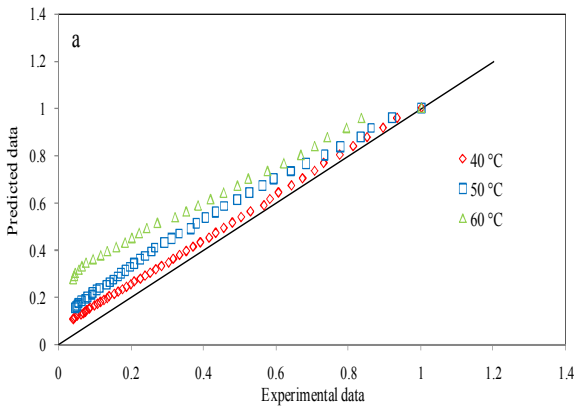
Model name	Model equation	Model constants	R^2	RMSE
Newton	$MR = \exp(-kt)$	k = 0.0089	0.9954	0.0230
Modified Page	$MR = \exp(-kt)^n$	k = 0.0126, n = 0.7074	0.9873	0.0487
Henderson and Pabis	$MR = a\exp(-kt)$	k = 0.0092, a = 1.0407	0.9880	0.0500
Wang and Singh	$MR = 1 + at + bt^2$	a = -0.0067, b = 0.00001	0.9918	0.0213

R^2: Coefficient of determination; RMSE: Root-mean-square error

This matter is also proven by comparison of Fig 7 with Fig 3. As it can be seen from the Fig. 7, an overestimation obtained by fitting the best model (Newton mode) to the experimental data, so that this overestimation increased with increase in temperature and decrease in thickness. Erenturk *et al.* (2004) reported the same results for thin-layer drying of Echinacea Angustifolia root. They reported that the feed-forward neural network based estimation was more concise (R^2 = 0.999) even than the best mathematical model used (modified page) (R^2 = 0.993). For two varieties of green malt, Aghajani *et al.* (2012) found that the estimated moisture ratio by feed-forward back propagation neural network was more accurate than Page's model. Also, similar results which imply the high precision of neural network based modes for prediction of moisture content been reported (Huang and Chen, 2015; Khazaei *et al.*, 2013; Momenzadeh *et al.*, 2011; Nadian *et al.*, 2015; Yousefi *et al.*, 2013a). No specific work was found in the case of estimation of moisture content using GMDH-type neural network, but many researchers have reported the remarkable accuracy of this method in other fields (Abdolrahimi *et al.*, 2014; Ahmadi *et al.*, 2007; Atashrouz *et al.*, 2015; Najafzadeh, 2015).

Conclusions

In this study, drying kinetics of thin-layer papaya fruit was investigated experimentally. Besides, a comparative study between a regression analysis and GMDH for estimation of moisture ratio (MR) during drying process was performed. Newton model indicated the closest results to the experimental data among the four thin-layer mathematical models considered. Higher R2 and lower RMSE values calculated for GMDH proved the higher performance of GMDH for prediction of moisture content. It should be noted that the results obtained are only valid in the experimented range and are not necessarily correct outside of that. In brief, in a wider range of operating conditions the validity of the mathematical methods could be higher than that of the GMDH adjusted to a restricted range of conditions. Altogether, it can be concluded that due to the high precision, GMDH- type neural networks can be applied for on-line state estimation and control of drying processes in industrial operations successfully



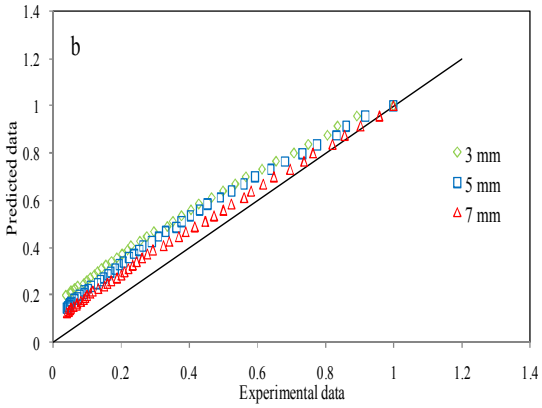


Fig. 7. (a) Comparison of actual and predicted data by Newton model for papaya fruit slices with 3 mm thickness, (b) comparison of actual and predicted data by Newton model for papaya fruit slices at 50 °C

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نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۵۷-۷۴۷

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 747-757

تخمین محتوای رطوبتی خربزه درختی با استفاده از مدلسازی GMDH حین خشک شدن لایه نازک

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تاریخ دریافت:۱۳۹۴/۰۹/۰۲
تاریخ پذیرش:۱۳۹۴/۱۲/۱۵

چکیده

در این تحقیق یک مدل هیبریدی شبکه عصبی-GMDH جهت تخمین محتوای رطوبتی قطعات خربزه درختی در حین خشک شدن با هوای داغ در یک خشک کن کابینتی تعیین شد. برای این منظور پارامترهای زمان خشک کردن، ضخامت قطعات و دمای خشک‌کردن بعنوان ورودی تعریف گردید و مقدار نسبت رطوبتی (MR) به عنوان خروجی تخمین زده شد. دقیقاً ۵۰ درصد داده‌ها جهت آموزش و ۵۰ درصد دیگر برای تست کردن مدل استفاده شد. بعلاوه، چهار مدل ریاضی مختلف بر داده‌های آزمایشگاهی برازش داده شدند و نتایج این مدلسازی با GMDH مقایسه گردید. مقدار ضریب تبیین (R^2) و جذر میانگین مربعات خطا (RMSE) بدست آمده برای مدل GMDH به ترتیب ۰/۹۹۶۰ و ۰/۰۲۲۰ بدست آمد، در حالی که برای بهترین مدل ریاضی (مدل نیوتن) این مقادیر به ترتیب برابر ۰/۹۹۵۴ و ۰/۰۲۳۰ تعیین شد. پس می توان نتیجه گرفت که مدلسازی با GMDH کارایی بالاتری نسبت به مدل ریاضی در تخمین محتوای رطوبتی قطعات لایه نازک خربزه درختی دارد.

واژه‌های کلیدی: خشک کردن، GMDH، خربزه درختی، شبکه عصبی

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Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 758-769

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۶۹-۷۵۸

The effects of extraction technique on phenolic compounds extracted from fig (*Ficuscarica*) pulp andskin

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Received: 2015.11.28
Accepted: 2016.06.20

Abstract

Recently, Subcritical Water Extraction (SWE) has been well known as a green technology for extraction of bioactive compounds from plants. In this study, Subcritical water extraction, ultrasound assisted extraction (UAE) and shaker solvent extraction (SSE) were compared for extraction of phenolic compounds from fig (Ficuscarica) pulp and skin. Antioxidant activity of the extracts was evaluated using DPPH radical scavenging, reducing power and rancimat tests. Subcritical waterhad the highest ability for extraction of total phenolic content (65.89±0.21 and 80.79±0.09 mg of gallic acid equivalents per gram of extract respectively) and flavonoid compounds (7.51±0.33 and 10.1±1.02 mg of quercetinequivalents per gram of extract, respectively)from both pulp and skin.The lowest IC50 in DPPH radical scavenging and reducing power tests were related to SWE of skin extract of fig. Furthermore, in extraction of total phenol and flavonoid compounds, subcritical water extraction showed to be a more suitable method than other solvent extraction methods, both in pulp and skin.

Keywords: Antioxidant activity; Fig; Extraction; Ultrasound; Subcritical water extraction

Introduction

The Common Fig (Ficuscarica L.) is a tree native to the Middle East and the Mediterranean region, which belongs to botanical family Moraceae. The Common (Flaishman *et al*., 2008; Oliveira *et al.*, 2009)fig is an excellent source of minerals, vitamins and dietary fiber; fat and cholesterol-free and contain a high number of amino acids (Caliskan, 2015; Viuda-Martos *et al*., 2015). In addition of several health benefits which were previously reported (Lansky *et al*., 2008; Viuda-Martos *et al*., 2015; Weli *et al.,* 2015), figs are an excellent source of phenolic compounds.

Polyphenols are natural antioxidants and the most abundant secondary metabolites of plants that possess interesting properties, such as free-radical scavenging and inhibition of various oxidative stress in the body(Dai and Mumper, 2010).Plant-derived antioxidants are molecules, which donate electrons or hydrogen atoms. These compounds are able to form less reactive antioxidant-derived radicals, which are efficiently quenched by other electrons or hydrogen sources to prevent cellular damage therefore, they may delay and inhibit lipid oxidation, protect human cells against oxidative damage, lead to a reduced risk of several oxidative-stress associated degenerative diseases, such as cancer, cardiovascular or neurodegenerative diseases (Scalbert *et al*., 2005).When added to foods, these antioxidant compounds tend to minimize rancidity, retard the formation of toxic oxidation products, help to maintain the nutritional quality and increase their shelf life (Fukumoto and Mazza, 2000).

Phenolic compounds from plants has been traditionally extracted using solvent extraction or steam distillation techniques. Traditional methods of extraction are cost and time consuming protocols, and require large volumes of solvents (Teixeira et al., 2006).Recently several new methods have been applied for plant phenolic extraction such as supercritical fluid extraction (SFE)(Herrero et al., 2010; McHugh and Krukonis, 2013; Pereira and Meireles, 2010), pulse electric

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field assisted extraction (PEFE)(Vorobiev et al., 2005), high pressure assisted extraction (HPE)(Corrales et al., 2008) and matrix solid-phase dispersion (MSPD) (Capriotti et al., 2010; Dawidowicz and Rado, 2010), which are less labor intensive and more environmentally friendly. Despite the use of this new extraction techniques solid–liquid extraction (SLE) is still commonly used.

Subcritical water extraction (SWE), also called pressurized polarity water extraction or superheated water extraction, is a technique using water as extraction solvent at temperatures between 100 and 374°C with a pressure high enough to maintain water in liquid state (Ma et al., 2015). Previous studies have proved that it is a promising technique because of its short extraction time, decrease the organic solvent consumption, less volatile oil loss and increase the quality of extracts(Jayawardena and Smith, 2010; Kumar et al., 2011; Rodríguez-Meizoso et al., 2010).

In recent years, ultrasound-assisted extraction method has become an effective method for edible oils and fats from natural product extraction UAE is an inexpensive, simple and efficient alternative to conventional extraction techniques (Wang and Weller, 2006). The mechanism of UAE is attributed to mechanical and cavitation efficacies which can result in disruption of cell wall, particle size reduction, and enhanced mass transfer across cell membrane(Wang *et al*., 2013). The objective of this study is to compare antioxidant activity of the phenols extracted from the pulp and skin of fig by ultrasound-assisted aqueous extraction, Subcritical water extraction and solvent extraction

Materials and methods

Material

Fig fruit (*F. carica L.*) from Siyah variety collected from Gorgan city on September 2014. Canola oil was purchased from Alia Golestan company (Kordkooy,iran) All other chemicals used in this study were of analytical grade and were purchased from chemical suppliers.

Preparation of extracts

The figs (Siyah variety) were weighed and immediately peeled. The pulp was cut and made into flat sheets. Thereafter, the pulp and skin of fruit were shade-dried for 5 days followed by drying at 60°C in an oven for 24 hours to ensure complete drying (Memmert 100-800, Germany). The samples were then milled and sieved through No. 67. Samples obtained were kept in polyethylene bags

Solvent extraction

Ten grams of each sample was mixed with water-ethanol (70%) in a ratio of 1 to 10 and gently stirred. For a better extraction, the mixture was shaken (120 rpm) at dark at 25 °C for 24 hours on a shaker, then the supernatant was filtered by Buchner funnel and Whatman filter paper No. 1. The extracts containing solvent was poured in a glass plate and placed in oven at 40°C for 24 hours. After evaporation of the solvent, the extracts were placed in desiccator until constant weight and kept at -18°C for further analyses (Esmaeilzadeh Kenari *et al.,* 2014).

Ultrasound assistant extraction

Dried powders of sample (10 g) were mixed with ethanol (1:10). The mixture was sonicated for 20 min at 40 °C in an ultrasonic bath (Elma s 30 H model, total power consumption: 280 W, heating power: 200 W, operating at 37 KHz frequency and internal dimensions: 198 × 106 × 50 cm). The temperature was controlled and maintained at 40 °C by circulating water. The extract was filtered and subsequently evaporated using a rotary evaporator. The concentrated extracts were stored at -18°C until further analyses (Esmaeilzadeh Kenari *et al*., 2014).

Subcritical water extraction

Subcritical water extraction was carried out by a system consists of a distilled water tank, a pump (Comet type:MTP AX 2/70 m) providing pressure up to 170±5 bar, an extraction cell with 140 ml capacity, a heating coil, a pressure gauge and a temperature

control device. The powdered sample was loaded into the cell. Extraction was carried out at temperature of 160ºC for 30 minutes (Hassas-Roudsari et al., 2009). The impurities of liquid (extract) was removed using filter paper (Whatman paper No. 4) under vacuum condition. The filtered extracts were cooled and stored at -18ºC in dark polypropylene bags until used in the analysis(Shaddel *et al*., 2014; Sharifi *et al.,* 2013).

Determination of total phenolic content

Total phenolic content of each extract was determined by the Folin–Ciocalteu micro-method according to revised methods of Javanmardiet al. (2003). Briefly, in a 50 ml volumetric flask, 1 ml of a standard solution of gallic acid, 6 ml of methanol, 2.5 ml of the Folin-Ciocalteau reagent, and 5 ml of 7.5% Na2CO3 were added.The final volume was achieved by addition of distilled water. The solutions were stored overnight and the spectrophotometric analysis was performed at λ=765 nm. (PG-instrument, USA). The total phenol content of samples and canola oil were expressed as gallic acid equivalents per g of extract using the following linear equation based on the calibration curve:

$y= 0.0008x+0.029 \quad R^2= 0.094$

Where y is absorbance at 765 nm and x is concentrations of gallic acid equivalents (mg/g)(Capannesi *et al.,* 2000; Javanmardi *et al*., 2003).

Determination of total flavonoid content

Colorimetric aluminum chloride method was used for flavonoid determination. Briefly, 0.5 ml solution of each plant extracts in methanol were separately mixed with 1.5 ml of methanol, 0.1 ml of 10% aluminum chloride, 0.1 ml of 1 M potassium acetate, and 2.8 ml of distilled water, and left at room temperature for 30 minutes. The absorbance of the reaction mixture was measured at 415 nm with a double beam Perkin Elmer UV/Visible spectrophotometer (PG-instrument, USA). The calibration curve was prepared by preparing pure quercetin solutions at concentrations 12.5 to 100 mg/ ml in methanol.Total flavonoid content was calculated as quercetinper g of extract using the following linear equation based on the calibration curve:

$y= 0.0064x+0.0124 \quad R^2= 0.9982$

Where y is absorbance at 415 nm and x is concentrations of flavonoids compounds (mg quercetin /g extract)(Nabaviet al., 2012).

DPPH Radical-Scavenging Activity

Stable 2, 2'-diphenyl-1-picryl hydrazyl radical (DPPH) was used for determination of free radical-scavenging activity of the extracts. Different concentrations of each extracts were added, at an equal volume, to methanol solution of DPPH (100 μM). The samples were kept at room temperature in darkness and after 15 min the absorbance of each sample was measured at 517 nm and the percentage of scavenging activity was calculated from the equation 1. The experiment was repeated for three times. IC50 values denote the concentration of sample, which is required to scavenge 50% of DPPH free radicals (Aksoy *et al*., 2013).

$$DPPH\ scavenging\ activity\ (\%) = \frac{Absorbance\ of\ control - Absorbance\ of\ sample}{Absorbance\ of\ control} \quad (1)$$

Reducing power

Ability of extracts to reduce iron (III) was evaluated using the method of Yildirim *et al*.(2001). Samples (2.5 ml) were mixed with 2.5 ml of phosphate buffer (0.2 M, pH 6.6) and 2.5 ml of potassium ferricyanide (K3Fe (CN) 6; 10 g/L) and incubated for 30 min at 50°C. Then 2.5 ml of trichloroacetic acid (100 /L) were added to the solution and centrifuged for 10 min. Finally, 2.5 ml of supernatant was combined with 2.5 ml of distilled water and 0.5 ml $FeCl_3$ (1 g/L). The absorbance of samples was measured at 700 nm. Higher absorbance means higher reducing power (Yildirim *et al.,* 2001).

Determination of the thermal oxidative stability index (Rancimat test)

One mg/ml of each sample was mixed with 100 ml pure canola oil (without antioxidant) and then oxidative stability measured by Rancimat (Metrohm, 743, Switzerland) test based on the AOCS method (2007). The air flow rate and the temperature was set at 20 m3/h and at 110 °C, respectively.

Statistical analysis

Each experiment was carried out at least in duplicate and measurement performed at least in triplicate. Statistical analysis of data was performed using Microsoft Excel. Analysis of variance was calculated using the SPSS program with a confidence level of 0.05, to find any significant difference between treatments.Duncan multiple range test (MRT) was used for mean separation at P< 0.05 where treatment effect was significant

Result and discussion

The effect of extraction on phenolic and flavonoid compounds

Analysis of variance (ANOVA) showed that the techniques used for extraction of phenolic compounds in skin and pulp of the fig were significant different (P<0.05). Subcritical water method in both skin and pulp samples showed the highest amount of total phenolic (80.79±0.09 and 65.89±0.21 mg gallic acid/g of extract, respectively) and flavonoid (10.1±1.02 and7.51±0.33 mg quercetin/g of extract, respectively) contents whereas there was no difference between UAE and SSE (Table 1).

Table 1- Total phenol and flavonoids of pulp and skin of fig extract with different extraction methods

Extraction technique	Total Phenol mg gallic acid/g of extract		Total Flavonoid mg quercetin/g of extract	
	pulp	skin	pulp	skin
SSE	58.35±0.05^{b}	68.59±1.02^{b}	2.04±0.13^{b}	4.29±0.12^{b}
UAE	58.84±0.13^{b}	70.09±0.32^{b}	2.06±0.23^{b}	4.32±0.12^{b}
SWE	65.89±0.21^{a}	80.79±0.09^{a}	7.51±0.33^{a}	10.1±1.02^{a}

Means with different letters within column indicate significance difference at $P < 0.05$.
SSE: Shaker Solvent Extraction; UAE: Ultrasonic Assisted- Extraction; SWE: Subcritical Water Extraction

Flavonoids are strong inhibitors of hydroxyl and peroxide radicals. These compounds can influence on free radicals even when they form complexes with metal ions (Koda *et al*., 2008). Flavonoid compounds have pharmaceutical, antibacterial and anti-oxidation properties. Quercetin is a flavonol which is one of the most powerful natural antioxidants and a major component known in figs (Solomon *et al.*, 2006). Antioxidant properties of flavonoids, especially quercetin, are rendered through metal ion chelating, radical scavenging, and stimulating the expression of protective enzymes (Baghel *et al*., 2012). Therefore, measurement of these compounds in figs deems very important.

Higher efficiency of SWE in the extraction of flavonoids also reported by earlier studies (Ko *et al*., 2011; Liang and Fan, 2013; Rangsriwong *et al*., 2009). Extraction of a wide range of flavonoids by common extraction methods is limited due to poor solubility in water. By application of subcritical water, the polarity, viscosity, surface tension, and disassociation constant of subcritical water are significantly lowered compared to water at ambient temperature and pressure, with more similar chemical properties to those of organic solvents. The temperature and pressure of subcritical water extraction provide higher penetration rate that improves its efficiency (Rangsriwong *et al*., 2009). Higher efficiency of SWE also could possibly be related to the effect of hydrolysis reaction caused by the increase in the ionization constant (Kw) of water at subcritical conditions.

Extraction time considerably decreased in ultrasonic process (from 24 h in SSE to 20 min in UAE) due to the positive effect of cavitation

although no significant difference was detected between the methods in terms of amount of phenolic and flavonoid compounds. Solid–liquid extraction is assisted by ultrasounds leading to formation of cavitation bubbles. The collapse of these bubbles near the cell walls is expected to cause cell disruption along with good penetration of the solvent into the cells through the ultrasonic jet action. This process leads to an intensification of mass transferand improved solvent penetration into the plant tissue (Da Porto *et al.,* 2013). Nevertheless, extraction conditions (e.g. time, temperature, solvent) greatly influence on the efficiency of extraction of phenolic compounds and flavonoids in plant tissue. Similar results which compared ultrasound and solvent methods, were in consistent with our results (Chemat *et al.,* 2004; Da Porto *et al.,* 2013; Kimbaris *et al*., 2006; Milić *et al.,* 2013; Vinatoru *et al*., 1997).

The effect of extraction on DPPH Radical-Scavenging Activity

DPPH scavenging activity assay is widely used to evaluate the ability of compounds to scavenge free radicals or donate hydrogen, and determine the antioxidant activity in foods (Bidchol *et al*., 2011). Subcritical water extraction of fig pulp at concentration of 1 mg/ml showed the highest radical scavenging activity (65.66 ± 1.54%) while a sharp decline in antioxidant activity was observed with higher concentrations (e.g. 1.5 and 2 mg/ml) (Figure 1). This extracts showed the highest inhibition at lower concentrations. While the other extracts with increasing concentrations, increased antioxidant activity. Subcritical water extraction of fig skin at concentrations of 0.5, 1, 1.5 and 2 mg/ ml and UAE and SSE extract at concentrations of 2.5 and 3 mg/ml had the highest percentage of inhibition. Radical scavenging activity in the UAE- and SSE-extracts from both skin and pulp of fig was dependent on concentration where a higher radical scavenging was achieved with higher concentrations of phenolic and flavonoid compounds; this effect might be owing to higher amount of hydroxyl groups and consequently, increased probability of hydrogen donation to free radicals (Sanchez-Moreno *et al*., 1999). However, radical scavenging activity of subcritical water extracts decreased with higher extract concentrations. A logic behind this observation is the reaction between released chemicals in solvent leading to formation of new compounds and interference in identification of target compounds in higher concentration (Plaza *et al*., 2010).

IC_{50} is defined as a concentration of the extract required to scavenge 50% of DPPH radicals. Subcritical water extract of skin revealed the lowest IC50 (0.45±0.02 mg/ml); in other word, it is the best extract to scavenge free radicals. On the contrary, subcritical water extract of pulp had significantly higher IC50(0.65±0.09 mg/ml) valuesthan other treatments (figure 2).

The effect of extraction on reducing power

Reducing property is generally defined as the ability ofdonating a hydrogen atom and thereby breaking aradical chain.Furthermore, reluctant react with peroxideprecursors and prevent the formation of peroxides [45]. Thus, samples with higher reducing powers aremore able to donate electrons. The reducing powers ofdifferent samples are shown in Fig. 3 (a,b). In all concentrations, SWE of fig pulp and skin had the highest reducing power, UAE and SSE had no significant difference. The results showed that the compounds in fig skin extracts were good electron or hydrogen donors and could successfully terminate radical chain reactions. So, it can be considered a good alternative to synthetic antioxidants in the diet. These results were consistent with Gou *et al*. (2003) who evaluated the antioxidant activity of the skin and the pulp and kernel of twenty-eight common fruit in China via reducing power analysis and reported that fruit peels and kernels had higher antioxidant activity than pulps (Guo *et al*., 2003).The results also showed the advantages of SWE because with higher temperature, the dielectric constant of water reduces leading to lower polarity of water. Therefore, compounds with differentpolarities including a variety of

flavonoids can be extracted via SWE, which increases the reducing power of extracts. Increasing concentrations lead to increase in the reducing power of extracts due to the increased amount of phenolic compounds present in the extract. These data largely confirm the DPPH test. The only difference is that a better distinction of antioxidant activities of extracts with varying concnetrations is achieved through reducing power assay. Since this method is usually used to measure the antioxidant capacity of hydrophilic compounds (Pérez-Jiménez et al., 2008)and also because of the nature of hydrophilic compounds in the figs extracts (due to the presence of anthocyanins), this method seems more accurate to measure the antioxidant activity fig extract.

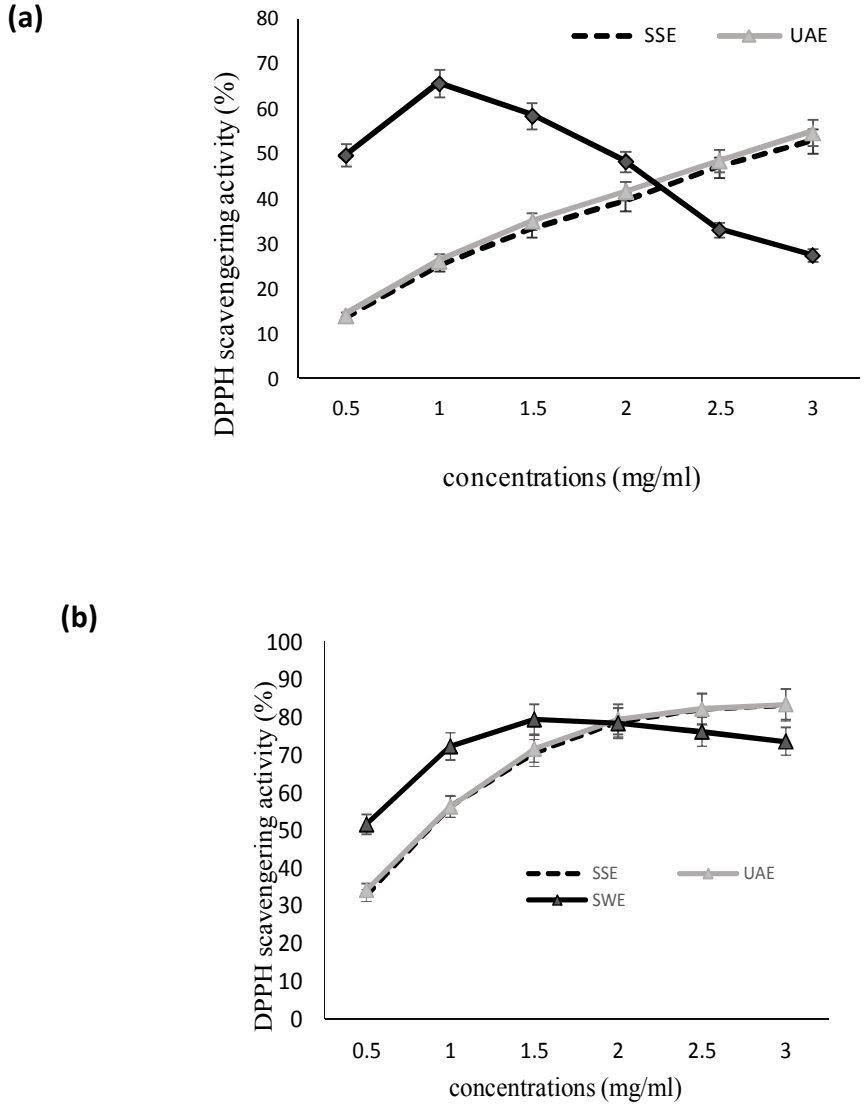

Fig. 1. DPPH scavenging activity of fig extract with different extraction methods: (a) fig pulp and (b) fig skin (SSE: Shaker Solvent Extraction; UAE: Ultrasonic Assisted Extraction; SWE: Subcritical Water Extraction)

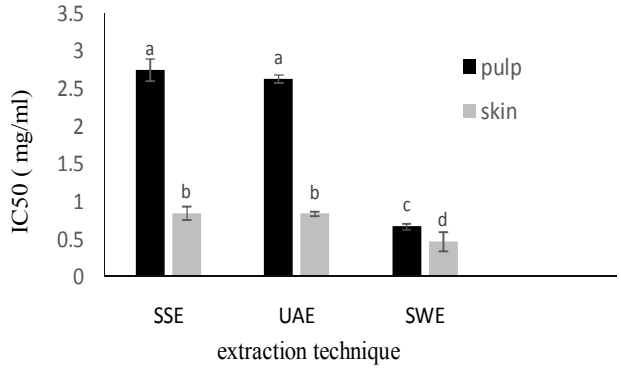

Fig. 2. IC_{50} of extracts in DPPH assay with different extraction methods (SSE: Shaker Solvent Extraction; UAE: Ultrasonic Assisted Extraction; SWE: Subcritical Water Extraction)

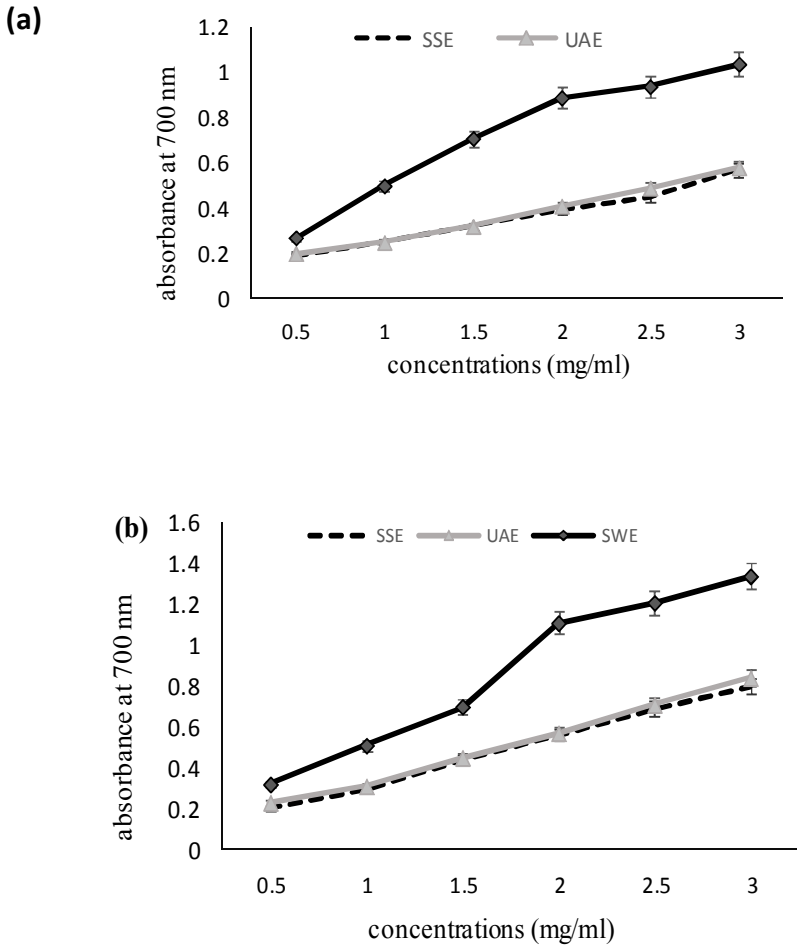

Fig. 3.Reducing power of fig extract with different extraction methods: (a) pulp and (b) skin (SSE: Shaker Solvent Extraction; UAE: Ultrasonic Assisted Extraction; SWE: Subcritical Water Extraction)

Figure 4 shows IC_{50} in reducing power assay (mg/ml). In the case of reducing power, the IC_{50} value presents the concentration at which the absorbance is 0.5. Similar to DPPH assay, Subcritical water extracts in both skin and pulp samples showed significantly the lowest IC_{50} (0.90±0.1 and 0.96±0.05 mg/ml) and the highest reducing power.

Antioxidant activity of the extracts in edible oil was measured based on the electrical conductivity of water in addition to the accumulation of volatile compounds from oxidation, especially carboxylic acids under accelerated oxidation. Oxidative stability index (OSI) is defined as oil stability time at a given temperature. The results has shown that the effect of the extraction method was significant on oxidative stability and thus antioxidant activity ($P<0.05$). In this study, UAE showed higher stability among other extracts (Figure 5). This can be due to differences in methods of extraction and the resulting difference is in the type of phenolic compounds in the extracts. These factors are important in solubility of the extracts in oil and hence in the oxidative stability of the oil.

Conclusion

The result presented in this study show that the subcritical water extraction method is an alternative for extraction of several phenolic and flavonoid compounds from skin and pulp of fig, and more efficient than both solvent extraction method and ultrasound. Subcritical water extracts of skin and pulp of fig showed higher antioxidant activities in the DPPH radical scavenging and reducing power assays, while in rancimat test ultrasound method was found to yield more antioxidant extracts. This difference can be justified by varying nature of the methods of measuring antioxidant activity. Additional research and development studies are necessary to thoroughly compare subcritical extraction with other recent methods.

Acknowledgment

The authors acknowledge department of food science and technology of Sari University of Agricultural Sciences and Natural Resources for providing financial support to this research work.

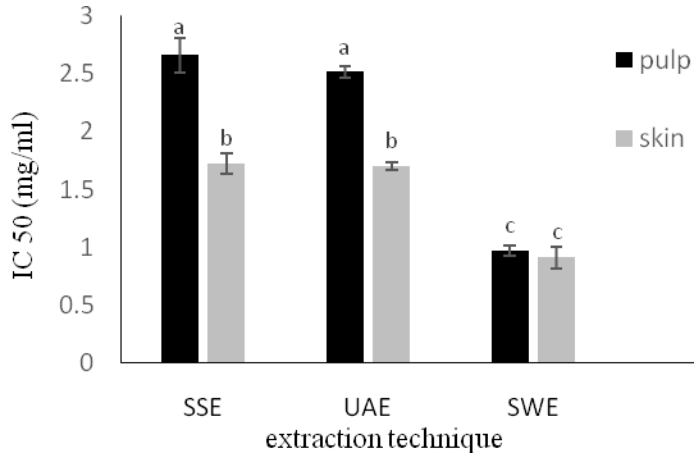

Fig. 4. IC_{50} of extracts in reducing power assay with different extraction methods (SSE: Shaker Solvent Extraction; UAE: Ultrasonic Assisted Extraction; SWE: Subcritical Water Extraction)

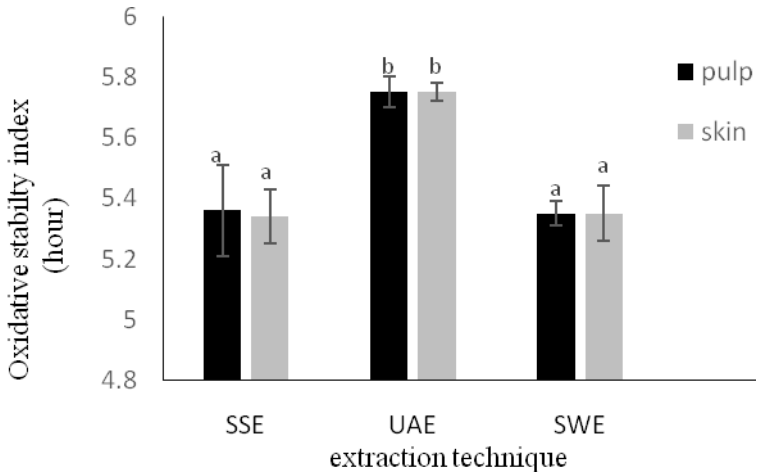

Fig 5- Oxidative stability index of pulp and skin extract with different extraction (SSE: Shaker Solvent Extraction; UAE: Ultrasonic Assisted Extraction; SWE: Subcritical Water Extraction)

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نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۶۹-۷۵۸

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 758-769

اثر روش‌های استخراج بر ترکیبات فنولی استخراج‌شده از پوست و پالپ انجیر

الهه مقصودلو[۱]- رضا اسماعیل‌زاده کناری [*۲]- زینب رفتنی امیری[۳]

تاریخ دریافت:۱۳۹۴/۰۹/۰۷
تاریخ پذیرش:۱۳۹۵/۰۳/۳۱

چکیده

اخیرا استخراج آب زیر بحرانی (SWE) به عنوان یک تکنولوژی سبز برای استخراج ترکیبات زیست فعال گیاهان شناخته شده است. در این مطالعه، استخراج آب زیر بحرانی، استخراج به کمک اولتراسوند (UAE) و استخراج حلالی همزنی (SSE) جهت استخراج ترکیبات فنولی پوست و پالپ انجیر مقایسه شدند. فعالیت آنتی‌اکسیدانی عصاره‌ها با آزمون‌های مهار رادیکال DPPH، قدرت احیاکنندگی و رنسیمت ارزیابی شد. آب زیر بحرانی نشان داد که بالاترین توانایی را در استخراج ترکیبات فنولی کل پالپ و پوست (به ترتیب، ۰/۲۱±۶۵/۸۹ و ۰/۰۹±۸۰/۷۹ معادل میلی‌گرم گالیک اسید در گرم عصاره) و ترکیبات فلاونوئیدی (به ترتیب، ۰/۳۳±۷/۵۱ و ۱/۰۲±۱۰/۱ معادل میلی‌گرم کوئرستین در گرم عصاره) دارد. همچنین، کمترین IC50 در آزمون‌های مهار رادیکال DPPH و قدرت احیاکنندگی به عصاره‌ی آب زیر بحرانی پوست انجیر مربوط بود. بنابراین، آب زیر بحرانی روش مناسب‌تری برای استخراج ترکیبات فنولی و فلاونوئیدی کل پوست و پالپ انجیر می‌باشد.

واژه‌های کلیدی: فعالیت آنتی‌اکسیدانی، انجیر، استخراج، اولتراسوند، استخراج آب زیر بحرانی

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Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 770-778

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۷۸-۷۷۰

Using artificial neural networks to predict thermal conductivity of pear juice

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Received: 2015.01.30
Accepted: 2016.06.20

Abstract

Thermal conductivity is an important property of juices in the prediction of heat- and mass-transfer coefficients and in the design of heat- and mass-transfer equipment for the fruit juice industry. An artificial neural network (ANN) was developed to predict thermal conductivity of pear juice. Temperature and concentration were input variables. Thermal conductivity of juices was outputs. The optimal ANN model consisted 2 hidden layers with 5 neurons in first hidden layer and the second one has only one neuron. The ANN model was able to predict thermal conductivity values which closely matched the experimental values by providing lowest mean square error (R^2=0.999) compared to conventional and multivariable regression models. However this method also improves the problem of determining the hidden structure of the neural network layer by trial and error. It can be incorporated in heat transfer calculations during juices processing where temperature and concentration dependent thermal conductivity values are required.

Keywords: Artificial Neural Network, Thermal conductivity, Fruit juices, Pear

Introduction

Thermal conductivity is an important property of juices in the prediction of heat- and mass-transfer coefficients and in the design of heat- and mass-transfer equipment for the fruit juice industry. Accurate thermal conductivity data and their variation with operating conditions (over wide temperature and concentration regions) are needed for various research and engineering applications in any branch of the food industry, such as developing food processes and processing equipment, the control of products, filters, and mixers, engineering calculations on evaporation rates, pumping, and pipe requirements, mixing requirements, quality evaluation; and an understanding of the structure of food and raw agricultural materials (Magerramov *et al*. 2006).

As the thermal conductivity of juices strongly depend on concentration and temperature, and due to natural differences between the fruits, it is nearly impossible to experimentally determine and tabulate the thermal conductivity of fruit juices for all possible conditions and compositions. However, most existing thermal conductivity measurements for fruit juices are at room temperature and very limited concentration range. Therefore an appropriate correlation and prediction models for the thermal conductivity of juices, as a function of temperature and concentration, to cover the entire range of temperature and concentration is necessary.

For this reason there has been consistent effort spent in developing generalized correlations to predict thermal properties of food materials for the use in process design and optimization. In recent years, mathematical modeling and computer-based numerical analyses have become the main tools for understanding and predicting processing phenomena.

Magerramov *et al*. (2006) have been presented and modeled thermal conductivity data as a function of concentration and/or process temperature. They also proposed 5 semi theoretical methods for the prediction of thermal conductivity of pear juice. Among them, the multi parametric Model (equation 1) with AAD = 0.1 to 0.2 %, where AAD is the average absolute deviation)) is best represented by the present experimental

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thermal conductivity data, but the predicting capability of equation 2 (AAD = 0.6 to 0.7%) is much better than that of others. Moreover, in this equation the minimum experimental thermal conductivity information at a reference temperature is needed to predict the values of the thermal conductivity of juices at high temperatures. Equation 2 can be recommended to calculate the combined effects of the temperature and concentration on the thermal conductivity of juices over wide ranges of temperature and concentration just using the values of thermal conductivity at reference temperature T0. It was found that the prediction equation 1 and 2 can be adopted with satisfaction.

$$\lambda(T,x) = 0.5794 - 3.7520 \times 10^{-3}x + (9.6237 \times 10^{-4} - 7.5953 \times 10^{-7}x)T + (-2.7390 \times 10^{-6} + 2.2198 \times 10^{-8})T^2 \quad (1)$$

$$\frac{\lambda(T,x)}{\lambda(T_0,x)} = \left(\frac{T}{T_0}\right)^m \quad (2)$$

Where λ is the thermal conductivity, x is the concentration, and T is the temperature, could be adopted with satisfaction.

Artificial Neural Network (ANN) modeling is increasingly accepted and is an interesting method for the estimation and prediction of food properties and process related parameters. Several researchers used Artificial Neural Network technique for predicting thermal conductivity of fruits and vegetables, bakery products and foods (Hussain and Rahman, 1999; Mittal and Zhang, 2000; Sablani *et al*., 2002; Sablani and Shafiur Rahman, 2003; Hussain and Shafiur Rahman, 2003; Rai *et al*., 2005a,b; Shafiur Rahman *et a*l., 2012).

However, little work has been conducted on the prediction of thermal conductivity of fruit juices using ANN. Consequently, the objective of this work was to develop an ANN model to predict the thermal conductivity of pear juice of known temperature and composition. Comparisons of the thermal conductivity prediction by ANN with the conventional analytical model described in the literature have also been made in this work.

Materials and methods

Experimental methods

Experimental data

Many researchers have measured thermal properties of fruit and vegetable juices such as thermal conductivity byvarious techniques. Thermal conductivity data needed for development of the ANN model were obtained from the thermal conductivity data set of pear juice (66 samples) were prepared by Magerramov *et al.* (2006). A total of 66 data points for pear juice at a temperature range of 20 to 120 °C and concentrations up to 50 °Brix were used (Table 1). According to Table 1, the thermal conductivity of pear juice considerably increases with temperature.

Model development

The development of a neural network model involves: the generation of (or compilation of available) data required for training/testing, the training/testing of the ANN model, the evaluation of the ANN configuration leading to the selection of an optimal configuration, and validation of the optimal ANN model with a data set not used in training before. The flow chart of methodology for developing ANN architecture is described in Figure 1.

Artificial Neural Networks (ANN)

Artificial Neural Networks (ANN) provides a range of powerful new techniques for solving problems in sensor data analysis, fault detection, process identification and control. The major advantages of using an ANN model are that it works only with input - output data, does need a well-defined algorithm to convert an input into an output, but a representative collection of examples is necessary to offer the desired output(Heaton, 2005).A single model can be used to generate multiple outputs. Once the neural network model has been adequately trained and validated, it is able to make predictions on new set of input data, but not used in the developing of the model (Curteanu, 2011). Due to their capabilities, ANNs can be used on a wide range of processes and systems from various domains (Kamali, M. Mousavi,

2008, Pirdashti *et al*.2013).Basic component of a neural network is the neuron, also called "node". Figure 2 illustrates a single node of a neural network. The inputs are represented by a1, a2 and an, and the output by Oj. There can be many input signals to a node. The node manipulates these inputs to give a single output signal (Lübbert and Simutis, 1994).

The values w_{1j} , w_{2j} , and w_{nj}, are weight factors associated with the inputs to the node. Weights are adaptive coefficients within the network that determine the intensity of the input signal. Every input (a_1, a_2, . . .,a_n) is multiplied by its corresponding weight factor (w_{1j}, w_{2j}, . . . , wnj), and the node uses summation of these weighted inputs (w_{1ja1}, w_{2ja2}, . . . , wnjan) to perform further calculations. In the initial setup of a neural network, weight factors usually are chosen randomly according to a specified statistical distribution. The other input to the node, bj, is the node's internal threshold, also called bias. This is a randomly chosen value that governs the node's net input through the following equation (Nasr *et al*., 2012):

$$u_i = \sum_{i=1}^{n} (w_{ij} * a_i) + b_j \qquad (3)$$

The node's output is determined using a mathematical operation on the node's net input. This operation is called a transfer function. The transfer function can transform the node's net input in a linear or non-linear manner. In the present work Sigmoid transfer function was applied:

$$f(x) = \frac{1}{1 + e^{-x}} \qquad 0 \leq f(x) \leq 1 \qquad (4)$$

The neuron's output, O_j, is found by performing one of this function on the neuron's net input, u_j. Neural networks are made of several neurons that perform in parallel. The weight factors and thresholds are adjusted in training process. Training is the process by which the weights are adjusted systematically so that the network can predict the correct outputs for a given set of inputs (Sadrzadeh et al. 2009). There are many different types of training algorithms. From all the types of networks enumerated above, feed-forward multilayered networks (multilayer perceptron, MLP) is the most used because is general and simply to apply (Wilamowski, 2009). In addition, advantages of MLP are also the easiness of programming and good results often provided (Fernandes and Lona, 2005). In the mathematical field, the universal approximation theory (Cybenko theorem) states that the standard MLP with a single hidden layer that contains finite number of neurons with arbitrary activation functions are universal approximate on a compact subset of R^n, property which makes it attractive to various researchers. MLP is composed of an input layer with a number of neurons corresponding to the input variables, one or more hidden layers and an output layer whose number of neurons corresponds to the number of output variables. Figure 3 shows the structure of this kind of ANN.

Table1- Experimental thermal conductivities (Wm-1K-1) of pear juices as a function of temperature for various concentrations Magerramov et al. (2006).

	Concentration(°Brix)					
T(K)	14	19	25	30	40	50
293.15	0.545	0.526	0.503	0.485	0.450	0.408
303.15	0.553	0.535	0.511	0.493	0.458	0.417
313.15	0.561	0.543	0.519	0.500	0.466	0.425
323.15	0.568	0.551	0.526	0.508	0.473	0.433
333.15	0.575	0.558	0.534	0.514	0.480	0.441
343.15	0.581	0.565	0.540	0.521	0.487	0.448
353.15	0.587	0.571	0.547	0.527	0.493	0.456
363.15	0.593	0.576	0.553	0.532	0.499	0.462
373.15	0.598	0.581	0.559	0.538	0.504	0.469
383.15	0.603	0.585	0.564	0.542	0.508	0.476
393.15	0.607	0.589	0.568	0.547	0.513	0.481

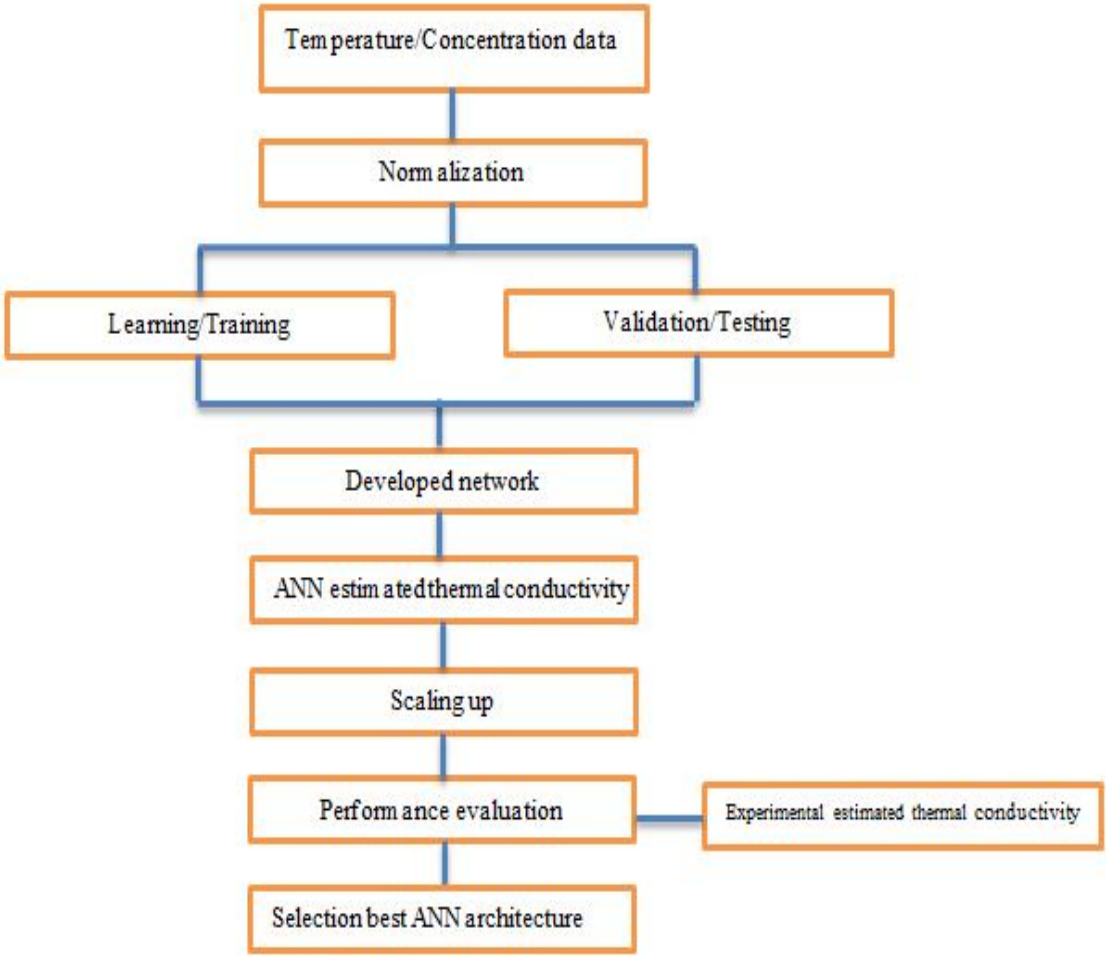

Figure1. Methodology for developing ANN architecture

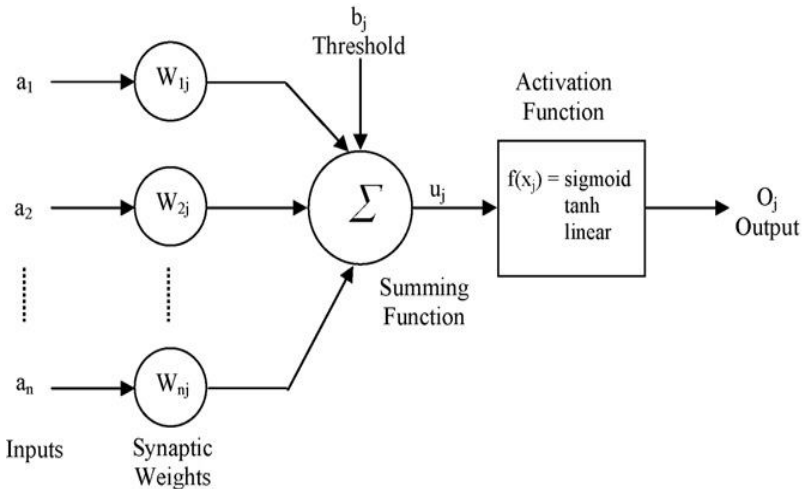

Figure2. Single node anatomy (Sadrzadeh *et al.*, 2009).

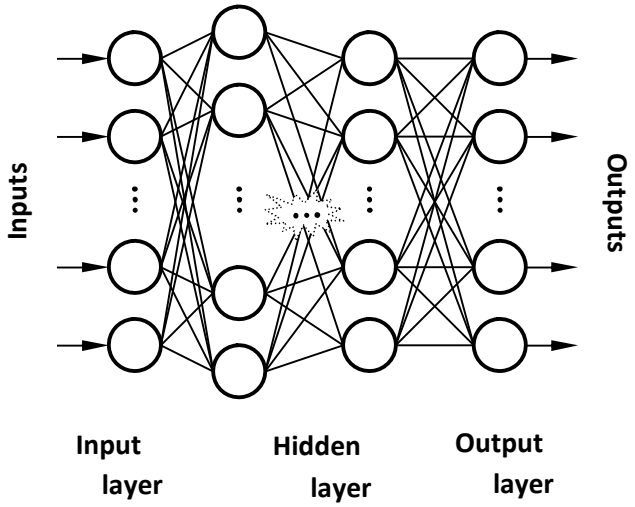

Figure 3. Structure of multilayer perceptron

Concerning the number of layers and neurons, several considerations have to be taken into account. Using a single hidden layer, a given degree of accuracy is attained only in the limited cases as the number of nodes becomes very large. For most complex cases, additional layers are necessary for a good fit and an improved generalization capability (Fernandes and Lona, 2005, Pirdashti *et al.* 2013). One of the most common classes of training algorithms for feed-forward neural networks is called back propagation (BP). Many other methods have been developed based on BP. Three subsets of data are used to build a model: training, validation and testing subsets. Training data set is used in training procedure. Validation data set is used to check the generality of network. If the network is trained sufficiently, the network output will differ only slightly from the actual output data. In initial steps of training, errors of both training and validation data are reduced. After several steps, the error of training data decreases while that of validation data increases. As a result, the network is over trained and its generality decreases. Hence, the training process must be continued until the validation data error decreases. Testing data set is used to test the trained network for unseen patterns (whose results are known for researcher but not used in training procedure). The network generalizes well when it sensibly interpolates these new patterns (Sadrzadeh *et al.* 2009).

For the prediction of thermal conductivity of pear juice, a feed-forward multi-layer neural network with input, output and hidden layers was used in this study which is shown in Figure4.

Results and Discussion

Based on ANN model, the input layer has 2 neurons and the output layer has only one neuron. Hidden layers are composed of two layers that the second one has only one neuron. The number of the neurons in the first hidden layer has to be selected by trial and error to minimize the mean relative error between the actual and the predicted thermal conductivity. In this study, the Levenberg-Marquardt algorithm with five neurons in the hidden layer was used to train the network. The network uses the sigmoid transfer function in the hidden layer, the linear activation function in the output layer.

Seventy present of data (46 samples) were randomly selected to train the network and 15 % (10 samples) were used for validation process and the remaining 15% were used for testing process. In the study, two hidden layer nodes were chosen to select the best production results. To reveal the credibility of prediction from the optimal ANN, predicted versus experimental values of thermal

conductivity was plotted (Figure 5). The results demonstrate very good agreement between the predicted and the experimental values of thermal conductivity ($R^2 = 0.999$).

Also, some statistical parameters are used for better comparison of the models. These statistical parameters are Normalized Bias (NB), Standard Square Error (SSE), Mean Square Error (MSE), Root Mean Square Error (RMSE) and *R*-square (R^2) which are described in Equations (6)–(10) (Draper and Smith (1998)., Armstrong and Collopy (1992)., *Cameron et al., 1997)*. They are used for the fitness investigation and error determination of the ANN model compared to equation 2.

where n is the number of experimental points; y_i^{exp} and y_i are the experimental and predicted values of thermal conductivity,respectively.Quantitative comparisons of the models using these statistical parameters are summarized in table 2, respectively.

$$NB = \sum_{i}^{n} \frac{(y_i - y_i^{exp})}{y_i^{exp}} \times 100 \quad (6)$$

$$SSE = \sum_{i}^{n} (y_i - y_i^{exp})^2 \quad (7)$$

$$MSE = \sum_{i}^{n} \frac{(y_i - y_i^{exp})^2}{n} \quad (8)$$

$$RMSE = \sqrt{\sum_{i}^{n} \frac{(y_i - y_i^{exp})^2}{n}} \quad (9)$$

$$R^2 = \frac{\sum_i^n (y_i^{exp} - y_{mean})^2 - \sum_i^n (y_i - y_i^{exp})^2}{\sum_i^n (y_i^{exp} - y_{mean})^2} \quad (10)$$

Table 2. Prediction accuracy of the models developed from the data set

	Statistical parameters				
	NB	SSE	MSE	RMSE	R^2
Model					
Eq.1	-9.6632	3.61×10^{-1}	5.4642×10^{-3}	7.392×10^{-2}	0.985
Eq.2	-0.1657	6.4625×10^{-4}	9.7916×10^{-6}	3.129×10^{-3}	0.996
ANN	-0.0037	1.454×10^{-5}	2.2028×10^{-7}	4.693×10^{-4}	0.999

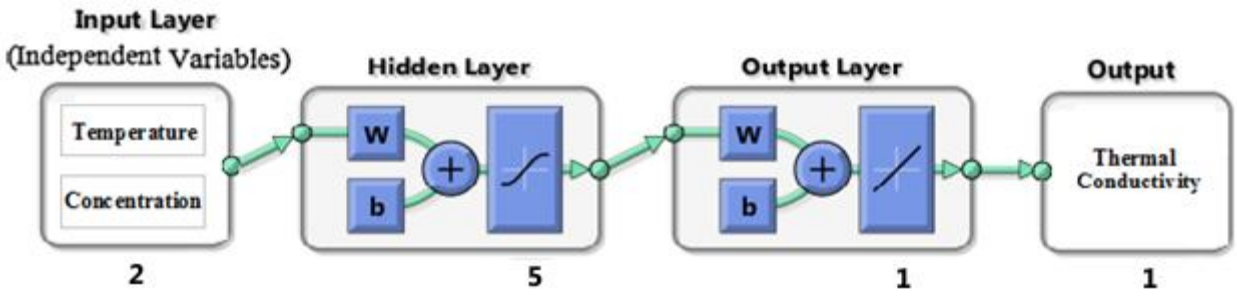

Figure 4. Schematic of multilayer neural network used to predict the thermal conductivity of pear juice

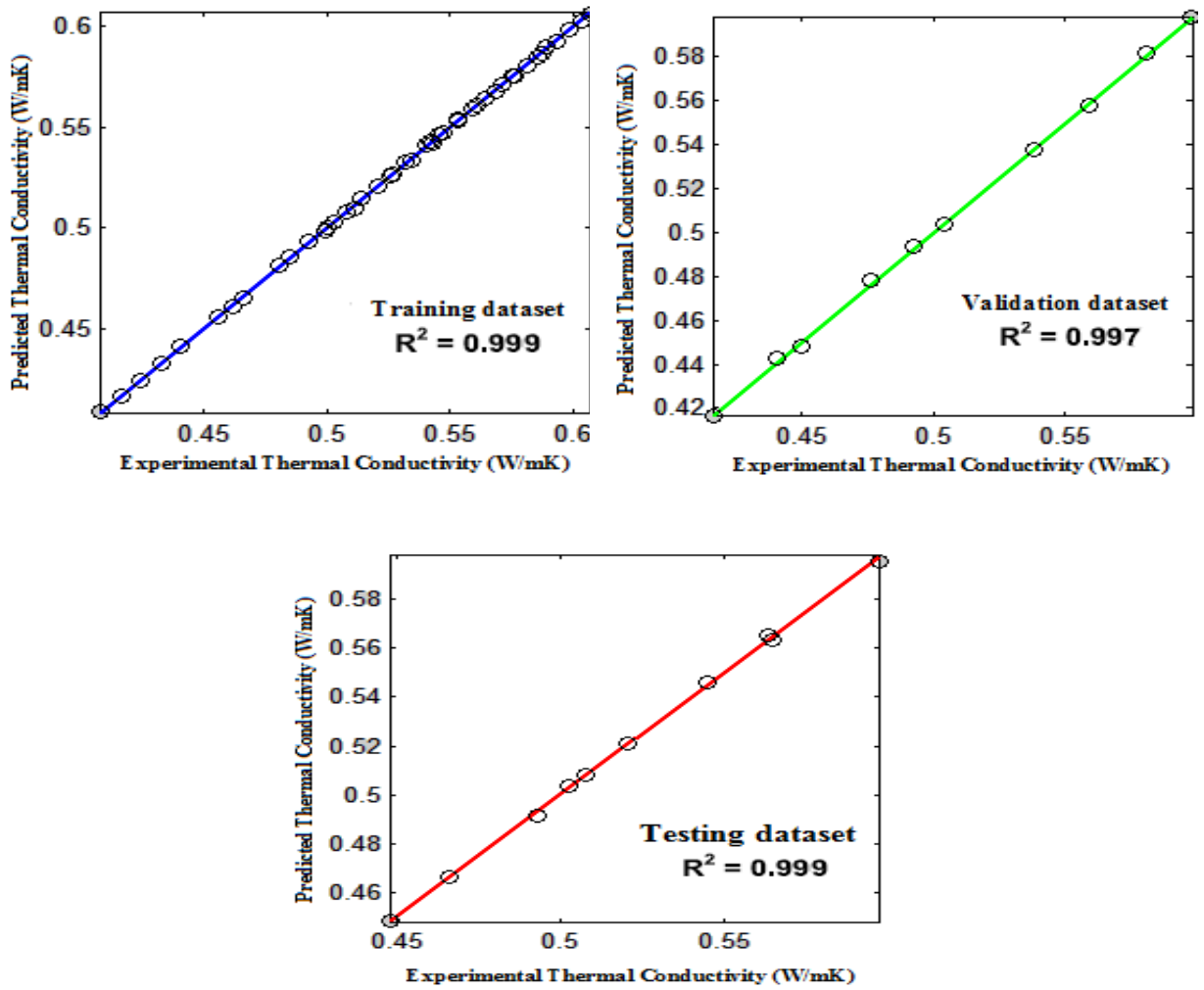

Figure 5. Correlation of experimental versus neural network values of thermal conductivity with training, validation and testing data set

Conclusion

A neural network based model was developed for the prediction of thermal conductivity of pear juice under a wide range of conditions of temperature and concentration. The optimal model, which consisted of 2 hidden layers and 5 neurons in first hidden layer, was able to predict thermal conductivity values. Empirical model was less accurate compared to neural network model in predicting the thermal conductivity. The ANN model can predict thermal conductivity of other juices when database be available.

where n is the number of experimental points; y_i^{exp} and y_i are the experimental and predicted values of thermal conductivity,respectively.Quantitative comparisons of the models using these statistical parameters are summarized in table 2, respectively.

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نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد ۱۱، شماره ۶، بهمن - اسفند ۱۳۹۴، ص. ۷۷۸-۷۷۰

Iranian Food Science and Technology Research Journal
Vol. 11, No. 6, Feb. Mrch. 2016, p. 770-778

استفاده از شبکه های عصبی مصنوعی برای پیش‌بینی هدایت حرارتی آب گلابی

زینب رفتنی امیری*[۱]، هنگامه درزی اربابی[۲]

تاریخ دریافت:۱۳۹۴/۰۷/۱۱
تاریخ پذیرش:۱۳۹۵/۰۳/۳۱

چکیده

هدایت حرارتی، یکی از ویژگی های مهم آب میوه ها برای پیش بینی ضرایب انتقال جرم وحرارت و هم چنین طراحی تجهیزات انتقال جرم و حرارت در صنعت آب میوه می باشد. شبکه عصبی مصنوعی برای پیش بینی هدایت حرارتی آب گلابی توسعه داده شد. دما و غلظت متغیرهای ورودی و هدایت حرارتی آب میوه متغیر خروجی بودند. مدل بهینه این شبکه شامل دو لایه پنهان با ۵ نرون در لایه اول و یک نرون در لایه دوم بود. مدل شبکه مصنوعی توانست مقادیر هدایت حرارتی را بسیار نزدیک به مقادیر اندازه گیری شده در آزمایش پیش بینی کند و در مقایسه با مدل های متعارف و رگرسیون چند متغیره از پایین ترین مجذور خطای میانگین (R^2=0.999)برخوردار بود. به علاوه با بکارگیری این روش می توان ساختار پنهان لایه ها در شبکه های عصبی را از طریق آزمون و خطا تعیین کرد.این روش می تواند در محاسبات انتقال حرارت در فراوری انواع آب میوه، جایی که نیاز به محاسبه هدایت حرارتی بر حسب دما و غلظت باشد، به خوبی مورد استفاده قرار گیرد.

واژه‌های کلیدی: آب میوه، شبکه عصبی مصنوعی، گلابی، هدایت حرارتی

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Iranian Food Science and Technology Research Journal

Vol. 11 No. 6 2016

Published by: Department of Food Science and Technology, College of Agriculture, Ferdowsi University of Mashhad, Iran.

Executive Manager: Poorazarang, H.

Editor-in-Chief: Razavi, Seyed M. A.

Executive Director: Taghizadeh, M.

Printed by: Ferdowsi University of Mashhad Press, Iran.

Address: The Iranian Food Science & Technology Research Journal, Scientific Publication Office, Food Science and Technology Department, Agriculture Faculty, Ferdowsi University of Mashhad, Iran.

P.O.BOX: 91775- 1163

Phone: (98)511-8795618-20(321)

Fax: (98)511-8787430

E-Mail: ifstrj@um.ac.ir

Web Site: http://jm.um.ac.ir/index.php/food_tech/index

This journal is indexed in ISC, SID, and MAGIRAN.

Contents

Ferdowsi University of Mashhad

Iranian Food Science and Technology Research Journal

Vol.11 No.6

2016

ISSN:1735-4161

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