Evaluation of Drying Methods With Respect to Drying Kinetics and Mineral Contents of Dill and Parsley

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ABSTRACT: *Dill (Anethum graveolens L.) and parsley (Petroselinum crispum Mill.) were dried by using sun and oven (50°C) drying methods. Oven drying decreased the drying time approximately 50% when compared to the sun drying method for both herbs. K, Ca, P, Mg and Na were the most abundant elements in dill and parsley samples. Oven dried samples had higher mineral values than that of the sun dried samples. Page, Modified Page, Midilli and Küçük and Diffusion approach were shown to give a good fit to the sun drying of parsley. The Midilli and Küçük and Verma models have shown a better fit to the experimental sun drying data of dill. Wang-Singh and Midilli and Küçük models gave the highest* r^2 *values for oven drying of parsley and dill, respectively.*

KEYWORDS: *Dill; Parsley; Mathematical modeling; Minerals; Drying kinetics.*

INTRODUCTION

Parsley (*Petroselinum crispum* Mill.) is a biennial plant growing to 0.3-0.6 m long. It is frequently used as a garnish or as a flavoring in salads and many cooked dishes and also used for medicinal purposes [1,2]. The dried leaves known as parsley flakes are particularly used in the instant food sector as an ingredient to flavor soups and sausages [3]. Dill (*Anethum graveolens* L.) is a biennial or annual plant belonging to the Umbelliferae family which is cultivated in temperate regions. Its' aromatic leaves are widely used in pickles, salads, sauces, fish, soups and in seasonings [1]. Due to their high moisture contents, in order to be better preserved parsley and dill need to be dehydrated through some drying process. Sun drying is not only the most common the method used to preserve foods but also has some problems of contamination and being weather and time dependent. Therefore using solar and hot-air dryers provides rapidity, uniformity, and hygiene [4,5]. Several drying methods have been developed in order to decrease the necessary energy and increase the biologic quality of the dried products [6]. Drying is the most important process causing substantial physico-chemical and sensory differences in plant product processes. Apart from their rich contents of vitamin C and beta carotene, herbs are an excellent source of mineral constituents whose importance in the human diet is indisputable. Some of them, such as potassium, sodium, phosphorus, calcium, magnesium or iron, are indispensable,

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in the sustainment of human health. Others such as copper or zinc are equally indispensable, but in this case, the interval between the acceptable and toxic levels is limited [7,8]. In recent years there has been a growing interest in mineral concentrations of foods, as the basic source of minerals for human [9]. The aim of this study was to determine the oven and sun drying kinetics of parsley and dill, and to evaluate the last products from the mineral contents point of view.

EXPERIMENTAL SECTION

Materials

Parsley (*Petroselinum crispum* Mill.) and fresh dill (*Anethum graveolens* L.) herbs were purchased from a local market in Konya, Turkey. Plant materials were kept in cooled bags while transporting to the laboratory. The moisture content of the herb was immediately measured on arrival. HNO_3 used in the mineral assay was of analytical grade (Merck, Germany). Prior to each of drying experiments, the thick stems of herbs were separated.

Methods

Drying of herbs

Oven drying

Samples were distributed uniformly as a thin layer on the trays and dried in an oven at 50ºC for 12 hours [10].

Open Sun drying

Samples were distributed uniformly as a thin layer on the trays and dried under direct sunlight at temperatures between 18-25ºC for 13 hours in May in Konya, Turkey [10]. The mass of the sample was measured in every 1 hour during oven and sun drying (*Günhan*, 2005; *Maskan*, 2002) using a digital balance, measuring to an accuracy of 0.001 g [11]. The moisture content of the plant material was measured by drying in an oven at 105ºC for 24h. The initial moisture content of the plant material was determined as 77.15% (kg[H_2O]/kg[DM]). Experiments were repeated three times and mean values were used.

Mathematical modelling of drying curves

For mathematical modelling, the equations in Table 1 were tested to select the best model for describing the drying curve equation of the herbs during drying. The moisture ratios of samples during drying were calculated using the equation; $MR = (M - M_{e)}/(M_0-M_e)$ [12]. The regression was performed in Statistica computer program (Statistica for Windows 5.0). The coefficient determination (r^2), Sum Square Error (SSE) and Root Mean Square Error (RMSE) were calculated in order to evaluate the goodness of fit to the models. The lower the SSE and RMSE values and the higher r^2 values indicate the high fit of the model [13].

Determining the mineral composition

About 0.5 g dried and a ground sample was put into a burning cup and 15 mL pure HNO_3 was added. The sample was incinerated in a MARS 5 Microwave Oven (CEM Corporation, USA, 3100 Smith Farm Road, Matthews, NC 28105-5044) at 200ºC temperature and a solution diluted to a certain volume (50 mL) with distilled water. Mineral concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) [14].

Working conditions of ICP-AES:

Instrument : ICP-AES (Varian-Vista)
RF Power : 0.7-1.5 kW (1.2- 1.3 kW for Axial)
Plasma gas flow rate (Ar) : 10.5-15 L/min. (radial)
15 L/min. (axial)
Auxiliary gas flow rate (Ar) : 1.5
Viewing height : 5-12 mm
Copy and reading time : 1-5 s (max. 60 s)
Copy time : 3 s (max. 100 s)

RESULTS AND DISCUSSION

Drying characteristics of dill and parsley

Twelve different MR models were used to determine the moisture content as a function of drying time (Table 1). The variation of weight of the product as a function of time was followed. In Tables 2 and 3, specific drying times and rate for the sun and oven drying are presented. Plots of the moisture ratio versus time curves are shown in Figs. 1 and 2 which represent the experimental curve of drying characteristics of dill and parsley. The moisture content of the materials were very high during the initial phase of the drying which resulted in high drying rates due to the higher moisture diffusion. The drying rate decreased continuously throughout the drying time. Drying process of parsley and dill herbs were in falling rate period. By using oven drying method the drying time

Table 1: Mathematical models applied to the drying curve.

Model no.	Equation	Model name	References
1	MR=exp(-kt)	Lewis	(Ayensu, 1997)
2	MR=exp(-kt^y)	Page	Diamante and Munro, 1993)
3	MR=exp(-(kt)^y)	Modified Page	(Özdemir and Devres, 1999)
4	MR=a exp(-kt)	Henderson and Pabis	(Henderson and Pabis, 1961)
5	MR=a exp(-kt)+c	Logarithmic	(Yaldız et al., 2001)
6	MR=a exp(-k$_o$t)+b exp(-k$_1$t)	Two-term model	(Togrul and Pehlivan, 2002)
7	MR=a exp(-kt^n)+bt	Midilli and Kucuk	(Lahsasni et al., 2004)
8	MR= a exp(-kt)+b exp(-gt)+c exp(-ht)	Mod. Henderson and Pabis	(Karathanos, 1999)
9	MR= a exp(-kt)+(1-a) exp(-kat)	Two-term exponential	(Sharaf-Elden et al., 1974)
10	MR= a exp(-kt)+(1-a) exp(-kbt)	Diffusion approach	(Kasem, 1998)
11	MR=1+at+bt^2	Wang-Singh	(Wang and Singh, 1978)
12	MR= a exp(-kt)+(1-a) exp(-gt)	Verma	(Verma et al., 1985)

Table 2: Moisture contents (dwb) and drying rates of dill (A. graveolens L.) at specific drying times according to oven and sun drying methods.

Time	Oven drying		Sun drying	
t(h)	Moisture content	Drying rate	Moisture content	Drying rate
0	6.41	-	6.407	-
1	1.62	4.79	2.065	4.34
2	0.93	2.74	1.098	2.65
3	0.71	1.90	0.626	1.93
4	0.23	1.54	0.454	1.49
5	0.10	1.26	0.271	1.23
6	0.03	1.06	0.175	1.04
7	0.02	0.91	0.125	0.90
8	0.01	0.80	0.097	0.79
9			0.062	0.70
10			0.051	0.64
11			0.041	0.58
12			0.035	0.53

Table 3: Moisture contents (dwb) and drying rates of parsley (P. crispum Mill.) at specific drying times according to oven and sun drying method.

Time	Oven drying		Sun drying	
t(h)	Moisture content	Drying rate	Moisture content	Drying rate
0	6.69	-	6.69	-
1	1.82	4.87	1.50	5.19
2	0.92	2.88	1.07	2.81
3	0.52	2.06	0.70	2.00
4	0.36	1.58	0.48	1.55
5	0.11	1.32	0.30	1.28
6	0.07	1.10	0.21	1.08
7	0.03	0.95	0.17	0.93
8	0.01	0.83	0.14	0.82
9			0.11	0.73
10			0.08	0.66
11			0.07	0.60
12			0.06	0.55

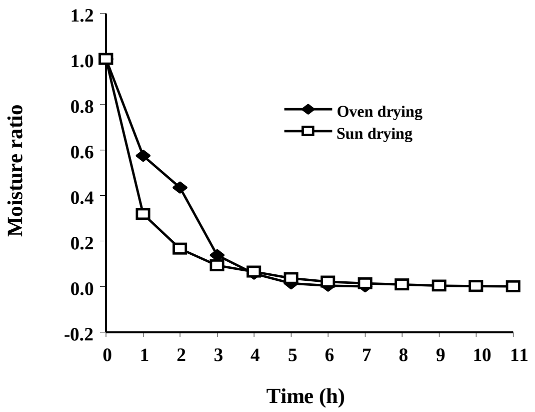

Fig. 1: Variations of moisture ratio as a function of time for oven and sun drying of dill.

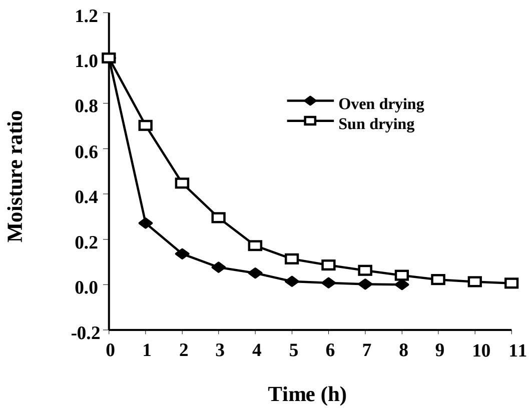

Fig. 2: Variations of moisture ratio as a function of time for oven and sun drying of parsley.

needed up to the moisture content of 6.3% (wwb) was 6 hours, while 11 hours needed to reach the same moisture content by sun drying of parsley. By oven drying method the drying time needed up to the moisture content of 3.04% (wwb) was 6 hours, while 12 hours needed to reach a closer moisture content (3.42% (wwb)) by sun drying of dill. At the end of 9 hours oven drying, parsley and dill materials had 1.30 and 0.82% (wwb) moisture content, respectively. At the end of 13 hours sun drying, parsley and dill materials had 4.59 and 2.12% (wwb) moisture content, respectively. The time was longer for sun drying of both herbs due to the low and fluctuating temperature during the drying period.

Evaluation of the models

These models exhibited a high coefficient of determination (r^2) values ranging between 0.9873-0.9978 for oven drying, 0.9913-0.9993 for sun drying of parsley and (r^2) values ranging between 0.9646-0.9944 for oven drying, 0.9954-0.9995 for sun drying of dill.

Table 4: Results of statistical analysis on the modelling of moisture contents and drying time for the oven dried parsley plant.

Model no.	Parameters	r^2	SSE	RMSE
1	k=0.3550	0.9873	0.0028	0.0529
2	k=0.2474 y=1.2914	0.9947	0.0012	0.0342
3	k=0.3390 y=1.2914	0.9947	0.0012	0.0342
4	k=0.3670 a=1.0374	0.9883	0.0026	0.0508
5	k=0.2470 a=1.1987 c= -0.1945	0.9969	0.0007	0.0262
6	k_0=0.3670 k_1=0.3670 a= 0.5187 b=0.5187	0.9883	0.0026	0.0508
7	k=0.2582 a=0.9938 b= -0.0111 n=1.1280	0.9970	0.0007	0.0258
8	k=0.3670 a=0.3458 b= 0.3458 g=0.3670 c=0.3458 h=0.3670	0.9883	0.0026	0.0508
9	k=0.4921 a=1.8005	0.9940	0.0013	0.0365
10	k=0.3550 a=0.1347 b= 1.0000	0.9873	0.0028	0.0529
11	a=-0.2537 b=0.0161	0.9978	0.0005	0.0221
12	k=0.1473 a=-18.0126 g=0.1546	0.9971	0.0006	0.0252

The statistical values are given in Tables 5, 6, 7 and 8. It is clear that Wang-Singh model gave the highest r^2 value (0.9978) and the lowest SSE and RMSE values for the oven drying of parsley. Page, Modified Page, Midilli and Küçük and Diffusion approach models gave the highest r^2 values for the sun drying of parsley. The r^2 value (0.9944) obtained from the Midilli and Küçük model was higher and SSE and RMSE values were lower than those obtained from other models for oven drying of dill. The highest r^2 values for the sun drying of dill were obtained from *Midilli* and *Küçük* (0.9995) and *Verma* (0.9994) models. Thus, these models may be assumed to present the oven and sun drying behaviours of dill and parsley herbs.

Mineral contents

The mineral contents of oven dried, sun dried and fresh parsley and dill herbs were given in Tables 9 and 10, respectively. K, Ca, Na, P, Mg, Fe and Al were the major minerals in fresh and dried samples of both parsley and dill herbs. The differences between Cd, Cu and Ni values of fresh and dried parsley samples were not statistically significant, as well as Li values of fresh and dried dill samples. Oven dried parsley samples had the highest Ag, Al, B, Ca, Fe, K, Li, Mn and Pb values. The remaining minerals had closer values in oven and sun dried samples. Pb values of fresh and sun dried parsley samples were not statistically significant. Ca, Cd, Fe, Mn, Sr and V values of oven and sun dried dill samples were not statistically different from each other. Al, B, K, Mg, Ni, P and Zn values of oven dried dill samples were higher than the values of sun dried samples. The differences between Na, Ag and Pb values of fresh and sun dried dill samples were not statistically significant. Cu values were higher in sun dried dill samples than the oven dried samples which may be attributed to the uncontrolled open air conditions of the sun drying process. Ca (11912.73 ppm), Cu (6.08 ppm), K (32437.16 ppm) and Zn (15.62 ppm) values of oven dried dill were closer, Fe (571.95 ppm), Li (2.79 ppm), Mn (60.42 ppm), P (8272.70 ppm) and V (46.62 ppm) values were higher and the remaining values were lower than the values (dry material) of Özcan [15]. Al (402.08 ppm), Cu (6.89 ppm), Mn (62.16 ppm), Ni (6.69 ppm) and Zn (34.68 ppm) values of parsley were closer to the values of *Özcan* [15]. *Akgül* [1] reported the mineral composition of dill as expressed in ppm was: Ca- 17840, Fe- 490, Mg- 4510, P- 5430, K- 33080, Na- 2080 and Zn- 30. Ca, Mg and Zn levels were higher than the results of the present study. The mineral composition of parsley in the same study as expressed in ppm was: Ca-14680, Fe- 980, K- 38050, Mg- 2490, P- 3510 and Zn- 50. Ca and Fe levels were higher than the results of the present study. Ca, Fe, K and Na values of fresh parsley were reported before as 1400 ppm, 600 ppm, 5500 ppm, and 600 ppm, respectively [16]. Ca, K and Na values were lower, but Fe value was higher

Table 5: Results of statistical analysis on the modelling of moisture contents and drying time for the sun dried parsley plant.

Model no.	Parameters	r^2	SSE	RMSE
1	k=0.2675	0.9913	0.0018	0.0424
2	k=0.1718 y=1.2972	0.9993	0.0001	0.0122
3	k=0.2572 y=1.2972	0.9993	0.0001	0.0122
4	k=0.2831 a=1.0636	0.9937	0.0013	0.0363
5	k=0.2311 a=1.1247 c= -0.0848	0.9971	0.0006	0.0244
6	k_0=0.2831 $k_{1=}$0.2831 a= 0.5318 b=0.5318	0.9937	0.0013	0.0363
7	k=0.1771 a=1.0054 b= -0.0005 n=1.2733	0.9993	0.0001	0.0120
8	k=0.2831 a=0.3545 b= 0.3545 g=0.2831 c=0.3545 h=0.2831	0.9937	0.0013	0.0363
9	k=0.2675 a=0.9999	0.9913	0.0018	0.0424
10	k=0.7055 a=-0.9697 b= 0.5586	0.9993	0.0001	0.0118
11	a=-0.1916 b= 0.0093	0.9966	0.0007	0.0267
12	k=0.1389 a=-23.5587 g=0.1426	0.9968	0.0007	0.0259

Table 6: Results of statistical analysis on the modelling of moisture contents and drying time for the oven dried dill plant.

Model no.	Parameters	r^2	SSE	RMSE
1	k=0.3874	0.9646	0.0093	0.0965
2	k=0.1452 y=1.8741	0.9938	0.0017	0.0406
3	k=0.3572 y=1.8741	0.9938	0.0017	0.0406
4	k=0.4130 a=1.0821	0.9685	0.0083	0.0912
5	k=0.2801 a=1.2509 c= -0.1983	0.9812	0.0050	0.0707
6	k_0=0.4130 $k_{1=}$0.4130 a= 0.5410 b=0.5410	0.9685	0.0083	0.0912
7	k=0.1182 a=0.9637 b= -0.0005 n=2.0155	0.9944	0.0015	0.0386
8	k=0.4130 a=0.3607 b= 0.3607 g=0.413 c=0.3607 h=0.4130	0.9685	0.0083	0.0912
9	k=0.3874 a=0.9999	0.9646	0.0093	0.0965
10	k=0.1528 a=-100.441 b= 1.0099	0.9809	0.0051	0.0712
11	a=-0.2786 b= 0.0190	0.9872	0.0034	0.0584
12	k=0.1512 a=-29.7134 g=0.1562	0.9809	0.0051	0.0712

than the results of the present study. These differences might be due to growth conditions, genetic factors, geographical variations and analytical procedures [17].

CONCLUSIONS

Oven drying decreased the drying time approximately 50% when compared to the sun drying method for both herbs. K, Ca, P, Mg and Na were the most abundant elements in dill and parsley samples. Oven dried samples had higher mineral values than the sun dried samples. The changes in the concentrations of minerals were dependent on the method and the drying temperature. Wang-Singh model gave the highest r^2 value for the oven drying of parsley. Page, Modified Page, Midilli and Küçük and Diffusion approach models gave the highest r^2 values for the sun drying of parsley. The r^2 value (0.9944) obtained from the Midilli and Küçük model was higher than those obtained from other models for oven drying of dill.

Table 7: Results of statistical analysis on the modelling of moisture contents and drying time for the sun dried dill plant.

Model no.	Parameters	r^2	SSE	RMSE
1	k=0.3016	0.9959	0.0008	0.0281
2	k=0.2341 y=1.1781	0.9991	0.0002	0.0135
3	k=0.2916 y=1.1781	0.9991	0.0002	0.0135
4	k=0.3102 a=1.0313	0.9965	0.0007	0.0261
5	k=0.2634 a=1.0740 c= -0.0621	0.9991	0.0002	0.0130
6	k_0=0.3102 $k_{1=}$0.3102 a= 0.5157 b=0.5157	0.9965	0.0007	0.0261
7	k=0.2402 a=0.9957 b= -0.0022 n=1.1265	0.9995	0.0001	0.0097
8	k=0.3102 a=0.3438 b= 0.3438 g=0.3102 c=0.3438 h=0.3102	0.9965	0.0007	0.0261
9	k=0.3955 a=1.6965	0.9990	0.0002	0.0138
10	k=0.4844 a=-219.184 b= 0.9974	0.9992	0.0002	0.0128
11	a=-0.2074 b= 0.0107	0.9954	0.0009	0.0300
12	k=0.1721 a=-14.7303 g=0.1782	0.9994	0.0001	0.0111

Table 8: Mineral contents of fresh, oven dried and sun dried parsley (mg/kg).

Minerals	Fresh parsley	Oven dried parsley	Sun dried parsley
Ag	0.03±0.18 iC	0.17±0.01 hA	0.14±0.16 hB
Al	78.13±21.13 gC	402.08±33.36 gA	327.03±22.14 gB
B	1.62±1.59 iC	19.09±1.14 hA	16.79±3.51 hB
Ca	3948.39±3504.69 bC	8968.00±390.53 bA	8706.36±353.11 bB
Cd	0.58±0.09 i	0.67±0.08 h	0.59±0.137 h
Cu	2.97±3.45 i	6.89±0.22 h	6.11±0.34 h
Fe	160.46±6.04 fC	271.85±41.78 fA	206.15±11.97 fB
K	6199.96±456.79 aC	35298.89±882.41 aA	34170.41±1234.59 aB
Li	3.99±0.50 iC	5.90±0.088 hA	5.65±0.444 hB
Mg	1244.22±520.62 dB	2650.53±234.96 dA	2503.38±187.09 dA
Mn	11.64±1.75 iC	62.16±2.90 hA	57.33±4.09 hB
Na	1933.00±920.17 cB	5658.70±200.25 cA	5607.08±452.251 cA
Ni	5.53±3.08 i	6.69±0.37 h	5.82±0.16 h
P	782.67±291.98 eB	2477.26±291.14 eA	2318.24±167.78 eA
Pb	0.84±0.19 iB	1.48±0.66 hA	1.07±0.46 hB
Sr	27.09±18.59 ghB	95.60±1.68 hA	90.86±3.86 hA
V	14.21±13.44 iB	31.02±1.01 hA	29.87±0.89 hA
Zn	21.24±25.39 iB	34.68±0.98 hA	30.79±1.80 hA

1) Mean±standard deviation
2) Different upper case letters in a row show statistically significant differences between treatments at 5% level probability.
3) Different lower case letters in a coloumn show statistically significant differences between mineral values at 5% level probability.

Table 9: Mineral contents of fresh, oven dried and sun dried dill (mg/kg).

Minerals	Fresh dill	Oven dried dill	Sun dried dill
Ag	0.057±0.05 gB	0.29±0.20 hA	0.06±0.01 hB
Al	57.17±7.65 gC	412.41±20.80 gA	370.91±10.88 gB
B	0.22±0.37 gC	15.21±0.78 hA	12.86±2.36 hB
Ca	3289.20±127.65 bB	11912.73±301.24 bA	11834.72±296.52 bA
Cd	0.45±0.03 gB	0.77±0.08 hA	0.67±0.03 hA
Cu	2.15±0.50 gC	6.08±0.40 hB	6.98±0.62 hA
Fe	239.15±6.23 fB	571.95±24.89 fA	511.95±57.16 fA
K	4749.01±122.83 aC	32437.16±759.58 aA	29330.50±1737.50 aB
Li	2.46±0.28 g	2.79±0.19 h	2.57±0.11 h
Mg	900.93±69.45 eC	3223.97±228.96 dA	2467.19±101.90 dB
Mn	17.99±2.90 gB	60.42±3.16 hA	60.30±5.35 hA
Na	1401.77±237.19 cB	1953.11±222.51 eA	1514.33±214.37 eB
Ni	3.31±0.14 gC	5.83±0.27 hA	5.55±0.69 hB
P	1164.05±206.33 dC	8472.70±438.37 cA	7649.35±352.46 cB
Pb	1.59±0.37 gB	1.84±0.12 hA	1.56±0.63 hB
Sr	20.76±1.63 gB	53.45±2.25 hA	53.12±2.70 hA
V	10.51±0.44 gB	46.62±1.69 hA	44.78±3.45 hA
Zn	7.13±1.09 gC	15.62±4.29 hA	13.30±1.29 hB

The highest r^2 values for the sun drying of dill were obtained from Midilli and Küçük and Verma models. In addition to its long time and environmental dependent process, sun drying is not recommended from the hygienic and nutritious qualities of the final product.

Nomenclature

a, b, c,g,h	Empirical constants in drying models
k, k_0, k_1	Empirical constants in drying models
MR	Moisture ratio, dimensionless
M	Moisture content at any time
M_e	Equilibrium moisture content
M_0	Initial moisture content
N	Positive integer
RMSE	Root mean square error
r^2	Coefficient of determination
SSE	Sum square error
t	Drying time, h
y	Empirical constant in drying models

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