Effect of adulteration on honey properties

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Abstract

Honey samples belong to clover plants (Trifolium alexandrinanum) were obtained from private Beehives at Gharbia governorate in June 2010. Adulteration of honey was obtained by the addition of four different materials (starch, glucose, molasses, and distilled water) with different concentrations (1, 3, 6, 12, and 24%). Physico-chemical and rheological characteristics of pure and adulterated honey samples were investigated. The samples were found to differ from each other in refractive index (R.I), moisture content, total soluble solids (T.T.S), density, specific weight, capillary action, surface tension and pH. The rheological properties of pure and adulterated honey were analyzed using Brookfield viscometer over a range of 10-100 rpm and 25ºC, pure honey exhibited Newtonian behavior, while adulterated honey exhibited non-Newtonian pseudoplastic behavior.

Keywords: honey adulteration, physiochemical properties. rheological properties, viscosity, flow behavior of honey.

Introduction

Honey is natural complex food product produced by bees from nectar of plants and from honeydew. It is a unique sweetening agent that can be used by humans without processing, (Ahmed et al., 2007). The composition and properties of honey vary with the floral and honeydew sources utilized by honeybees, as well as regional and climatic conditions (Lazaridou et al., 2004). Honey syrup preserves human health and shields them from various diseases. It is defined as a pure and natural product that does not include any other substances, (Wikipedia, 2008).

Honey adulteration is a complex problem, which has a significant economic impact; it can be occurred by the addition of different materials. Adulteration, or the addition of foreign substances to honey such as; molasses, starch solution, glucose, sucrose, water and inverted sugar, were studied by (Sharbt and Abdel- Fattah, 1994. Ruoff and Bogdanov, 2004. Bogdanov, 2010). Physiochemical characteristic of Egyptian honey were studied by (Ibrahim et al., 1978 and Roushdi et al., 1979). The results indicated that the total soluble solid varied from 81.5 to 83.0%, pH value was 4.0 and viscosity value was 60.00 C.P. Meanwhile, (Al-Khalifa and Al–Arify 1999) determined that the total soluble solids values was 82.20 – 84.33%, refractive index was 1.4948 – 1.5019, water insoluble solids was 0.02 – 0.59 %, pH value 3.70-6.06 and viscosity was 104-376 cp. at ten unfurl Saudi honeys.

Kamal, et al., (2002) determined the physiochemical parameters i.e. refractive index, specific gravity, water insoluble solids and total soluble solids….etc. The biochemical variation in the composition of honey due to floral type shows that Ziziphus honey had higher pH. Whereas, Trifolium honey contained the higher moisture content. Saif-ur -Rehman, et al., (2008), determined that physical properties, conductance, surface tension, and pH using digital instruments. The most abundant minerals found in Pakistani honey samples were K, Na, Ca, Mg, Fe, Zn, Cu, Ni and Co, with K accounting for almost 83% of the total mineral composition. Most Pakistani honey samples met international standards. However, some samples showed altered parameters, reflecting possible adulteration. A considerable change in viscosity was observed only in adulterated honey samples containing more than 50% of a saturated sugar solution.

The water content as a function of the refractive index at 20ºC were taken and plotted based on a simple regression and the following equation was obtained, (Abu Jdayil et al., 2002).

$W = 608.277 - 395.743 R.I.$

Where, W is the water content in g/100g honey and R.I. is the refractive index

The rheological properties of honey, like many other physical properties, depend on many factors, including composition and temperature. One of the major factors is the water content. Generally, the viscosity of honey decrease with water content, (Zaitoun, et al., 2000). The rheological properties of honey also depend on the composition of individual sugars, and the amount and type of colloids present in honey (Bhanadari, et al., 1999).

Di'az, et al., (2005) studied the rheological properties of Galician honey and determined the effect of water content upon the apparent viscosity value, it was observed that a clear decrease in the viscosity value as water content increased. The effect of temperature upon the viscosity value was also analyzed in different honeys where its water content had been modified.

The objective of this work is to determine the effect of adulteration on the physical properties. These properties database can be used to design a simple taste detection tool of honey adulteration.

2. Materials and methods

2.1. Material:

Honey samples belong to clover plants (Trifolium alexandrinanum) were collected from private beehives at Gharbia governorate in June 2010.

2.2. Methods:

Pure honey was adulterated by the addition of four different materials (starch solution 3%, glucose syrup 20%, molasses and distilled water) with different concentrations (1, 3, 6, 12, 24%) each concentration were added separately. Three replicates were taken to determine the physiochemical properties of honey (refractive index, moisture content (%), total soluble solids (%), density ($g.cm^{-3}$), specific weight ($cm^3.g^{-1}$), capillary action (mm), surface tension ($N.m^{-1}$) and pH value) and the rheological properties.

2.2.1. Refractive index (R.I)

Refractive index was determined using a digital refractometer. Before doing the measurements, the refractometer was calibrated using distilled water in accordance with the instrument's instructions.

2.2.2. Density (ρ) and specific weight:

The density of a substance is its mass per unit volume. Meanwhile, specific weight is its volume per unit mass.

2.2.3. Surface tension (σ)

Surface tension calculated from the following equation:

$$\sigma = \frac{h\, r\, \rho\, g}{2}$$

Where, h= Solution height on capillary tube, cm

r = Capillary tube radius,(1.15×10^{-3} cm)

ρ= Solution density, $g.\ cm^{-3}$

g = Standard gravity (constant) = 9.80 $m.s^{-2}$

2.2.4. pH value

pH values were determined using pH meter

2.2.5. Rheological properties

A Brookfield Digital Rheometer, Model DVIII Ultra and spindle No. HA-07 was used to measure the apparent viscosity of pure honey and adulterated honey samples. Samples were placed in a beaker. The temperature of honey samples was controlled by a thermostatic water bath provided with the instrument. The apparent viscosity of honey samples were studied at 30°C and different rotational speeds (10-100 rpm).

Shear rate was calculated using the following equation (Brookfield Manual, 1998):

$$\gamma = [\frac{2\pi \ R_c^2}{60(R_c^2 - R_b^2)}]rpm$$

Where, γ = Shear rate, 1/sec
R_c = Container radius, (2.5cm)
R_b = Spindle radius, (0.15cm)

3. Results and Discussions

3.1. Physiochemical properties:

Table (1) shows the physiochemical properties of pure honey and adulterated honey by adding of starch, glucose, molasses and distilled water.

Table 1: Physical characterization of adulterated honey samples.

Adding material	Conc. (%)	Refractive Index	Moisture content (%)	Total Soluble Solids (%)	Density ($g.cm^{-3}$)	Specific weight ($cm^{-3}.g^{-1}$)	Capillary action (mm)	Surface tension ($N.m^{-1}$)	pH value
Pure Honey		1.4911	78.6	21.4	1.407	0.7107	15.04	0.1194	3.76
Starch solution		1.432	97	3%	1.016	0.9841	36.72	0.2107	6.41
Starch solution 3%	1	1.4892	21.2	78.8	1.4031	0.7127	15.60	0.1236	3.77
	3	1.4859	23.7	76.3	1.3953	0.7167	19.68	0.1551	3.71
	6	1.4849	26.6	73.4	1.3836	0.7228	22.87	0.1787	3.75
	12	1.4729	27.9	72.1	1.3601	0.7352	23.40	0.1798	4.2
	24	1.4514	36.6	63.4	1.3132	0.7615	24.07	0.1785	4.06
Glucose syrup		1.371	77.6	22.4	1.156	0.8654	33.74	0.2202	4.59
Glucose syrup 20%	1	1.371	20.7	79.3	1.4045	0.7120	15.06	0.1194	3.68
	3	1.4903	24.1	75.9	1.3995	0.7146	16.85	0.1332	3.73
	6	1.4805	27.6	72.4	1.3919	0.7184	17.62	0.1385	3.73
	12	1.4849	28	72	1.3768	0.7263	17.94	0.1395	3.66
	24	1.4784	39.6	60.4	1.3467	0.7426	18.32	0.1393	4.02
Molasses		1.4739	26.8	73.2	1.437	0.6955	27.94	0.2269	4.67
Molasses	1	1.4893	22.2	73.2	1.4073	0.7106	16.10	0.1279	3.95
	3	1.4899	20.9	77.8	1.4079	0.7103	19.70	0.1566	3.97
	6	1.4902	21.9	79.1	1.4089	0.7098	20.87	0.1660	3.94
	12	1.488	21.7	78.1	1.4107	0.7089	21.66	0.1726	3.98
	24	1.4869	22.7	78.3	1.4144	0.7070	21.99	0.1756	4.11
Distilled water		1.335			1	1	36.38	0.2055	7
Distilled water	1	1.4889	21.4	77.3	1.4029	0.7128	15.10	0.1196	3.68
	3	1.4881	24.9	75.1	1.3948	0.7169	15.40	0.1213	3.73
	6	1.4822	26.6	73.4	1.3826	0.7233	15.93	0.1244	3.86
	12	1.4703	27.9	72.1	1.3582	0.7363	15.95	0.1224	4.07
	24	1.4565	29.2	70.8	1.3093	0.7637	17.71	0.1309	4.19

3.1.1. Refrective Index (R.I), moisture content and total Soluble Solids (T.T.S)

The refractive index values were obtained for pure honey and adulterated honey with the addition of different concentrations of starch, water, Glucose and molasses. The results indicate that there is a slight difference in refractive index values. The moisture content of pure honey should be between 14% and 18%; although this number depends heavily upon the season and geographical conditions, (Saif-ur-Rehman, et al., 2008). The result indicates that moisture content varied from 21.2% to 36.6% for adulterated honey by the addition of starch, from 20.7 to 39.6 for adulterated honey by the addition of glucose, and from 21.4% to 29.2% for adulterated honey by the addition of distilled water. Moisture content is approximately constant in addition of molasses.

The percent of total soluble solids decrease with increasing concentration of starch, molasses, glucose and distilled water.

3.1.2. Density (ρ) and Specific weight:

Density values depend on water content, pure honey has a higher density compared with the other adulterated samples except molasses. The results indicate that density decreases with increasing concentration of starch added to honey, the same trend was observed for adulterated honey by the addition of glucose and distilled water. Density values increases with increasing concentration of molasses added to honey.

Figure (1) shows the relationship between density of adulterated honey and different concentrations of starch, glucose, distilled water and molasses. The results were fitted to the following equations:

- Adulterated honey by adding starch
  $\rho_S = -0.0039C_s + \rho_H$
- Adulterated honey by adding glucose
  $\rho_g = -0.0025\,C_g + \rho_H$
- Adulterated honey by adding molasses
  $\rho_m = 0.0003\,C_m + \rho_H$
- Adulterated honey by adding distilled water
  $\rho_w = -0.0041\,C_w + \rho_H$

Where:

ρ_H is the pure honey density, (1.407g.cm^{-3}), C is the concentration of added material (starch, glucose, molasses and distilled water), ρ_s is the honey density with the addition of starch, ρ_g is the honey density with the addition of glucose, ρ_m is the honey density with the addition of molasses, and ρ_w is the honey density with the addition of distilled water.

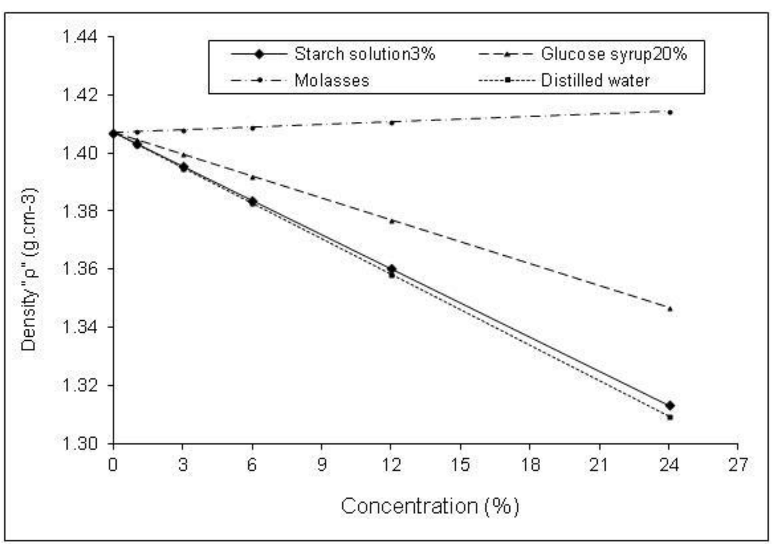

Fig. 1. Relationship between density of adulterated honey and different concentrations of added materials (starch, glucose, distilled water and molasses).

3.1.3. Capillary action (h) and surface tension (σ):

Table (1) shows the effect of adding different concentrations of starch, glucose, molasses and distilled water to pure honey on capillary action. The height of solution on capillary tube increases about 9.03, 3.28, 6.95, and 2.67 mm for starch solution, glucose syrup, molasses and distilled water with increasing concentration from 0, 1, 3, 6, 12, 24% respectively. The height of solution on capillary tube varied from 15.04 mm for pure honey to 24.07 mm for adulterated honey by adding starch 24%. The variation in height of capillary tube was not observed with adulterated honey by adding glucose syrup (3.28 mm) and distilled water (2.06mm).

The results were fitted to the following equations:

- Adulterated honey by adding starch

$$H_s = -0.036C_s^2 + 1.2152C_s + 15.386$$

- Adulterated honey by adding glucose

$$H_g = -0.012C_g^2 + 0.4174C_g + 15.139$$

- Adulterated honey by adding molasses

$$H_m = -0.0273C_m^2 + 0.9053C_m + 15.766$$

- Adulterated honey by adding distilled water

$$H_w = 0.0013C_w^2 + 0.0751C_w + 15.115$$

Where, H = height of capillary tube (mm)
C = Concentration of the added material

The results show that both solution height of capillary tube and density affects the surface tension values. Surface tension increases with increasing concentration of starch, glucose, molasses and distilled water.

Figure (2) shows the relationship between surface tension of adulterated honey and different concentrations of added materials (starch, glucose, molasses and distilled water). The results were fitted to the following equations:

- Adulterated honey by adding starch

$$\sigma_s = -0.0003C_s^2 + 0.0091C_s + 0.1224$$

- Adulterated honey by adding glucose

$$\sigma_g = -1\times10^{-04}C_g^2 + 0.0031C_g + 0.1203$$

- Adulterated honey by adding molasses

$$\sigma_m = -0.0002C_m^2 + 0.0072C_m + 0.1253$$

- Adulterated honey by adding water

$$\sigma_w = 7\times10^{-04}C_w^2 + 0.0003C_w + 0.11201$$

Where, σ = Surface tension value, ($N.m^{-2}$)
C= Concentration of added materials

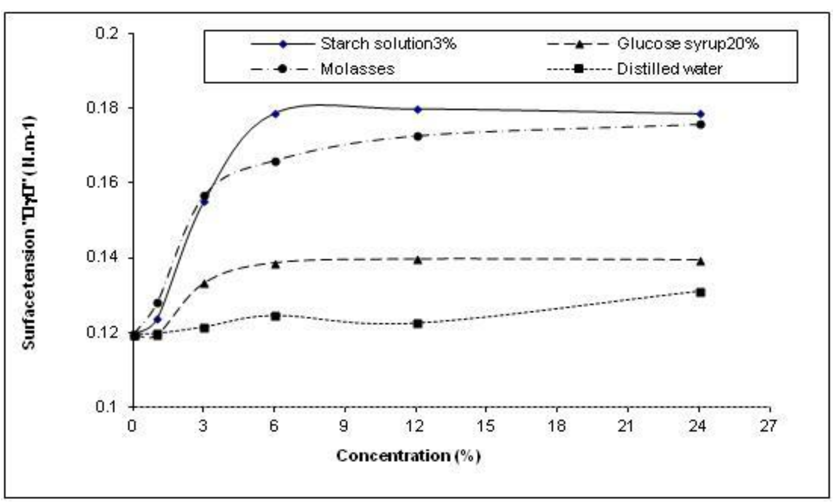

Fig. 2 Relationship between surface tension of adulterated honey and concentrations of starch, glucose, molasses and distilled water

3.1.4. pH value:

The result shows a slight variation in pH values at all concentrations of added materials. All studied honey samples were acidic in nature and the pH values were varied between 3.6 and 4.19. The acidity of honey developed due to presence of organic acids as previously discussed by (Ouchemoukh et al., 2006).

3.2. Rheological properties:

Freshly extracted honey is a viscous liquid; its viscosity depends on a large variety of substances and therefore varies with its composition and particularly with its water content.

3.2.1. Adulterated honey by adding Molasses

Figure (3) shows the shear rate-shear stress data of pure honey, molasses and adulterated honey by adding different concentrations of molasses (1, 3, 6, 12, 24%), the flow curves were fitted to power law model:

$$\tau = K\gamma^{n}$$

Where, τ is the shear stress, (Pa), K is the consistency index, γ is the shear rate, (s^{-1}) and n is the flow behavior index.

It was observed that pure honey exhibited Newtonian behavior with (K=9.1123) and (n=1.02), while molasses sample exhibited pseudoplastic behavior, as previously discussed by (Satindar, et al., 2002). Also, adulterated honey by adding different concentrations of molasses (1, 3, 6, 12, 24%) exhibited pseudoplastic behavior. As shown in Figure (3) the distance between the curves of honey and adulterated honey by adding 1% and 3% molasses are very small, resulting in two groups formed by pure honey and adulterated honey by adding (1, 3%) molasses, and the curves of adulterated honey by (3, 6, 12%) molasses, this may be due to structural change in honey samples as a result of adding different concentrations of molasses.

Figure (4) shows the relation between the apparent viscosity and shear rate of honey, molasses and adulterated honey by adding different concentrations of molasses. The results show that apparent viscosity decreases with increasing shear rate indicating shear thinning behavior, while apparent viscosity was approximately constant for pure honey indicating Newtonian behavior.

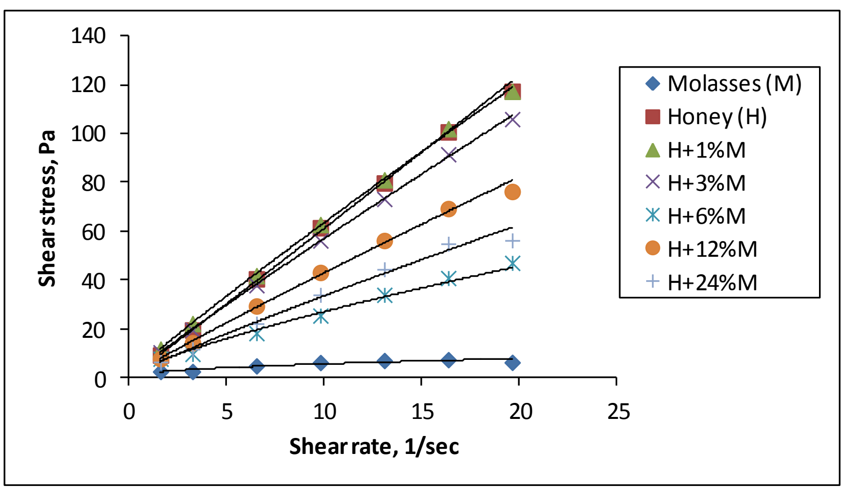

Fig. 3: Relationship between shear rate and shear stress for honey, molasses and adulterated honey by adding different concentrations of molasses.

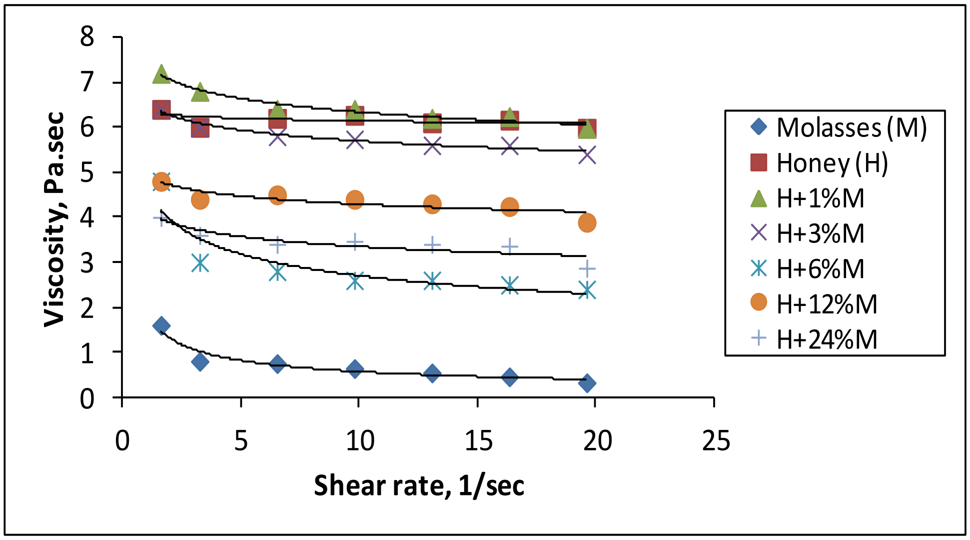

Fig. 4. Effect of adding molasses to pure honey on apparent viscosity.

3.2.2. Adulterated of honey by the adding starch

Commercial starch (3%) was added to pure honey samples with different concentrations (1, 3, 6, 12, 24%). Figure (5) shows the shear rate-shear stress data of pure honey, starch solution (3%) and adulterated honey by adding different concentrations of starch solution, the results indicate that all samples exhibited non-Newtonian pseudoplastic behavior. The distance between the curves at honey and adulterated honey with (1, 3, 6, 12, 24%) starch solution are very small, resulting in two groups formed by pure honey, starch solution and adulterated honey with (1, 3, 6, 12, 24%) starch, this may be due to structural change in honey samples as a result of adding different concentrations of starch.

Figure (6) shows that apparent viscosity decreases with increasing shear rate for adulterated honey by adding different concentrations of starch. At higher concentrations of starch added to pure honey the pseudoplasticity is turning out to be more visible.

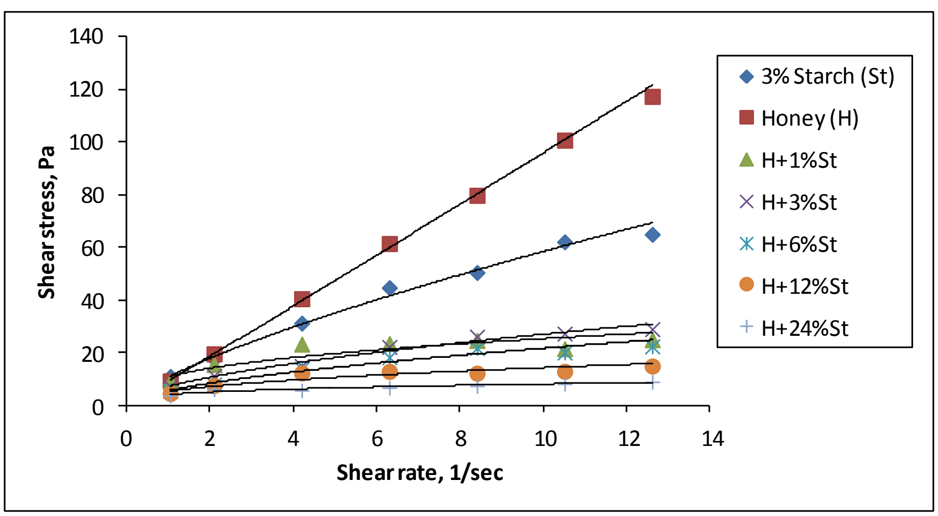

Fig.5. Relationship between shear rate and shear stress for honey, starch and adulterated honey by adding different concentrations of starch.

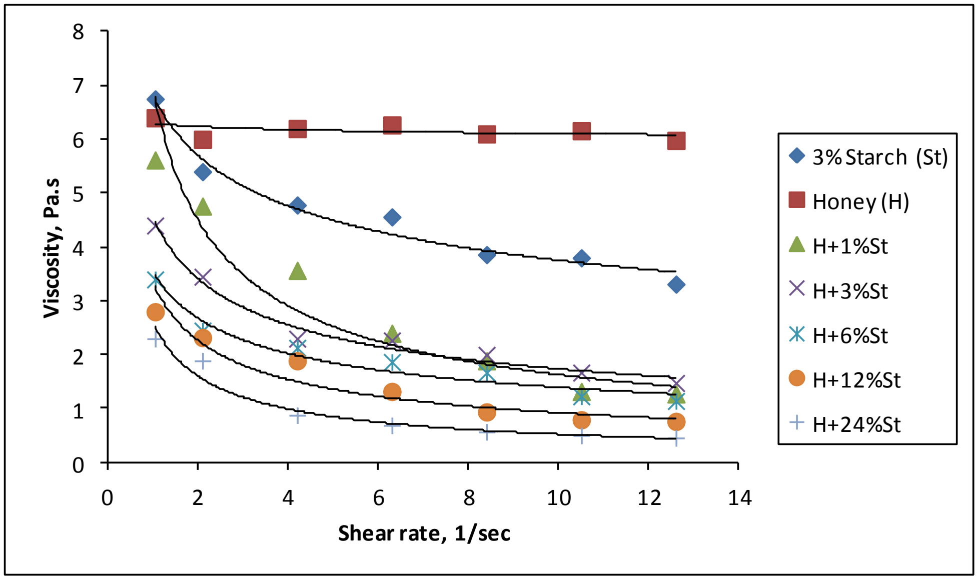

Fig. 6. Effect of adding different concentrations of starch solution to pure honey on apparent viscosity.

3.2.3. Adulterated of honey by the addition of distilled water

Water content is the main factor that influences the preservation of the honey's quality or its storage **(Di`az, et al., 2005)** . Different amount of distilled water (1, 3, 6, 12, and 24%) were added to pure honey. Figure (7) shows that all samples exhibited non-Newtonian pseudoplastic behavior at all amounts of water added.

The distance between the curves at honey and adulterated honey by adding (1, 3, 6, 12, 24%) distilled water are very small, this may be due to structural change in the honey samples with the addition of different concentrations of distilled water.

Figure (8) shows the relation between shear rate and apparent viscosity of adulterated honey by adding distilled water at different concentration (1, 3, 6, 12, 24%), the results indicates that apparent viscosity of honey decreases with increasing concentration of water. At adding different concentrations of distilled water to pure honey, the pseudoplasticity is turning out to be less visible.

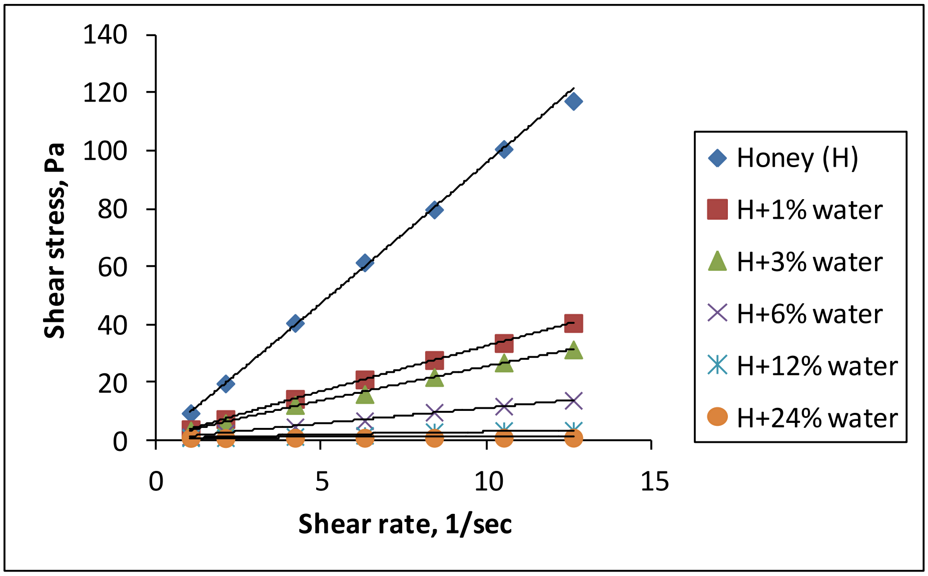

Fig.7. Relationship between shear rate and shear stress for pure honey and adulterated honey by adding different concentrations of distilled water.

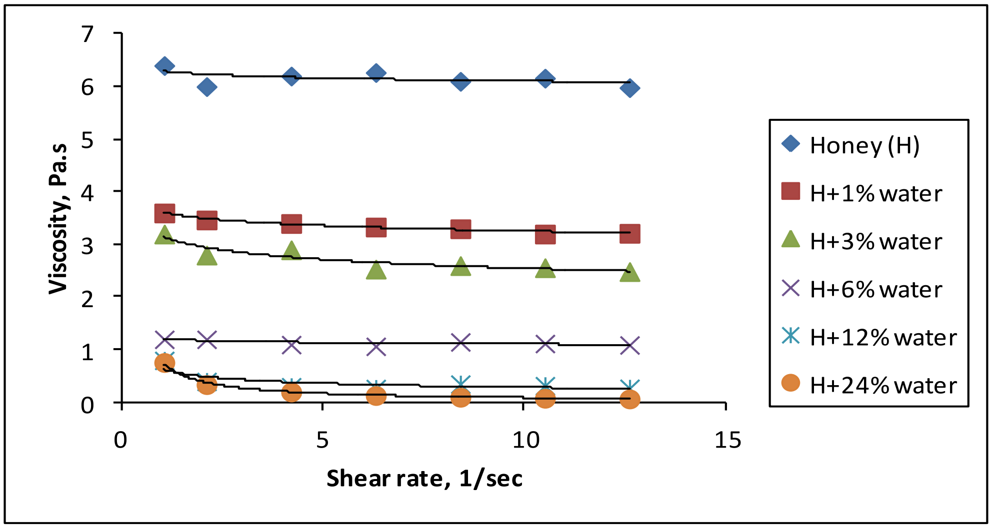

Fig. 8. Effect of adding different concentrations of distilled water to pure honey on apparent viscosity.

3.2.4. Adulterated of honey by the addition of glucose

Figure (9) shows the shear stress-shear rate data for glucose and adulterated honey by adding different concentrations of glucose (1, 3, 6, 12, 24%). The results indicate that these samples exhibited pseudoplastic behavior. The distance between the curves at honey and adulterated honey with (1, 3, 6, 12, 24%) glucose are very small, this may be due to structural change in honey samples as a result of adding different concentrations of distilled water.

Figure (10) shows that the apparent viscosity of glucose and adulterated honey by adding glucose decreases with increasing shear rate.

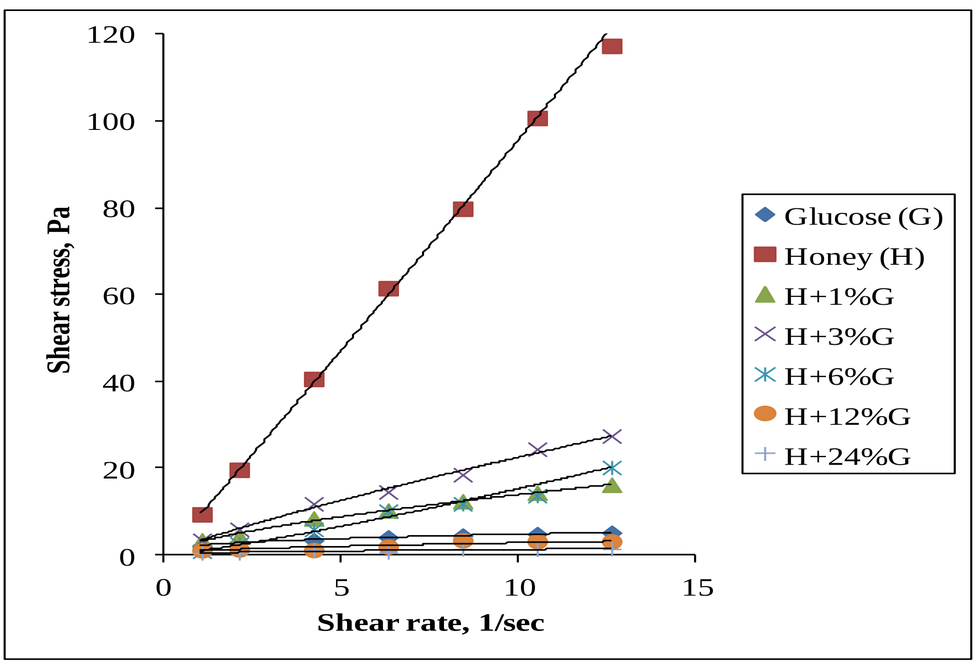

Fig.9. Relationship between shear rate and shear stress for honey, glucose and adulterated honey by adding different concentrations of glucose.

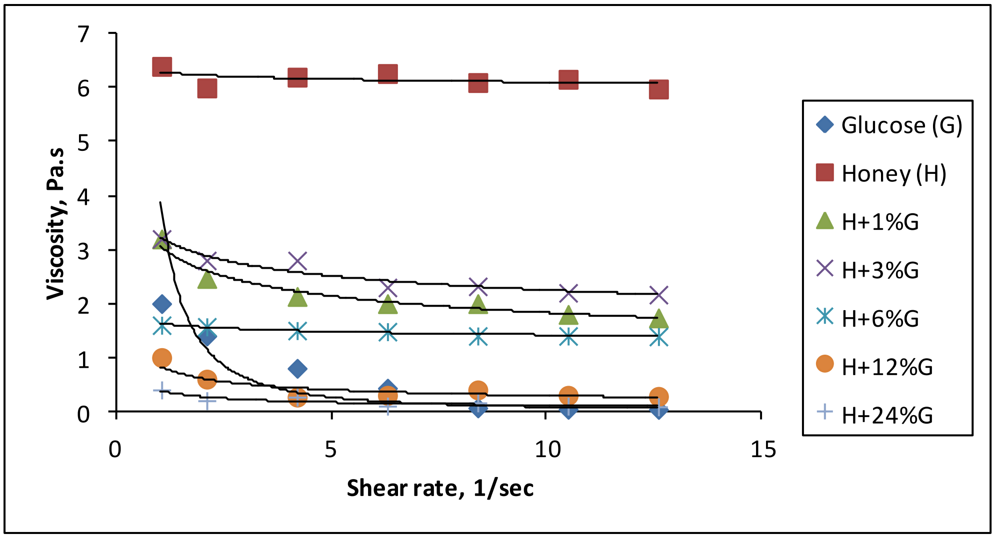

Fig. 10. Effect of adding glucose to pure honey on apparent viscosity.

Table (2) presents the parameters obtained by fitting to the power law model for pure honey and adulterated honey by adding different concentrations of starch, molasses, glucose and distilled water. The consistency indexes (K) of honey were affected by the addition of foreign material to pure honey. The flow behavior index is smaller than one for all adulterated honey samples this indicates a pseudoplastic behavior for adulterated honey.

Table (2) Parameters of Power law model for pure honey and adulterated honey samples.

Addition material	K (consistency index)	n (flow behavior index)
Pure honey	9.1123	1.0217
Starch solution (st)	10.621	0.74
H+1%st	10.883	0.3663
H+3%st	7.1178	0.5785
H+6%st	5.5312	0.5922
H+12%st	5.2063	0.4383
H+24%st	4.0628	0.2987
Glucose (G)	2.1645	0.339
H+1%G	3.0283	0.661
H+3%G	3.2351	0.8431
H+6%G	0.9114	1.2218
H+12%G	0.8571	0.5057
H+24%G	0.3686	0.5184
Molasses (M)	2.3404	0.4709
H+1%M	11.7	0.9326
H+3%M	9.005	0.94
H+6%M	6.5356	0.7616
H+12%M	7.4504	0.9403
H+24%M	6.1901	0.9064
Distilled water		
H+1%water	3.6114	0.9543
H+3%water	3.1506	0.9073
H+6%water	1.2009	0.963
H+12%water	0.6403	0.0491
H+24%water	0.7711	0.0491

Conclusion

Honey collected from clover plants (Trifolium alexandrinanum) was adulterated by adding four different materials (starch, molasses, glucose and distilled water). Adulterated honey varied in physico-chemical properties (refractive index (R.I), moisture content, total soluble solids (T.T.S), density, specific weight, capillary action, surface tension and pH value). The results showed that pure honey has Newtonian behavior, while adulterated honey exhibited non-Newtonian pseudoplastic behavior, which was fitted well to Power law model.

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