Effect of Ultrafiltration Permeate on the Quality of Chocolate Milk

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Abstract: The present study provides a new version of chocolate milk from a dairy liquid originated from skim milk and ultrafiltration (UF) milk permeate. The mixtures of chocolate milk containing milk permeate at different levels, were manufactured and stored at 4ºC for 2 weeks. Chemical, color characteristics, viscosity and sensory properties of various formulations were evaluated. Most of chemical analysis did not change before and after storage of chocolate milk with milk permeates. Results showed that the highest score of color was recorded for the (B4-B6) sample followed by (C7-C9) then (A1-A3) samples. The highest score of appearance was recorded for the (B4-B6) followed by (C7-C9) then (A1-A3) samples. Also, the highest score of viscosity were recorded for the (B4-B6) followed by (C7-C9) then (A1-A3) samples. From the previous results, it is obvious that results showed a decrease at the following order B6 > B5 > C9 > C8 > C7 > B4 > A3 > A2 > A1 regarding to L*, a*, b*, C*, H*, BI-values, chemical, viscosity and sensory evaluation. Finally, using milk permeate was able to produce a good quality chocolate milk. However, using the permeate has economic important because it considers valuable substitute to skim milk as partial or Whole replacement. Also, the added sugar can be reduced during manufacture as economic and healthy trend through reducing sugar in chocolate milk.

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Key words: Skim milk, Chocolate milk, milk permeate, ultrafiltration, viscosity and color.

1. Introduction:

Membrane separation technique is simple in operation and compatible with existing equipment and technology. Sample collection and concentration efficiency up to 100% can be achieved. Membrane technology has the potential for not only producing a superior product, but for considerable savings in capital and operating costs, by eliminating filter processes, cartridge filters and centrifuge. At present, membrane separation processes in general and ultrafiltration (UF) in particular has become more effective, in the separation of molecular solutions. The main reason for the emergence of UF as an industrial process is the breakthrough in polymer manipulation through blending of polymers (Vijayalakshmi et al., 2008). Due to these advantages the ultrafiltration technique is followed in this study. However, milk permeate, which penetrate the membrane during UF process of milk has been regarded as waste product, although it contains high level of lactose, soluble proteins, vitamins and minerals. However, because of its high nutrient content and its disposal can pose environmental problems, there is interest in finding a calue-added utilization for it. Chocolate milk has the same 15 essential nutrients as white milk, including the six bonebuilding nutrients of calcium, vitamin D, vitamin A, protein, magnesium and phosphorous. Other nutrients include: thiamine, riboflavin, niacin, vitamin B6, pantothenic acid, and zinc, vitamin B12 (cobalamin, carbohydrate and energy (calories). Here is a breakdown of each nutrients function. Chocolate milk is an excellent sports recovery beverage. Studies show that chocolate milk has the right combination of protein, electrolytes and carbohydrates to repair and recover after a workout. However, many studies have been shown that adding protein to the mix fit hasten recovery, accelerate of glycogen synthesis and improve endurance performance over carbohydrate ingestion alone(Saunders et al., 2004 and Valentine et al., 2006). Studies showed also that athletes ideally need a carbohydrate-to-protein ratio of 4:1[Ivy et al., 2003 and Romano et al., 2004]. With the recent growth in flavored milk sold, attention is needed to improve existing chocolate milks and guide new product introductions focusing on reduced calorie formulations (Boor, 2001). Chocolate milk has a great amount of carbohydrates more than that of plain milk, along with protein, electrolytes and other key nutrients, in quantities that commercial carbohydrate replacement drinks cannot match. Recently, some controversy has arisen over the efficiency of chocolate milk in recovery when taken after intense athletic workouts. Karp et al (2006) reported that chocolate milk is as good as or better than commercial sports drinks at helping athletes recover from strenuous exercise. The authors suggested that chocolate milk contains carbohydrates-to-protein ratio, which is ideal for helping refuel tired muscles after exercise at a high intensity during subsequent workouts. However, nutritionists have been criticized chocolate milk for its high fat and sugar content. The high fat content of chocolate milk may be delayed glycogen re-synthesis and decreased time to exhaustion due to a decreased gastric emptying rate and a consequent decreased carbohydrate absorption rate. Moreover, lactose in chocolate milk cannot be tolerated by lactose-intolerant and malabsorbers athletes, particularly if their gastrointestinal system grows more sensitive with exercise (Dehkordi et al., 1995). Also, chocolate milk contains oxalic acid, a compound occurring naturally in cocoa beans. Because of oxalic acid can combine with calcium in the intestine forming calcium oxalate, which is fairly insoluble, calcium absorption from chocolate milk has been questioned. Therefore, the object of the present intention was to study the effect of permeate by ultrafiltration of Cow's milk and storage at refrigerator on the chemical, color characteristics, viscosity and sensory evaluations of chocolate milk compared with those of conventional chocolate milk by skim milk. However, using the permeate has economic important because it considers valuable substitute to skim milk as partial or Whole replacement. Also, the added sugar can be reduced during manufacture as economic and healthy trend through reducing sugar in chocolate milk.

2. Material and Methods

Dry Ingredients:

Cocoa powder produced by Hintz Foodstuff Production GmbH Bremen, Germany. Sucrose and kcarrageenan were locally purchased. Vanilla produced by Dream Co., New Borg El-Arab City, Alexandria, Egypt.

Dairy Ingredients:

Fresh skim cow's milk (8.8% T.S) and milk permeate (5.5% T.S) were used.

Formulations:

Fresh skim Cow's milk 8.8 % T.S or mixtures of fresh skim milk and milk permeate (5.5% T.S). The dry ingredients of cocoa powder (1g/100 g mix), sucrose 5,6 and 7g/100 g mix). The mix was then homogenized using a double stage homogenizer (Rannie, Copenhagen, Denmark), with pressures of 1500 and 500 psi. After thorough mixing, formulations were heat treated at 72°C for 30 min and cooled. Finally, vanilla (0.05g/100 g mix) and (0.3g/100g mix) k-carrageenan were added. The final products were then filled into 250-mL glass bottles, and stored at 4°C for 2 weeks until analysis. Chocolate milk formulations are summarized in Table (1). Two sets of each batch were formulated.

Table 1: Chocolate milk formulation

Ingredients %	Formulations								
	A1	**A2**	**A3**	**B4**	**B5**	**B6**	**C7**	**C8**	**C9**
Skim milk	93.65	92.65	91.65	46.83	46.33	45.83	-	-	-
Permeate	-	-	-	46.83	46.33	45.83	93.65	92.65	91.65
Sucrose	5	6	7	5	6	7	5	6	7
Cocoa	1	1	1	1	1	1	1	1	1
K.carragenan	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Vanilla	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Total	100	100	100	100	100	100	100	100	100

Chemical analysis:

Chocolate milk mixtures samples were analyzed for moisture as given by A.O.A.C.(1990) and total nitrogen as described in IDF Standard (1986). Lactose was determined according to Barnett and Abdel-Tawab (1957). Carbohydrates content were calculated according to Abd El-Aziz et al. (2004). pH value was measured using a laboratory pH meter with glass electrode.

Determination of Chocolate milk viscosity:

Chocolate milk viscosity was measured using a coxial cylihder viscometer (Bohlin V88, Sweeden) attached to a workststion loaded with V88 viscosity program. Viscosity was measured at 32°C at shear rate N° (40) 5.75 E+2 1/s 1 minutes intervals. A total of 8 measurememts were carried out.

Colour:

Color was assessed using spectro-colorimeter (Tristimulus Color Machine) with the CIE lab color scale. This color assessment system is based on the Hunter L*-, a*- and b*- coordinates. L*- representing lightness and darkness, + a*- redness, -a*- greenness, + b*- yellowness and - b*- blueness (Hunter, LabScan XE – Reston VA, USA) in the reflection mode. The instrument was standardized each time with white tile of Hunter Lab Color Standard (LX No.16379): X= 72.26, Y= 81.94 and Z= 88.14 (L*= 92.46; a*= -0.86; b*= -0.16) (Sapers and Douglas, 1987). The Hue (H)*, Chroma (C)* and browning index (BI) was calculated according to the method of Palou et al, (1999).

Sensory Evaluation:

Chocolate milk formulations were sensory evaluated by seven member panel. Panelists ranked the samples using a 9-point hedonic scale, where 1 = extremely dislike, 5 = neither like nor dislike and 9 = extremely like. The sensory attributes included appearance, chocolate flavor, color, chocolate sweetness, sedimentation and viscous. Panelists were instructed to shake the bottles before the evaluation to suspend any settled cocoa particles in the bottom.

Statistical Analysis:

Results were statistically analyzed using the one way ANOVA, the GLM procedure (SAS Institute Inc., Cary, NC, USA). Duncan's Multiple Range Test was applied for comparison of the best formulation and control. The level of significance was set at $P < 0.05$. All data presented are means of three replicates.

3. Results and Discussion

Effect of storage at refrigerator and permeate UF on chemical analysis of Chocolate milk:

Data presented in Tables (2) showed that the pH in all chocolate permeate and / or skim milk were not changes, but it increased after process to 6.62 – 6.69 after tow weeks stored samples.

The total solids were the Lowest content in all chocolate produced by permeate milk (C7-C9) compared with chocolate produced by permeate milk and / or skim milk (A1-A3 and B4-B6). Also, total sugars lactose were the lowest content of chocolate produced by permeate milk (C8, C9) after 2 weeks storage. It could be considered as a source of protein, where, the percentage of protein was light changes in all samples after storage samples, as seen in table 2.

Table (2): Effect of permeate UF and storage on chemical analysis of Chocolate milk:

	pH	Total solids	Total protein	Total sugar
A1	6.57	16.9	2.86	12
A2	6.56	17.21	3.22	12.5
A3	6.58	18.76	3.39	13
B4	6.59	14.57	2.80	9.5
B5	6.58	15.1	3.20	11
B6	6.56	16.88	3.22	11.5
C7	6.57	11.52	2.68	8.0
C8	6.59	12.02	2.74	8.5
C9	6.58	13.93	2.86	10

Effect of storage at refrigerator and permeate UF on color characteristics of Chocolate milk:

Colour is usually defined by three coordination. There are various colour scales that can used to characterize colour: CIE-X,Y,Z; the L*,a*,b* ; and the Rd, a, b scales. Similarly, colour indexes and differences can be calculated from these values. The L*,a*,b* scale is recognized to show a better discrimination between small colour differences in the darker region of the colour space, providing good discrimination for saturated colours, as in the case of chocolate milk. For these reasons this scale is one of the most frequently used for food products (Francis 1989), however it is not so useful for light coloured samples (Anon., 1976).

The L* value represents a nonlinear mathematical approximation of the white – black response of the eye, ranging from 100 for a perfect white to 0 for a perfect black, and measures the luminosity of the sample. A positive value of a* indicates redness, and a negative value greenness. A plus value for b* indicates yellowness and a minus value blueness. There are other parameters derived from the Hunter-L*,a*,b* scale; the saturation index or chroma that indicates colour saturation and is proportional to its intensity, a/b ratio and the Hue angle among others (Anon., 1976; Francis, 1989 and Barreiro et al., 1997).The a/b ratio has been used as a quality specification for chocolate milk. The hue angle (tan -1 b/a) is another parameter frequently used to characterize colour in food products. An angle of 0 or 360 represent red Hue, while angles of 90, 180 and 270 represent yellow, green and blue Hue, respectively. It has been extensively used in the evaluation of colour parameters in green vegetables, fruits and meats (Barreiro et al., 1997).

Color characteristics measurement directly in the Chocolate with permeates milk or with skim milk samples with a Hunter Lab Ultra Scan revealed that color did not change over different samples addition and after storage at refrigeratore 4 ^{o}C (Table 3). In this case (L*-values) brightness decreased, (a*-

values) redness increased and (b*-values) yellowness decreased. Color is only part of the overall appearance, but is probably a major quality factor in Chocolate product. According to our results, the main color change in Chocolate was due to increase in different skim milk or permeate milk addition, which was in high correlation to browning measurement. The effects of different skim milk or permeate milk addition and storage of chocolate at refrigerator 4 ^{o}C in the inhibition of the browning reaction is showed in Table 3. It is obvious that different skim milk or permeate milk addition of chocolate increased the development of red colour a*. The browning index (BI) was calculated using the pre-mentioned equation (eqn.3), for chocolate produced by skim milk or permeate milk addition A1, A2, A3, B4, B5, B6, C7, C8 and C9 samples and the results represented in Table 3. It is clear that chocolate produced by permeate milk C7-C9 samples markedly highest the BI. But had a BI equivalent to 200.5, 231 and 194 respectively compared to 158, 182 and 200 in case of the chocolate produced by skim milk sample, as seen in Table 2. These results are in good agreement with those of Palou et al., (1999) and Genovese et al, (1997) All chocolate samples were also tested for the Hue angle (H*) as well as the Chromaticity (C*). Table 4, lists the values of H* and C* as well as a*-values for chocolate which has been produced by permeate milk higher than chocolate produced by skim milk, as seen in Table 3.

Table (3): Effect of permeate by UF and storage on colour characteristics in chocolate milk.

	L*	a*	b*	H*	C*	BI
A1	28	10	13	78.96	16.40122	158.3397
A2	24	10.9	12	47.75	16.21142	182.1109
A3	22.3	11	12	47.49	16.27882	200.0114
B4	28	10	11.2	48.24	15.01466	138.5359
B5	26	10.1	12.2	50.38	15.83824	163.8623
B6	21	10.3	12.6	50.74	16.27421	222.5869
C7	21.3	9	12	53.13	15	200.545
C8	21	10.5	13	51.07	16.71077	231.175
C9	23	11.9	11.8	44.76	16.75858	194.1233

Table (3) shows that permeate chocolate milk formulations were slightly more dark, more brownish and less brightness than skim milk chocolate. A wide brightness range going from too light to dark was also observed by Yanes et al., 2002 for commercial chocolate milk beverages.

Sensory evaluation:

Table (4): Effect of permeate UF and storage on sensory evaluation of chocolate milk

Sensory Properties	Final Remarks	Formulations								
		A1	A2	A3	B4	B5	B6	C7	C8	C9
Appearance	10	7^{D}	7.25^{C}	7.5^{C}	8.75^{B}	9.25^{A}	9.5^{A}	8^{B}	8.5^{B}	8.75^{B}
Color	15	10.5^{C}	10.75^{C}	10.75^{C}	14.25^{A}	14.25^{A}	14.25^{A}	11.25^{B}	11.5^{B}	11.75^{B}
Viscous	15	11.75^{D}	12.25^{C}	12.5^{C}	13.75^{B}	14^{A}	14^{A}	13^{B}	13.75^{B}	13.75^{B}
Flavor sweet	20	13.75^{D}	16.25^{C}	18.25^{A}	16^{C}	17.5^{B}	18^{A}	16.25^{C}	18^{A}	17.5^{B}
Flavor choc	25	21^{D}	21^{D}	21^{D}	23.25^{A}	22.75^{B}	22.75^{B}	22^{C}	22^{C}	22.25^{B}
Sediment	10	8.75^{B}	8.75^{B}	8.75^{B}	9.5^{A}	9.5^{A}	9.5^{A}	9.5^{A}	9.5^{A}	9.5^{A}

The organoleptic characteristics of the Chocolate with permeate milk or with skim milk samples (A, B and C) and storage for 2 weeks at refrigerator were evaluated as presented in the following Table 4. Results in Table (4) showed that the highest score of color was recorded for the (B4-B6) sample followed by (C7-C9) then (A1-A3) samples. The highest score of appearance was recorded for the (B4-B6) followed by (C7-C9) then (A1-A3) samples. Also, the highest score of viscosity were recorded for the (B4-B6) followed by (C7-C9) then (A1-A3) samples. Furthermore, chocolate produced by skim and permeate milk (B4-B6) followed by (C7-C9) then (A1-A3) samples was similar in gaining the best score for flavor sweet and flavor chocolate. Also, results in table (4) showed that the highest score of sediment was recorded for the (B4-B6 and C7-C9) sample followed by (A1-A3) samples, which all chocolate produced by permeate contents. Statistical analysis indicate that there were no-significant difference ($P<0.05$) between different concentration of sucrose (5, 6 and 7%) in chocolate produced by skim milk and / or permeate milk. Sugar content can be reduced from 7% to 5% in order to good out come the lactose that present in the permeate, consequently the using of permeate is valuable during the production regarding to lactose content. Also, minimize the west during cheese manufactures.

Table (4) showed that the formulation made without permeate added had a very low chocolate flavour. For all sensory attributes, formulations made with permeate UF had higher mean ratings compared to that prepared without permeate or with skim milk. Studies showed that, commercial chocolate milks vary widely in their sensory properties. Thompson et al., (2004) showed that consumer perception of chocolate flavor, sweet taste, and color intensities were not correlated to overall liking of chocolate milk, suggested that strong chocolate flavor, high sweetness, or dark color do not necessarily drive consumer liking. A wide variability was also observed in consumer acceptability of chocolate milks. Oliveira et al., (2004) evaluated the acceptance of commercial chocolate milk desserts. The results identified two main groups of consumers; one that preferred the products of a specific brand and another that preferred dietetic puddings.

Effect of storage at refrigerator on viscosity of Chocolate with permeates milk:

The viscosity (cP) was selected as a measure of chocolate produced by skim milk and / or permeates milk quality. However, the viscosity in all samples (A1, A2, A3, B4, B5, B6, C7, C8 and C9) was not change as long as time measurements until 460 seconds before and after storage, the results represented in Figures (1 and 2). It is clear that chocolate produced by permeate milk C1-C3 samples markedly highest the Viscosity, followed by chocolate produced by permeate milk and skim milk (B4-B6) then chocolate produced by skim milk (A1-A3) samples , as seen in Figures (1 and 2). However, chocolate produced by permeate milk C7-C9 causes such an increase in viscosity due to increasing of evaporating of water content.

Viscosity: The viscosity profiles of chocolate milk formulations (figures 1 and 2) showed a similar pattern although clear differences can be observed among them, as a result of a complexity of their flow behaviour depending on the fat content, the level of permeate added and both concentration and physical state of dispersed phase. The viscosity values were higher as permeate level increased. Chocolate milk formulation with high permeate was more viscous than others; while formulation with low permeate followed a viscosity pattern more closely to chocolate whole milk. The viscosity value of non-permeate or skim milk added formulation was the lowest compared to permeate added formulations. This formulation, exhibited a fluid-like behaviour. A similar trend was given by Yanes et al., (2002) for commercial chocolate milk beverages. Chocolate milk is complex suspension system, which comprises milk or dairy fluid as dispersion phase and several solid ingredients (cocoa particles, sugar, stabilizers, etc.) as dispersed phases. The rheological properties of chocolate milk are based on the flow behaviour of the dispersion phase and the dispersed solid ingredients interacting with the dispersion phase and with each other. This interaction which gives raises the complicated rheological properties. k-carrageenan is the most common stabilizer used in chocolate milk formulations Langendorff et al., 2000 and Spagnuolo et al., 2005 . However, permeate by UF also exhibited a great potential in stabilizing the dispersion of cocoa particles in experimental formulations. This may be due to the ability of permeate by UF to bind water molecules and form a particle gel.

Conclusion:

From the previous results, it is obvious that results showed a decrease at the following order B6 > B5 > C9 > C8 > C7 > B4 > A3 > A2 > A1 regarding to L*, a*, b*, C*, H*, BI-values, chemical, viscosity and sensory evaluation. Finally, using permeates milk without or with skim milk was able to produce chocolate good quality.

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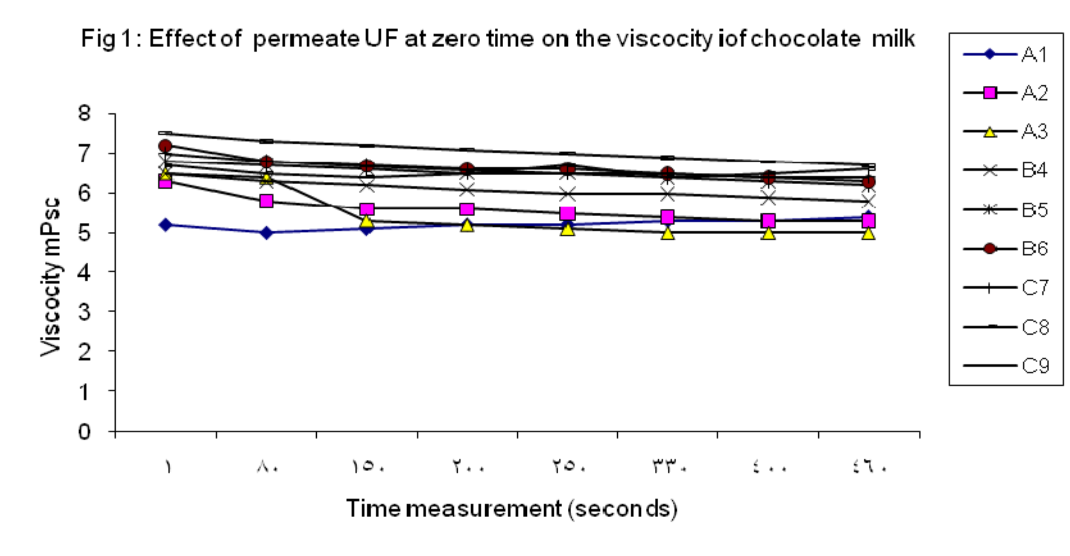

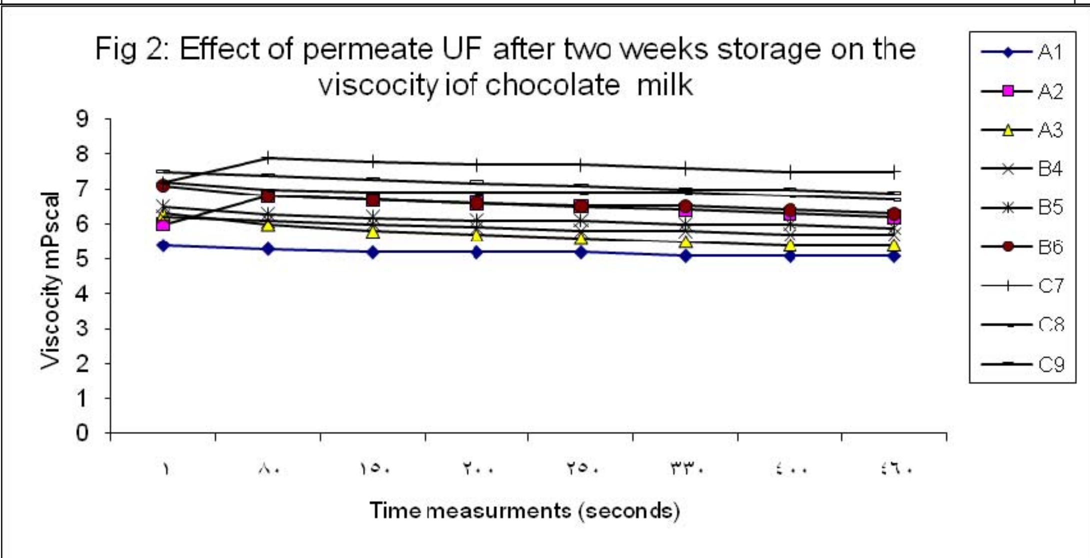

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