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DISTRIBUTION OF SOME HEAVY METALS FROM MILK TO ACIDIC AND ENZYMATIC COAGULATION CURD AND THE PRESENCE OF THESE METALS IN KAREISH AND MISH CHEESES

Zeinab A. M. El-Atawy
Animal Production Research Institute, Agriculture Research Centre

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***ABSTRACT**: This study was carried out to compare the extent of curd recovery of metals in cases of acidic and enzymatic coagulations. Milk has been obtained from local market of Great Cairo, where it has been skimmed and pasteurized. After coagulation and whey drainage, acidity, pH, total solids and four metals (aluminium "Al", iron "Fe", zinc "Zn" and lead "Pb") were estimated in the obtained curd. The above-mentioned metals and total solids were also estimated in milk and whey.*

Acidity percentage increased, while pH values decreased in acidic coagulation curd in addition to increase in moisture content and yield, while decreased total solids recovery level in the curd which increased in the whey on the contrary of the enzymatic coagulation curd.

Metal recovery percentage in acid curd was generally lower than that of enzymatic curd. On the other hand, loss of these metals in acidic coagulation whey was higher than that of the enzymatic one.

For completing this study, sixty samples of Kareish and Mish cheeses were obtained from five different districts from the local market of Great Cairo as well as thirty samples from five different dairy plants for detecting the levels of the four metals. It was found that the four mentioned metals contents were higher in Kareish cheese than Mish cheese, and in the local market samples than that of the dairy plants samples. For Kareish cheese, aluminium, iron, zinc and lead contents were 6.31, 41.11, 27.90 and 0.325 ppm for local market samples, and 5.55, 38.89, 25.97 and 0.267 ppm for samples of the plants respectively. The contents of these metals in Mish cheese were 5.20, 36.95, 24.16 and 0.236 for local market samples , and 4.62, 34.16, 21.09 and 0.205 for samples of the plants respectively.

It can be concluded that the manufactured cheese or the ready-made cheese did not conform with the standard levels. So, it is advisable to make all the precautions to avoid the metallic pollution as it causes a great hazard to human health. Also, it is advisable to make acid-coagulation cheese to decrease the metallic contents in cheese and increase loss in whey.

Key words: *Pollution, Heavy metals, Kareish cheese, Mish cheese.*

INTRODUCTION

Different health hazards are now widely spread due to pollution, particularly the metallic one. The sources of metallic pollution are multiple including that comes through food. Milk and dairy products, especially cheese, are frequently exposed to a relatively high metallic pollution. Heavy metals are stable and bioaccumulative. Most of the heavy or toxic elements are widely spread in the environment and contaminate the food products during the production processes. Beijer and Jernelov (1986) stated that metals differ from other toxic substances in that they are neither created nor destroyed by human body.

Aluminium is found in trace elements in biological organisms (Abrams and Murrer, 1993). Its accumulation leads to interference with normal neurological functions and causes behavioral difficulties, e.g. Alzheimer's disease (Moon & Marlow, 1986 and Mc Lachlan et al., 1996). Aluminium also can interfere with phosphate absorption leading to hypophosphatemia (Savory and Wills, 1992). It is also deposited on the mitochondria of osteoblasts and inhibits formation of bone phosphates (Mc Dowell, 1992). In cases of aluminium human toxicity, the target organs are the lungs, bones and central nervous system (De Boni et al., 1976 and Morrow, 1992).

Iron toxicity is characterized by excessive deposition of storage forms of iron in tissues accompanied by high plasma iron and cellular damage to the intestinal mucosa (Goyer and Clarkson, 2001). Chronic iron toxicity symptoms include disturbances in liver functions, diabetes mellitus, endocrinal disturbances and cardiovascular effects. At the cellular level, lipid peroxidation increases which causes membrane damage to mitochondria, microsomes and other cellular organelles.

Zinc toxicity causes gastrointestinal distress, diarrhea, adverse changes in DHL/LDL cholesterol ratios and impaired immunity which have been reported following ingestion of beverages standing in galvanized cans or from the use of galvanized utensils (Kelly, 1999). Extensive intake of zinc may aggravate marginal copper deficiency (Groyer and Clarkson, 2001).

The dissolution of lead from piping and tanks is influenced by the length of time the milk stays in contact with these utensils and the chemical properties of the milk itself, i.e. pH, temperature, and chloride and nitrate concentrations. Absorbed lead can be accounted for in the skeleton, liver and kidney (ATSDR, 1999). Lead inhibits enzymes dependent on the presence of the free sulfhydryl groups for their activity, e.g. biosynthesis of heme. Pathological changes in the kidneys and clinical signs of cardiac diseases are frequently observed in both chronic and acute toxicities. The neurological effects of lead were among the first to be recognized, and symptoms in humans include optical nerve atrophy , tremors and wrist drop, with structural and functional changes in peripheral nerves (Goyer and

Clarkson, 2001). There is a relationship between increased level of lead and the incidence of malignancies (Bery and Burbank, 1972).

The present work aimed to study the extent of curd recovery percentage of some metals in cases of acidic and enzymatic coagulation. Also, the metallic pollution degree of Kareish and Mish cheeses collected from the local market and some dairy plants were studied.

MATERIALS and METHODS

Milk: Fresh buffalo's milk was obtained from the local market in Great Cairo then skimmed and pasteurized (72°C/15 Sec.). The total solids content was 11.67%.

Starter Culture: Zabady starter was obtained from the dairy unit, Dairy Technology Department , Animal Production Research Institute.

Rennet: Rennilase 150 L, Novo, Denmark. The rennet was added at a rate of 1 ml/100 kg milk. The metal contents of the rennet were 1.05, 58.13, 8.94 and .0225ppm for Al, Fe, Zn and Pb respectively.

Cheese Manufacture: Acidic and enzymatic coagulations were carried out for Kareish and Domiatti cheeses manufactures according to Fahmi & Sharara, (1950) and Fahmi, (1960). The curd and whey were weighed. Manufacture and handling were under care to avoid metallic pollution. Triplicates were carried out for each treatment.

Collected Cheese Samples: Sixty samples of Kareish and Mish cheeses (30 samples of each) were randomly collected from five different districts of the local market in Great Cairo. Also, thirty samples of Kareish and Mish cheeses from five dairy plants were collected (6 samples from each plant).

Chemical Analysis: Total solids, titratable acidity and pH values were carried out according to Ling (1963).

Determination of heavy metals: Aluminium, iron, zinc and lead contents were determined using atomic absorption spectrophotometer according to Moyer (1999).

All determinations were carried out in duplicates.

RESULTS and DISCUSSION

It was noticed a higher titaritable acidity and lower pH value in acidic coagulation treatment in comparison to the enzymatic one as a result of starter activity . Acid curd had higher moisture content, attained weight and lower drained whey on contrary to the enzymatic one (Table 1). This may be probably resulted from relatively permanent structure formed in acid gels in comparison with that of rennet gels. Rennet coagulation involves the formation of a more compact network with an increased number of bonds and flocculated micelles (Varnam and Sutherland, 1994). Thus, rennet curd keeps more milk constituents which consequently led to increase in total

Table (1): Effect of acid and enzyme coagulation on some proportions, recovery and loss of total solids.
(Averages of triplicates for each treatmens).

Parameters / coagulation method	Cheese curd %					Whey %		
	Acidity	pH value	T.S.	Yield	Recovery	T.S.	Yield	Loss
Acid	1.410	4.330	33.830	20.160	58.440	5.860	78.150	39.240
Rennet	0.270	6.180	38.020	19.230	62.650	5.300	79.380	36.050

solids and recovery percentage in the curd. However, high amount of small particles and soluble constituents of milk solids were withdrawn from the acid curd in the drained whey, denoting higher total solids and percentage loss in the whey as a result of the low rigid, and low compact acid curd.

Table (2) shows that the curd contained lower metals contents in both acid and enzyme coagulations than the corresponding drained whey. These findings agreed with Metwally (1993). Acid cheese curd generally kept lower proportions of heavy metals and expelled more amount than enzymatic curd. These were observed from the recovery and loss percentages of metals in curd and whey. These findings agreed with Kebary et al. (1992) who stated that calcium and phosphorus levels were lower in acid-coagulated curd than rennet-coagulated one. Varnam and Sutherland (1994) reported the same trend.

From the same table, it is evident that metal recovery percentages in cheese curd gradually increased for alumunium, iron, zinc and lead on contrary to the loss of whey. This may be due to the relative atomic mass of these metals, i.e. 27, 55.9, 65.4 and 207.2 respectively.

Sieber and Daniel (1996) found that the concentration of aluminium is in the orders of 0.1 mg/L in milk and more than 1 mg/kg in dairy products. Levels of aluminium, in the products of this study, were higher than that obtained by Sieber and Daniel (1996). El-Kenany et al. (2001) illustrated higher percentages of aluminium, iron and lead in comparison to that found in this study, which may be attributed to the added salts. Fouzy (2000) found a low lead level with an average of 0.0908 ppm in market Domiatti cheese. Zinc levels, as shown in table (2), were higher than the results found by El-Kenany et al. (2001).

It is clear from table (3) that, the averages of heavy metal contents of Kareish and Mish cheeses from local market were higher than that from the dairy plants. This may be attributed to that milk and cheese are

more exposed to metal pollution through processing, handling and packaging. Mish cheese contained lower contents of metals than Kareish cheese. This may be due to high acidity and consequently excretion of metals from cheese to the whey. Ibrahim (1991) and El-Kenany et al. (2001) reported that pickled cheese contained lower metal contents than the corresponding fresh one.

All of the cheese samples from the Egyptian market in this study were not in line with the Egyptian standards (2000) which are 1.5 and 0.1 ppm for iron and lead respectively. Fayed et al. (1993) reported that milk and its products, including Domiatti cheese, contained levels of heavy metals greatly exceeding the acceptable levels which are recommended by the International Dairy Federation (1979). The daily mineral requirements for humans of iron and zinc are 10 -15 and 12 – 15 mg respectively (Mc Dowell, 1992). Doull (2001) stated that the limit values for aluminium, iron, lead and zinc are 2, 1, 0.15 and 5 m/M respectively.

Table (2): Effect of acid and enzyme coagulation on distribution, recovery and loss of some heavy metals (ppm) in the curd and whey. (Averages of triplicates for each treatmens).

Parameters \ Metals		Al	Fe	Zn	Pb
Milk		4.180	59.560	43.220	0.431
Acid coagulation					
	Curd	2.480	39.590	31.450	0.358
	Recovery %	11.910	13.400	14.670	16.750
	Whey	4.560	63.580	45.520	0.440
	Loss%	85.250	83.420	82.310	79.860
Enzyme coagulation					
	Curd	2.900	46.020	36.430	0.417
	Recovery %	13.340	14.860	16.210	18.600
	Whey	4.410	61.580	44.160	0.424
	Loss%	83.750	82.070	81.110	78.090

Table (3): Average of some heavy metals (ppm) in collected Karish and Mish cheese in Egypt

Metals / Samples	Al	Fe	Zn	Pb
Local market:				
Karish cheese (30)	6.310	41.110	27.900	0.325
Mish cheese (30)	5.200	36.950	24.160	0.236
Dairy plants:				
Karish cheese (15)	5.550	38.890	25.970	0.267
Mish cheese (15)	4.620	34.160	21.090	0.205

No. of samples in each group is shown in between brackets

From this study, it can be concluded that acid coagulation cheese reduces the heavy metal hazards and increases the safety limit in the resultant cheese. Heavy metal concentration must be monitored in the dairy products, starting from milk production, raw materials used and environmental pollution throughout processing, packaging and during dealing in the market.

It is recommended to apply strict inspection to reduce the hazards of the heavy metals.

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توزيع بعض المعادن الثقيلة من اللبن إلى خثرة التجبن الحمضى والإنزيمى ومستويات تلك المعادن فى الجبن القريش وجبن المش

زينب عبدالحميد محمد العطوى

معهد بحوث الإنتاج الحيوانى – مركز البحوث الزراعية

الملخص العربى

أجريت تلك الدراسة لمقارنة مدى إحتفاظ الخثرة بالمعادن فى حالة التجبن الحمضى والإنزيمى، حيث تم الحصول على اللبن من السوق المحلى بالقاهرة وأجريت له عملية الفرز والبسترة. وبعد تمام التجبن وترشيح الشرش، تم تقدير الحموضة والأس الأيدروجينى والجوامد الكلية فى الخثرة الناتجة بالإضافة إلى تقدير أربعة معادن هى الألومنيوم والحديد والزنك والرصاص، وقد تم أيضا تقدير الجوامد الكلية والمعادن فى اللبن والشرش.

وقد تبين إرتفاع النسبة المئوية للحموضة، وإنخفاض قيم الأس الأيدروجينى فى خثرة التجبن الحمضى، مع إرتفاع محتوى الرطوبة والتصافى. كما إنخفض معدل إحتفاظ الخثرة بجوامد اللبن مع زيادة الفاقد منها فى الشرش، وذلك على العكس فى الخثرة الناتجة من التجبن الإنزيمى.

وقد إتضح أن النسبة المئوية لإحتفاظ الخثرة بالمعادن تقل فى الخثرة الحمضية بصفة عامة عنها فى الخثرة الإنزيمية. وعلى العكس من ذلك كان الفاقد فى الشرش فى حالة التجبن الحمضى أعلى منه فى حالة التجبن الإنزيمى.

وإستكمالا لتلك الدراسة، فقد تمت دراسة مدى تواجد المعادن الأربعة فى ستين عينة من الجبن القريش وجبن المش من خمس مناطق مختلفة من السوق المحلى بالقاهرة الكبرى، علاوة على ثلاثين عينة من خمس شركات للألبان.

وقد وجد أن المحتوى من المعادن فى الجبن القريش أعلى من نظيره فى جبن المش، كما كان فى عينات جبن الأسواق المحلية أعلى من عينات جبن شركات الألبان حيث إحتوى الجبن القريش من السوق المحلى على ٦,٣١ ، ٤٤,١١ ، ٢٧,٩٠ ، ٠,٣٢٥ جزء فى المليون ،

بينما إحتوى جبن الشركات على ٥,٥٥ ، ٣٨,٨٩ ، ٢٥,٩٧ ، ٠,٢٦٧ جزء فى المليون من الالومنيوم والحديد والزنك والرصاص على التوالى . أما جبن المش فكان المحتوى ٥,٢٠ ، ٣٦,٩٥ ، ٢٤,١٦ ، ٠,٢٣٦ جزء فى المليون فى عينات السوق المحلى بينما كان ٦٢و٤ ، ١٦و٣٤ ، ٠٩و٢١ ، ٢٠٥و٠ جزء فى المليون فى عينات جبن الشركات بالنسبة للمعادن الأربعة على التوالى .

من ذلك يتضح أن الجبن الناتج سواء المصنع أو الذى حصل عليه من الأسواق لا يطابق المواصفات القياسية، ولذلك ينصح بعمل الإحتياطات الكاملة لتجنب التلوث بالمعادن لعظم خطورة ذلك على صحة الإنسان، كما ينصح بصناعة الجبن بالتجبن الحمضى لتقليل محتوى المعادن فى الناتج مع زيادة الفاقد فى الشرش.