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Changes in Mineral Distribution During Preparation and Processing of Milk Products

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Abstract

Many important physiological functions, which are essential for our existence are performed by the minerals. As milk and milk products are very good sources of bioavailable calcium, phosphorus and many other minerals. Processing treatments make milk products healthier, safer, tastier and with enhanced shelf-life. Present work aims at study of change in total and soluble mineral content, when milk is converted into various milk products, undergoing various processing treatments like heating, pH change, desiccation, fermentation etc. Milk is converted into *dahi, paneer* and cheese..

Keywords: Mineral, Milk-Products*, Dahi, Paneer*, Cheese, Processing, Treatments.

Introduction

Minerals perform various vital physiological functions which are essential for the existence of human beings. Milk and milk products are rich sources of bioavailable calcium (Scholz et al.,2020). Phytic and oxalic acids, Long chain saturated fatty acids, form insoluble complexes with calcium and decrease calcium absorption (Mulet-Cabero et al., 2021). Calcium from milk and fermented milk products is more easily absorbed in the intestine than the calcium from phytate -oxalate rich vegetables and cereals. Phosphorus present in milk and milk products (negatively charged) has been reported to influence calcium absorption and retention (Markoska, T et al., 2020). Preparation and processing make food healthier, safer, tastier and more shelf-stable. During preparation of milk products, processing can also be detrimental, affecting the nutritional quality of minerals in milk products. The mineral composition in milk products depends on various factors like -heating, pH, fermentation, concentration, coagulation, desiccation etc.

Khoa is a concentrated milk product prepared traditionally by heat desiccation of milk in an open shallow pan with continuous stirring. It is a main intermediate base for a variety of sweets like Gulab jamun, burfi, Pela, kalakand etc. Annual production of*Khoa* is around 6 lakh tons (Brahmini, B. et al., 2021), utilizing about 9 million tons of annual milk production. The aim of this study was to update mineral composition and distribution of milk and various milk products- *Dahi, Paneer*, Cheese and *Khoa*. It gathers information on change in mineral distribution on the following aspects: (1) mineral retention during preparation of *paneer* from buffalo milk; (2) mineral retention during preparation of cheddar cheese from cow milk; (3) change in distribution of minerals (soluble and colloidal) during preparation of *dahi* from buffalo milk; and (4) change in mineral composition during preparation of *Khoa* from buffalo milk.

Minerals in five samples of each product with their respective milks (from which products were prepared) procured from experimental dairy, NDRI Karnal were analyzed by FAAS, except phosphorus, which was analyzed spectrophotometrically.

Objective of the Study

The aim of this study was to update mineral composition and distribution of milk and various milk products- *Dahi, Paneer* and Cheese. It gathers information on change in mineral distribution on the following aspects: (1) mineral retention during preparation of *paneer* from buffalo milk; (2) mineral retention during preparation of cheddar cheese from cow milk; (3) change in distribution of minerals (soluble and colloidal) during preparation of *dahi* from buffalo milk.

Review of Literature

Fractionation Procedure: Fractionation of whole milk between colloidal and soluble phase was done as suggested by Fransson & Lonnerdal (1983).

Paneer is a traditional dairy product, which is prepared by coagulating buffalo or a blend of cow and buffalo milk and pressing the resulting coagulum (Ammu, V et al., 2020). It resembles un-ripened cheese prepared either from whole milk or skim

milk. It is extensively used for the preparation of a large number of culinary dishes. About 5% of total milk produced in India is converted into paneer. Annual production of Paneer is estimated to be 0.2 million tons. It is a valuable source of fat, vitamins and bone minerals. For making good quality paneer, buffalo milk is recommended as it contains higher amounts of casein and minerals (Ca and P) which are responsible for imparting firm and rubbery body to paneer than cow milk. Two changes were studied during conversion of paneer from buffalo milk.

The coagulation process in paneer is due to the chemical and physical changes in casein brought about by the combined effect of heat and acid. During paneer formation, large structural aggregates of casein, milk fat and coagulated serum proteins along with some whey are formed. During this, the main changes that take place are:(i) progressive removal of tricalcium phosphate from the surface of casein and its conversion into monocalcium phosphate and soluble calcium salt and (ii) progressive removal of calcium from calcium hydrogen caseinate to form soluble calcium salt and free casein. When the pH of the milk system drops, the colloidal particles become isoelectric i.e. the net electric charge becomes zero to form “Zwitter-ion”. Under such circumstances the dispersion is no longer stable; the casein gets precipitated and forms a coagulum (Goulding, D. A et al., 2020). This mechanism may play a crucial role in the manufacture of a superior quality paneer from buffalo milk compared to cow milk. Calcium content of buffalo milk is higher as compared to cow milk which results in greater linkages between casein micelles which in turn result in firm body and close textured paneer from buffalo milk vis a vis cow milk. As solubility favours absorption and thus bioavailability, therefore paneer is especially good for weak, elderly and diabetic patients. Compared to paneer, there is greater retention in cheddar cheese.

Cheddar cheese is a hard variety of cheeses having high nutritional value which includes proteins, fat, vitamins and essential body minerals like Ca, P, Mg, Na etc. (Khanal, B.K.S. et al., 2019). Quality of cheddar cheese depends on starter culture, manufacturing technology and composition of milk. Cheese is prepared from milk having a dynamically balanced mixture of protein, fat, carbohydrates, vitamins, water, lactose and water-soluble minerals. Generally, cheddar type of cheese is produced from cow’s milk. In this study, changes in mineral retention and effect on their solubility while converting milk to cheese have been studied. Although the mineral solubility may change during ripening (due to proteolysis and other biochemical changes), that aspect has not been studied in the present work. The majority of the whey proteins, lactose and water are separated out in the form of whey. Since the moisture portion of cheese is actually whey, we do retain small amounts of whey proteins and lactose in the final cheese, proportionate to the moisture content. However, it is obvious that the fat and casein content of the milk will be the key constituents of milk that will contribute the most towards the yield of cheese (Chakraborty, Pet al.,2021).

As in *Paneer*, during cheese making also, serum proteins, lactose and minerals are lost in whey. Mineral elements in milk which are of importance in the cheese making process are calcium and magnesium salts with phosphate and citrate. Calcium along with phosphates makes it complex with caseins. Calcium content of milk greatly influences rennet coagulation time, strength of the clot and body and texture of cheese. The quantity of calcium affects the size of the casein. Variation in the concentration of calcium as well as magnesium, phosphates, citrates, and sodium have a direct influence on RCT of milk. More soluble phosphates, citrates and sodium and less soluble calcium and magnesium and also low proportion of casein bound calcium give slow coagulation of milk by rennet.

Indian *curd / dahi* is a very important cultured indigenous milk product consumed by large sections of the population throughout India, due to its organoleptic properties like characteristic flavour, refreshing taste and improved digestibility. It has therapeutic, anticholesterolemic and anticariogenic properties beyond their basic nutritive value. *Dahi* has been strongly recommended for curing ailments like dyspepsia, dysentery and other gastrointestinal disorders (Ayurveda). It also improves appetite and vitality. Bacterial production of lactic acid from lactose of milk is the most important step in the preparation of *dahi*. Special advantage of consuming *dahi* is for the lactose intolerant people who cannot digest milk due to lack of lactase (1,4-β-galactosidase -lactose splitting enzyme). Low pH causes important changes in the composition, structure and reactivity of casein micelles

also modifies mineral equilibrium. The acidic nature of *dahi* will have a positive effect on the gastrointestinal absorption of calcium. About 8% of the total milk produced in India is used to prepare the traditional fermented milk product *dahi.*

The bioavailability of a nutrient from a particular food has been defined as the degree to which a nutrient from food is absorbed and utilized in the body for various physiological processes. Several food components are able to form soluble or insoluble complexes with minerals and trace elements under gastrointestinal conditions thereby increasing or decreasing the bioavailability of these components in complex food products. *Dahi,* a fermented dairy product containing more lactic acid which affects bioavailability and solubility of minerals. Fermented milk products may form soluble ligands with trace minerals in the gastrointestinal tract, thus enhancing the absorption of trace minerals like iron and zinc. Acidic conditions favour minerals to be in free form (ionic) Research reports point out that the digestibility of milk is only 32% after an hour in the digestive tract, whereas 91% of curd is digested within the same period of time (Roy, D et al., 2020).

Bioavailability of calcium: In *dahi* maximum minerals (major as well as trace) were found in non-sediment able fraction (soluble form). It is a fact that mineral absorption does not depend solely on the amount of the element present in dairy products but also on the other factors like solubility (Singh, M., et al., 2019). Mineral availability in dairy products is affected by the nature of the complex. The chemical form of the mineral may influence bioavailability: free /soluble forms are well absorbed, whereas those bound are poorly. Latest technological treatments used for the dairying products are known to modify the concentration of various chemical forms present in milk (Nunes, L., & Tavares, G. M.2019).

It is used in daily diet as a potential source of B-complex vitamins, folic acid, and riboflavin. *Dahi* is rich in lactic acid bacteria and demonstrates the probiotic effect, which helps in intestinal health as it helps in controlling diarrhoea in children. Lactic acid bacteria produce bioactive compounds such as diacetyl, hydrogen peroxide, and reuterin suppress the normal growth of undesirable flora, especially E. coli, Bacillus subtilis, and Staphylococcus aureus (Özogul, F., & Hamed,I (2018).

Diets that contain both high calcium and phosphate are of particular concern as studies have shown that in diets high in both calcium and phosphate; insoluble magnesium-calcium-phosphate complexes are formed, impairing absorption. One example of a diet high in minerals found to impair magnesium bioavailability would be one high in both milk and phosphorus-containing carbonated beverages, such as colas. For those with a regular daily intake of carbonated beverages, it may be wise to find additional sources of magnesium to supplement intake and prevent deficiency. Researchers have noted that high intake of sodas have placed many members of the population at risk for magnesium deficiencies. Consuming these beverages with food, as well as common drinks such as coffee and tea, ultimately reduces the amount of magnesium available to the body. Researchers have noted that high intake of sodas have placed many members of the population at risk for magnesium deficiencies. Consuming these beverages with food, as well as common drinks such as coffee and tea, ultimately reduces the amount of magnesium available to the body. Bioactive peptides derived from the tryptic digestion of casein, known as casein phosphopeptides (CPP), possess physicochemical properties that enable the chelation of various bi- and trivalent minerals, thereby enhancing mineral solubility in the lower small intestine.

Hypothesis

The present study is to investigate benefits of fermented milk products- dahi, paneer and cheese. Microorganisms responsible for fermentation are associated with many health benefits, so these microorganisms should be given proper attention. Most commonly used is LAB i.e. lactic acid bacteria. In the fermentation process these microorganisms synthesize minerals, vitamins and produce biologically active peptides (peptidase, proteinase etc.). Microorganisms in fermented foods improve gastrointestinal health and mitigate the risk of cardiovascular diseases and type 2 Diabetes. The most commonly consumed fermented milk foods in India are curd, dahi, cheese, lassi and paneer.

Methodology

Fractionation Procedure: Fractionation of whole milk between colloidal and soluble phase was done as suggested by Fransson & Lonnerdal (1983) with modification. The method is depicted in Figure 1. Raw milk samples were defatted by centrifugation (4000 *g*, 10 min, 4°C) and skim milk was ultrafiltered with Amicon® Ultra-15, 10KDa Centrifugal Filter Devices (Merck, Germany) using centrifuge (5000 *g*, 40 min, 25°C). The retentate was discarded and permeate was analyzed for soluble minerals

Sampelling

Milk samples were collected from apparently healthy animals from the NDRI Livestock Research Center. All the milk products prepared in the referral lab.,NDRI Karnal.. Water with conductance 0.055 mhos/cm was used in the study. Nitric acid, hydrochloric acid of analytical grade was procured from Merck KGaA, Dramstadt, Germany. NIST traceable standard solutions for all the elements and lanthanum chloride were purchased from Sigma-Aldrich Inc., St. Louis, USA.

Tools Used

Major mineral elements such as calcium, magnesium, sodium and potassium were quantified using method suggested by International Organization for Standardization (ISO: 8070, 2007) and trace minerals such as zinc, iron, copper and manganese were determined by AOAC official method (AOAC 999.11, 2008) using atomic absorption spectrophotometer (Model: AA-7000; Shimadzu, Japan). Phosphorus was estimated spectrophotometrically at 820 nm (ISO 9874: 2006 (E)).

Statistics Used in the Study

All the data were analyzed with average values having standard deviations.

Analysis

.Table : Ash content of milk and the milk products.

No.	Milk and Milk Products	Ash (%)
1.	Cow milk	0.74±0.021
2.	Buffalo milk	0.83±0.015
3.	*Dahi* (B.M.)	0.89±0.019
4.	Cheese (C.M.)	2.94±0.108
5.	*Paneer* (B.M.)	2.27±0.018

Table: Mineral Retention during preparation of *paneer* from buffalo milk.

Element	Total and Soluble	Milk (mg/100g) (TS =17.35%)	*Paneer* (mg/100g) (TS =34%)	Mineral Retention (%) (TS = 34%)
Calcium	T	206.06 ± 1.86	617.57± 3.88	52
	S	40.87±1.11	186.64±1.04	
Phosphorus	T	117.13±0.38	358.88± 0.188	53
	S	38.37±0.21	118.41±0.47	
Magnesium	T	22.28±0.9	35.55± 0.528	28
	S	11.31±0.09	18.51± 0.33	
Sodium	T	48.57 ±2.41	46.25±3.11	16.5
	S	47.18±2.17	45.12± 0.94	

Potassium	T	121.86±0.285	109.1±0.56	15.5
	S	117.11±2.87	105.17± 0.95	
Iron	T	0.21±0.002	0.662±0.33	55
	S	0.0522±0.002	0.27±0.006	
Zinc	T	0.536±0.013	2.039±0.062	66
	S	0.064±0.001	0.264± 0.004	
Copper	T	0.077± 0.001	0.169± 0.019	38
	S	0.038± 0.003	0.105±0.005	
Manganese	T	0.032±0.001	0.109± 0.004	59
	S	0.0052±0.001	0.027±0.003	
Ca / P	T	1.76	1.72	
	S	1.06	1.6	

Table: Change in soluble fraction (%) of minerals during preparation of *paneer* from buffalo milk.

Mineral Element	Solubility (%) in buffalo milk	Solubility (%) in *paneer*
Calcium	19.8	30.22
Phosphorus	32.75	32.99
Magnesium	50.76	52.06
Sodium	97.14	97.55
Potassium	96.1	96.4
Iron	24.76	41
Zinc	11.94	12.95
Copper	49.35	62
Manganese	16.25	24.77
Ca /P ratio	1.06	1.6

Table: Mineral Retention during preparation of cheese from bovine milk.

Element	Bovine milk (mg/100 g) TS= 11.65%	Cheese (mg/100g) TS = 55%	Mineral Retention (%) On dry matter basis
Calcium	127.52±1.86	739.32±1.25	67.5

Phosphorus	90.28±0.61	522.64±0.665	67.4
Magnesium	10.94±0.07	36.99±0.185	39.4
Sodium	51.13±0.56	631.0±1.88	+43
Potassium	147.3±4.06	119.42±0.51	9.4
Iron	0.11±0.004	0.642±0.004	68
Zinc	0.57±0.007	3.18±.056	65
Copper	0.052±0.001	0.273±0.002	61
Manganese	0.037±0.002	0.231±0.006	73
Ca/P	1.41	1.41	

Result and Discussion

Change in mineral content during conversion of milk to *paneer*:

Retention of minerals: Calcium, phosphorus, magnesium, sodium, potassium, iron, zinc, copper and manganese was determined on a dry matter basis in paneer (TS = 66%) from buffalo milk with total solids 17.35%. During paneer making, serum proteins, lactose and minerals are lost in whey. It was observed that mineral retention in paneer was in the range of 15.5 to 66%. The maximum retention of minerals was observed in case of calcium and phosphorus wherein about 52-53% of their content retained in paneer. Among the various minerals, sodium and potassium were the least retained minerals as only 15.5 to 16.5% of their content retained in paneer. Low value of sodium and potassium can be due to their higher solubility (97%,93%) in milk, causing maximum loss in whey during paneer making.

Change in soluble fraction: The results indicated that there is increase in the content of all soluble mineral fractions when milk is converted to *paneer*. The increase was significant in case of calcium and all the trace minerals i.e. Fe, Zn, Cu and Mn. On the other hand, increase in soluble fractions of Mg, Na and K was not significant during preparation of paneer from buffalo milk. For calcium increase in soluble fraction was from 19.8 to 30.25%, in phosphorus 32.75 to 32.99, in magnesium from 50.76 to 52.06%, in sodium 97.14 to 97.55%, in potassium from 96.1 to 96.4%, iron from 24.76 to 41 %, in zinc from 11.94 to 12.95%, in copper from 49.35 to 62%, and in manganese from 16.25 to 24.77%. Ca / P ratio of soluble fraction of raw buffalo milk was found 1.06 whereas in paneer it was 1.6.

Change in mineral content during conversion of milk to cheese:

Retention of minerals: The contents of calcium, phosphorus, magnesium, sodium, potassium, iron, zinc, copper and manganese were determined on a dry matter basis. The average total solids content in cheddar cheese and cow milk was observed to be 55 and 11.65%, respectively. Minerals retention for calcium, phosphorus, magnesium, sodium, potassium, iron, zinc, copper and manganese were 67.5%, 67.4%, 39.4%, + 43%, 9.4%, 68%, 65%, 61%, 73%, respectively. The Calcium / Phosphorus ratio remained the same. During the conversion of milk to cheese, lowering the pH takes place which alters protein interactions and thus affecting cheese functionality. At pH greater than 5.0, calcium solubilization decreases protein-to-protein interactions. In contrast, at pH lower than 5.0, the acid precipitation of proteins overcomes the opposing effect caused by increased calcium solubilization and decreased calcium content of cheese, and protein-to-protein interactions increase. About 96% of the casein, 93% of the milkfat, and 60% of the calcium will be retained in the curd of Cheddar cheese.

Change in mineral content during conversion of milk to *dahi:*

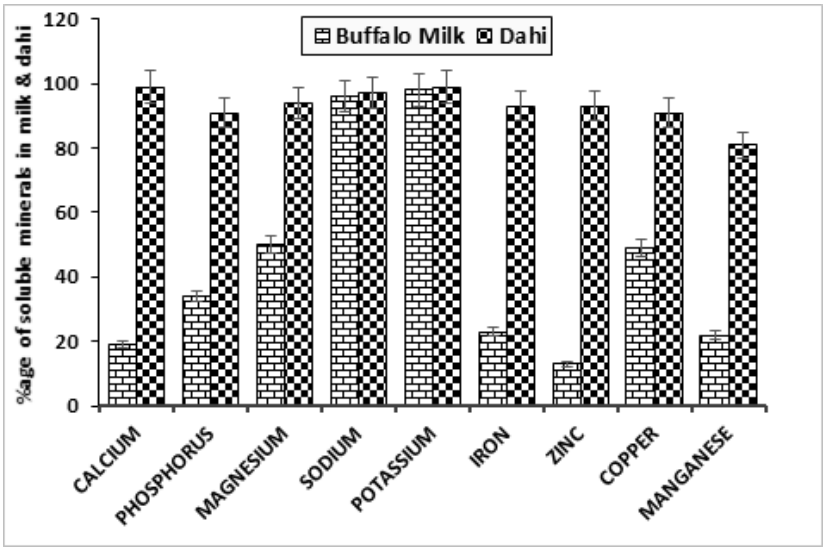
Change in soluble mineral fraction (Milk to *Dahi*): A significant increase in solubility was observed in various minerals when buffalo milk is converted to *dahi*. For calcium increase in soluble fraction was from 19 to 99%, in phosphorus 34 to 91, in magnesium from 50 to 94%, in sodium 96 to 97%, in potassium from 98 to 99%, iron from 29 to 93 %, in zinc from 13 to 93%, in copper from 49 to 91%, and in manganese from 22 to 81% (Ca / P ratio of soluble fraction of raw buffalo milk was

found 1.02 whereas in *dahi* it was 1.97. The mineral content remains constant after fermentation, the product obtained improves calcium bioavailability (García-B et al., 2020) and favours the absorption of these nutrients in the gastrointestinal tract. Fermentation of milk significantly increased zinc bioavailability. Zinc bioavailability in *dahi* is increased, improved bioavailability of the trace mineral may be attributed to greater solubility of zinc due to presence of bioactive peptide i.e. CPPs resulting from casein hydrolysis (Mohan, J. et al., 2018). *Dahi* is characterized by a nutritionally good ratio of calcium to phosphorus (1.4:1) (Singh, M et al., 2019) which are the favourable factors for promoting better bioavailability of calcium.

In *dahi,* maximum minerals (major as well as trace) were found in non-sedimentable fraction (soluble form) (Table and Figure). It is a fact that mineral absorption does not depend solely on the amount of the element present in dairy products but also on the other factors like solubility (Singh, M., et al., 2019). Mineral availability in dairy products is affected by the nature of the complex. The chemical form of the mineral may influence bioavailability: free /soluble forms are well absorbed, whereas those bound are poorly. Latest technological treatments used for the dairy products are known to modify the concentration of various chemical forms present in milk (Nunes, L., & Tavares, G. M.2019).

It is used in daily diet as a potential source of B-complex vitamins, folic acid, and riboflavin. *Dahi* is rich in lactic acid bacteria and demonstrates the probiotic effect, which helps in intestinal health as it helps in controlling diarrhea in children. Lactic acid bacteria produce bioactive compounds such as diacetyl, hydrogen peroxide, and reuterin suppress the normal growth of undesirable flora, especially E. coli, Bacillus subtilis, and Staphylococcus aureus (Özogul, F., & Hamed,I (2018).

Figure: Change in soluble fraction of minerals during preparation of *dahi* from buffalo milk



More than 50% of the calcium, phosphorus, iron, zinc and manganese retained in paneer when milk is converted into paneer. Increase in solubility of all the minerals studied (0.24%-16.24%) was indicated during conversion of buffalo milk into paneer, especially Iron, copper, calcium and manganese. Soluble Ca /P ratio was increased from 1.06 to 1.6 during conversion of buffalo milk to paneer. More than 60% of the calcium, phosphorus, iron, zinc, copper and manganese retained in cheese when milk is converted into cheese.

Conclusion

Marked increase in the solubility of all the minerals (81-99%) was observed on conversion of milk into dahi. *Dahi* and *Paneer,* fermented dairy products containing more of acid (lower pH than milk) affects bioavailability and solubility of minerals, but the total mineral content remains constant. These fermented milk products may form soluble ligands with minerals, especially trace minerals in the gastrointestinal tract, thus enhancing the absorption of the minerals, especially iron and zinc

Buffalo milk is a richer source of major and minor /trace minerals except iron, which are essential to provide the nutritional requirements to the human body.

Buffalo milk business should be promoted. Genetic potential of buffaloes in getting more milk of higher quality and experimenting the diversity of product especially indigenous products i.e. *dahi, paneer* in local as well as international market by better exploiting the unique properties of buffalo milk.

Suggestions for the future Study

Minerals play a vital role in human health, especially the soluble fraction which is better absorbed and more bioavailable.There is little research in this area. Thus, more emphasis should be given to the projects/ research on such studies.

Limitation of the Study

A limited variety of milk and milk products were analyzed due to paucity of time and funds.

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