Milk adulteration: Some Chemical Adulterants of Milk

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Abstract

Milk as naturally product is a complete food and can supply infants and adult with the daily requirement of nutrition. Any removal from or addition to milk without customer’s knowledge which known as adulteration will not only change its content but also cause hazard effect use of milk, adulterants is the substances used for adulteration. The common and first adulterant used for adulteration of milk is water for increase income. Following water adulteration; some adulterants will be added to mask the variation of properties of adulterated milk as sucrose, starch, ammonium sulfate, carbonate, sodium hydroxide and chloride. Others will introduced to milk for increasing shelf life as formalin, hydrogen peroxide, benzoic, salicylic and boric acid. Another dangerous material added to milk for hiding the true protein content as urea, ammonium sulfate and melamine. The serious health risk of these adulterants are gastrointestinal complains, liver and kidney damage. Nowadays our world become little town so people must be aware about this risk and milk adulteration, also these must be opposed by authorities rules for prevention the health risk of milk adulteration.

Introduction

Milk is the fluid secreted by the female of all mammalian species, primarily to meet the complete nutritional requirement of the neonate, and it is the major component in human diets in many parts of the world, as the milk is a complete food and source of essential nutrients, including carbohydrate, protein, fatty acids, calcium, phosphorus and magnesium. The milk constituents can affect dairy products performance and quality. Therefore, the industries usually define milk quality based on the nutrient levels, mainly protein and fat. These parameters have been used to calculate the payout to the supplier (Embrapa 2014). Unfortunately, adding non authentic nutrients has been used to adulterate milk and, consequently increase economic gain (Moore et al. 2012). In 2011, more than 735 million tons of milk were produced around the world (including cow, buffalo, sheep, goat and camel milk). USA was the largest producer, with 87.5 millions of tons, and Brazil was the fifth major producer (31.7 millions of tons). However, as fast as the production and demand for milk have grown, a larger frequency of sophisticated milk adulterations has been reported in different countries (Embrapa 2014).
Adulteration is defined as the removal or replacement of milk components and addition of substances without a purchaser’s knowledge, including water, whey, sucrose, starch, salt, sodium hydroxide and formaldehyde (Bansal and Singhal 1991, Santos et al. 2013a). Moreover melamine which is a nitrogen rich compound commonly used in manufacture of plastics, laminates, glues and adhesives and is not an ingredient in food, it was reported as present in Chinese powdered milk and infant formula in 2008 (Domingo et al. 2015). The addition of adulterating substances to milk by unscrupulous producers in order to raise their profits is not a new subject, but recently, it has attracted more attention worldwide. In Brazil, two major milk adulteration scandals were recently reported by the Federal Police. In 2007, the so-called “Operacão Ouro Branco” (White Gold Operation) reported the use of sodium Citrate, sodium hydroxide, sodium chloride, sucrose, phosphates, carbonates, bicarbonates and hydrogen peroxide to correct milk defects, such as high acidity and microbial growth, and to increase its volume (Hoorfar 2012). In 2013, the “Operacao Leite Com penado” (Compensated Milk Operation) revealed the utilization of fertilizers containing urea and formaldehyde to mask water addition in milk (UOL 2014). 100 samples of Brazilian UHT milk have been analyzed and detected high rates of non-conformities, such as 55% for urine, 44% for formaldehyde, 30% for hydrogen peroxide and 12% for chlorine (Souza et al. 2011). Milk adulteration is banned due to its ill effects on health (Beall and Scofield 1995). Adulteration of food products specially milk is a major problem and may lead to severe health problems. Gastrointestinal problems like gastric ulcer, colon ulcer, diarrhea, and electrolyte disturbance may be caused by carbonates in milk (Beall and Scofield 1995). Hydrogen peroxide adulteration disturbs the antioxidants activity in the body that causes disturbance in natural immunity, which leads to increase aging (Clare et al. 2003). Weakening, sensory disturbances and loss of acquired speech may be developed by presence of ammonia in milk. Blood pH and acid base balance in the body may be disturbed by the presence of chlorides in milk (Hu and Murphy 2004). Damages of liver and lung tissues and increasing of total oxidant capacity by formalin was stated (Aydin et al. 2015). Melamine was added to milk to elevate falsely assay results for protein content. A variety of toxic effects from melamine, including nephrolithiasis, chronic kidney inflammation, and bladder carcinoma, all have been studied in animals (Kai-ching Hau et al. 2009).

The article in our hands aims to spot the light about different chemicals used for adulteration of milk.

1- Water

Water is the most common adulterants used for increasing the milk volume by dilution, resulting in the decrease of nutrition substances, such as protein and solid content (Adam 2009, Santos et al. 2012). (Santos et al 2013b) reported the adulteration of milk with
water and so water is the most common milk adulteration in raw milk (Chanda et al. 2012). Water was used without any consideration to its health whether contaminated or not and this may lead to stomatitis to the consumers also some seller used to sell their milk as cold milk by adding ice which may presser the milk for a long time (Adam 2009). The water adulterated milk changed in its properties and seller need to mask this change. This will be done by addition of other substances which have health risks.

**Detection of added water**

Water is the most common adulterants and its presence can be detected by testing the freezing point of milk the AOAc Specifies a freezing point for normal milk of −0.550°C (Kamthania et al. 2014). But the preservative’s addition and other soluble matters like sugar and salts decrease the freezing point of watered milk and thus false detection of adulteration (Kamthania et al. 2014). Water adulteration can also be detected by putting a drop of milk on a polish slanting surface, the drop flows slowly leaving a white trail behind it if it was a pure milk. The adulterated one will flow immediately without leaving a mark.

**2- Starch**

Starch is one of the most component that is added to adulterate milk as starch is used as thickener, increasing the solid content of adulterated milk. Milk adulteration with starch was recorded (Adam 2009, Chanda et al. 2012). Then Citrate (other adulterants) is used as stabilizer and preservative, aiming to avoid precipitation of nutrients (Abbas et al. 2013).

**Detection of starch in milk**

The test to detect starch in milk used iodine solution, addition of which turns the milk solution to blue black color due to the formation of starch–iodo complex, in the presence of starch (Kumar et al. 1998).

**3- Cane sugar**

The common sugar present in milk is lactose. Table sugar like sucrose is added to the milk to increase the carbohydrate content of the milk and thus the density of milk will be increased. So the milk can now be adulterated with water and it will not be detected during the lactometer test (Miralles et al. 2000). Sucrose is used to restore the normal analytical values of adulterated milk in physicochemical tests and to improve its sensory properties (Kasemsumran et al. 2007, Santos et al. 2013b, Zhanget al. 2014). Cane sugar adulteration for milk was stated (Sanjeevani et al. 2011, Chanda et al. 2012, Abbas et al. 2013).

**Detection of cane sugar**

Sugar will react with the resorcinol to give a red colored precipitate, indicating the presence of Table sugar in milk (Miralles et al. 2000).
4- Preservatives: formaldehyde, acids and hydrogen peroxide.

a. Formaldehyde
Since the reduction of nutritional value due to water addition increases the risk of microbial contamination, Formaldehyde one of the preservatives used for preserving adulterated milk from microbial contamination, Formalin (40 percent aqueous solution of formaldehyde) is the most common preservative added to milk. The addition of any kind of preservative to milk is legally prohibited. Determination of formalin in milk samples was revealed (Chanda et al. 2012, Abbas et al. 2013). Formaldehyde decreased serum/tissue total antioxidant levels, it also increases total oxidant level, oxidant and apoptosis index (Aydin et al. 2015).

Detection of formalin
Formalin reacts with Sulfuric acid and ferric chloride to give a purple colored ring at the junction of the milk layers, indicating the presence of formalin adulteration in milk (Panda And Bindla 1998).

b. Acids
Generally acids like Benzoic acid and Salicylic acid is used as a preservative in food industry. It is added to milk to preserve and thus increase the shelf life of milk (Abbas et al. 2013).

Detection of acids
Presence of these acids can be detected by adding concentrated sulphuric acid and ferric chloride, which when reacts with benzoic acid and salicylic acid give buff colored and violet colored reaction products respectively.

c. Hydrogen peroxide
This is another preservative which is frequently used in milk to prolong its keeping quality. Hydrogen peroxide adulteration disturbs the antioxidants activity in the body that causes disturbance in natural immunity, which leads to increase aging (Clare et al. 2003).

Detection of Hydrogen peroxide
Add to about 5 ml of milk (suspected sample) in a test tube, and 5 drops of a 2 percent solution of paraphenylenediamine. A blue color is developed in presence of hydrogen peroxide. Hydrogen peroxide in destroyed when milk is heated or stored for a long period. (Recio et al. 2000).

5- Carbonate
Carbonate added to milk for neutralizing the developed acidity in milk adulteration of milk with carbonate is stated by (Sanjeevani et al. 2011, Chanda et al. 2012, Abbas et al. 2013).
Detection of carbonate

The qualitative detection of carbonate by the addition of 0.1% alcoholic solution resoalic acid that will produced red colore (Miralles et al. 2000).

6- Ammonium sulphate

Ammonium Sulphate is a chemical fertilizer, which is added to milk to raise the density of watered milk and increases the lactometer reading by maintaining the density of milk. Ammonium Sulphate adulterated milk was revealed by (Arora et al. 2004, Abbas et al. 2013).

Detection of ammonium sulphate

Ammonium sulphate in milk can be detected by adding sodium hydroxide, sodium hypochlorite and phenol, the reaction of the three reagents with ammonium sulphate results in formation of deep blue colour. The deep blue color is generated when the amine reacts with phenol in the presence of hypochlorite in an alkaline environment, results in the formation of a complex which is blue in color (Kumar et al. 2002).

7- Salt

Sodium chloride (common salt) other substances which added to make up the density (lactometer reading) of watered milk. Presence of salt to milk was revealed by (Arora et al. 2004, Abbas et al. 2013).

Detection of salt

2 ml of milk and add 0.1 ml of 5 percent potassium chromate and 2 ml of 0.1 N silver nitrate. Appearance of Yellow precipitate indicates the presence of sodium chloride (Kamthania et al. 2014).

8- Nitrogen-rich compounds: Melamin and urea.

Bovine milk contains around 80% casein and 20% whey proteins of high biological value (Freitas et al. 2009). Sellers of milk aim to increase the volume produced and delivered to the market by adding water, this alters its composition and reduces its nutritional quality. The reduction in protein concentration is one of the most significant effects. As a consequence, unethical producers add nitrogen-rich compounds to correct the apparent milk protein content. Fraudulent producers introduce new alternatives that cannot be detected by established techniques. The addition of nitrogen compounds to milk to increase/correct protein content – can be attributed to the official method adopted worldwide (AOAC International 1980) to control milk protein content, which determines total nitrogen and not protein nitrogen. For dairy products, total nitrogen must be converted to ‘total nitrogen proteins’ using a conversion factor (6.38) based on the nitrogen content of casein, as originally proposed by (Hammarsten and Sebelien 1892). A number of water-soluble nitrogen compounds such as melamine, ammonium sulphate and urea produce the
same analytical characteristics as proteins using the Kjeldahl method and can be used as milk or whey adulterants.

**a. Melamine**

![Chemical structure of melamine](image)

Melamine is an organic base commercially synthesized from urea and one of the water-soluble nitrogen compounds. Its high nitrogen content (66% by mass) makes it a potential milk adulterant; melamine was recently added to milk to mask its protein content as it elevates falsely its protein content by the Kjeldahl method (Figure 2). The use of melamine for this purpose is particularly harmful because of the formation of a very stable complex with cyanuric acid that crystallizes causing renal damage (Finete et al. 2013).

![Kjeldahl method](image)

Figure 2. Kjeldahl method, a universally used quantitative method for assessing protein content in food.

... an outbreak of urinary stones in infants and children consuming melamine- tainted milk in China, melamine compound became headline news. The nephrotoxic effects of melamine now warrant the attention of nephrologists, pediatricians, urologists, and radiologists. Studies concerning the toxicity of melamine taken orally in humans are nonexistent. Toxicity data mainly come from studies in sheep, cat, dog, mice, and rat. Toxicity can be an acute or chronic (Hau et al. 2009).
Detection of melamine

A combination of results of Kjeldahl and spectrophotometric methods should be used to screen for milk adulteration by melamine (Finete et al. 2013).

b. urea

urea is a natural component of milk. Cow milk contains about 50 mg/100 ml urea whereas buffalo milk it is present to the extent of 35 mg/100 ml in average on the other hand urea is a chemical fertilizer, which is added to watered milk to raise its density (lactometer reading). Also urea is used in milk to elevate its SNF content. In adulterated milk the concentration is twenty times more (Kumara et al. 2000).

Detection of urea

To 5ml milk add equal volume of 24% trichloroacetic acid (TCA) to precipitate fat and proteins of milk then filter and collect filtrate after that take 1 ml filtrate and add 0.5 ml sodium hypochlorite (2%), 0.5 ml sodium hydroxide (2%) and 0.5 ml phenol solution (5%) and mix. A characteristic blue or bluish green colour develops in presence of added urea whereas pure milk remains colourless.

Conclusions

Consumers must be aware about milk adulteration and its health risk, Fraudsters must be informed about the health risk of food adulteration. On the other hand authorities must enact rules to prevent this problem.

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