Heavy metal and trace element residues and health risk assessment in raw milk and dairy products with a trail for removal of copper residues

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A B S T R A C T

This study was conducted to determine the residues of Lead (Pb), Cadmium (Cd), and Copper (Cu) in raw milk of different species and dairy products, and to estimate the dietary intake of such metals, as well as to evaluate the potential health hazards of these metals to humans through consuming milk and dairy products. On the other hand, we made a trial to remove copper residues using adsorption properties of the resin. Therefore, a total of 120 random samples of milk and dairy products, including 80 samples of raw milk of different species from different dairy shops, and farms in Sharkia Governorate, Egypt, in addition to 20 samples for each of UHT milk and Kariesh cheese, were collected. Pb and Cu residues in the examined samples were ranged from 1.85–2.78, 0.009–0.81ppm, respectively, while Cd was detected only in raw goat's milk and kariesh cheese samples. However, it is worth to clear that Pb was recorded the highest levels in the examined samples, since most of samples were over the permissible level of 0.1 mg/kg established by Egyptian Standard. Human health risk associated with consuming milk and other examined dairy products was identified using Target Health Quotient (THQ) showed that Pb is the most dangerous element measured in these products as its value was more than one in 66.7% of samples. In the present study, performance of IMAC HP resin was assessed for the first time for removal of Cu ions from artificially contaminated raw cow's milk, although it is used extensively to purify water from heavy metals. It was noticed that the removal efficiency of Cu ions increased with higher resin concentration, and increasing time, as maximum removal percent (76.89%) was achieved by using 0.8 g/L. IMAC HP resin after 45 min. Finally, it was concluded that this type of resin is suitable for the adsorption of Cu ions from artificially contaminated raw milk.

Keywords: *Heavy metals, Milk, Resin, Atomic absorption spectrophotometer*.

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1. INTRODUCTION

Heavy metals are widespread materials present in our nature and become easily accumulated in different food chains as they are non-biodegradable (Aslam et al., 2011). Metal contents of milk and milk products can be classified into two groups, essential elements that are required but only at low doses as copper (Cu), iron (Fe), and zinc (Zn). The second one is non-essential elements that have no biological role including arsenic (As), lead (Pb), and cadmium (Cd) (Khan et al., 2013).

These toxic metals are considered generally air pollutants which are produced and diffused into it mainly from various industrial activities (WHO, 2007), from which they are reached soil, plants, foods, and waters causing their contamination with these metals (Bilandzic et al., 2011). Therefore, they enter into the food chain easily, as dairy animals ingest them while grazing in the pasture from contaminated concentrate feeds, or even from water. Then, in the animal these metals are transferred to milk (Maas et al., 2011). Food considered the main route of exposure as it is representing about 90 % of the total intake (WHO, 2007). In milk and different milk products, presence of Pb and Cd residues is of specific interest, as their presence even in low amounts, Pb to poisoning and other great disorders in the body (Ghorbel-Abid et al., 2010). Also, they are considered potential carcinogens (Zhuang et al., 2009).

On the other hand, Cu is one of the essential micronutrients for normal function of our body, as it is required for the absorption of iron and as cofactor of some enzymes that are essential for different vital processes in the body (Solaiman et al., 2001). However its intake in higher amounts above the safe levels recommended by the international organizations may cause hazardous effects to the human health and this is mainly occur due to presence of Cu with high levels in animal feed (Licata et al., 2012).

Therefore, it is necessary to examine milk and its products for the presence of the residual concentrations of different metals and assessed their potential health hazards to ensure consumer health. For this purpose, determining the dietary intake of each metal and comparing it with the permissible limits set by regulatory agencies is important (Leblanc et al., 2000). Moreover, the target hazard quotient (THQ) is one of the approaches that had been recommended for evaluating the potential health hazards of intake of various pollutants on human (US EPA, 2000).

Additionally, there are many techniques have been developed for metals removal such as chemical treatment, flocculation, coagulation, membrane separation, filtration and adsorption (Geise et al., 2010, Yargeau and Zeman, 2012, Gupta et al., 2013 and Madsen, 2014). Adsorption is one of these methods that has some advantages, including simple design, low cost, and absence of sludge formation. Many natural and synthetic materials have been used to remove heavy metals in this technique, including clay, seaweed and biomass, activated carbon, and mesoporous silica (Chen et al., 2010). Resin is a novel chelating ion exchange used for removal of heavy metals by the adsorption method depending on their high selectivity in binding metal ions as reported by many studies (Dinu and Dragan, 2008, Alyüz and Veli, 2009 and Lasheen et al., 2017).

Therefore, the major aim of this study was to determine the contamination levels of Pb, Cd, Cu, in different types of raw milk and milk products and to assess their potential health hazards for human using target health quotients (THQ). Finally, the removal of Cu from artificially contaminated raw milk by using the adsorption properties of a suitable chelating ion exchange (CIE) resin was investigated.

2. Materials and methods

2.1. Collection of samples

A total of 120 random samples of milk and milk products, including 80 samples of raw milk of different species (sheep, goat, cow, buffalo, 20 samples for each) from different dairy shops, and farms in Diarb Negm and Zagazig, Sharkia Governorate, in addition to 20 samples for each of Ultra heat treated (UHT) milk and Kariesh cheese, were collected in clean polyethylene bags and in its original container from different farmers, dairy shops, and supermarkets. Each sample was labelled to identify the source, site and date of sampling. The samples transported to the laboratory without delay in an ice box and stored at -2°C until analysis.

2.2. Preparation and analysis of the collected samples

Each prepared sample was digested according to (Tsoumbaris and Papadopoulou, 1994) until obtained a clear solution. Samples were filtered and diluted to 25 ml with deionized water and filtered through whatman filter paper No. 42. All filtrated samples were analyzed for presence Pb, Cu, and Cd by using Buck Scientific Atomic Absorption Spectrophotometry (AAS) model 210VGP at wavelengths of 217, 228.8, 324.8, nm respectively. It was applied at the Atomic Absorption Unit of the Central Laboratory in the Faculty of Veterinary Medicine, Zagazig University. Three replicates were done, and the result was the average of these replicates.

2.3. Calculations

2.3.1. Calculation of Estimated daily intake of metals (mg/kg.bw/day) (EDI)

The daily intake of the examined heavy metals for an adult person (60 kg BW) from consumption of milk and cheese was calculated according to The Nutrition Institute, Cairo, (2007). Where the average daily consumption was considered to be 200 mL, and 45 gm of milk, and kareish cheese, respectively. Depending on the mean concentration of metal in food, the daily food consumption, and the body weight of the adult human.

2.3.2. Target hazard quotient (THQ)

The THQ for the consumers via consumption of polluted milk and cheese was evaluated depending on the determined dose and the reference oral dose (RFDO) for pollutant. When the THQ is less than one, it assumed that the inhabitant did not expose to adverse effects. The severity of health hazards is enhanced with increasing its value more than one (Zhuang et al., 2009).

2.4. Treatment process for metal removal from experimentally contaminated raw cow's milk

2.4.1. Materials

1- IMAC HB 333: weak acid cation exchange resin containing carboxyl group on an acrylic matrix according to (Nasef et al., 2002).

2- A standard solution of copper sulfate (tested metal).

3- PH adjustments were carried out by using 0.1N HCl and 0.1N NaOH.

2.4.2. Apparatus:

1- Atomic Absorption Spectrophotometry (AAS) model 210VGP at wavelengths of 228.8 nm

2-PH meter (Adwa kft, AD11, Romania)

3-Electric Shaker (SCILOGEX, MX-S)

2.4.3. Procedures:

The ion exchange experiments were performed, using different resin doses and contact periods during agitation at room temperature. The effect of each parameter was determined, while other parameters were kept constant. 3 liters of raw cow's milk were collected from a dairy farm at El-Sharkia Governorate, and immediately taken to the laboratory. At first, only 20 ml was taken from one liter for heavy metal analysis and determination of copper and calcium in raw milk without any addition. Then, 100 ml of synthetic solution of copper sulfate (100mg/L) was added into the second flask contained another liter of raw milk (Alyüz and Veli, 2009), from which 4 equal volumes (100 ml each) were transferred into clean and acid washed flasks. To each volume, IMAC HB 333 was added with different amounts 0.05, 0.2, 0.4, and 0.8g. PH adjusted at 6 by using 0.1N sodium hydroxide and 0.1N hydrochloric acid. Solutions were shaken continuously by using electric shaker at 200 rpm for 60 min. The milk of each volume was strained through several layers of cleaned gauze into another acid cleaned flask, for preventing the passage of resin beads. From each treated milk 10 ml subsample were taken and analyzed for metal content by spectrophotometer as mentioned above. The results were recorded.

The 3rd liter of raw milk was also experimentally contaminated with 100ml Copper sulfate of (100mg/L) and added IMAC HB 333 with a constant concentration that give the highest removal percentage in the previous part of the experiment. Then, samples were taken at various durations of agitation (5, 15, 30, 45 min.) and metal residues were analyzed. The results were recorded.

2.5. Statistical analysis

All the data analysed and Comparisons among means of different groups for each element were performed using ANOVA test using SPSS/PCT (Foster, 2001).

3. RESULTS

From the data shown in (table, 1), it is apparent that the average concentrations of Pb were 2.68, 2.04, 2.78, 1.85, 1.94 and 2.26 ppm in raw cow’s, buffalo’s, sheep’s, goat’s milk, UHT milk, and kariesh cheese, respectively, there was no observed significant difference between samples.

While Cd failed to be detected in all samples except raw goat’s milk, and kariesh cheese without observed significant difference between samples which were (0.02±0.005), (0.02±0.016) respectively. Concerning Cu residues, the highest mean values of Cu in our work was found in Kariesh cheese samples (0.81±0.09 ppm), while the lowest value was found in raw cow’s milk samples (0.009±0.008 ppm).

There was no significant difference between UHT, kariesh cheese, goat milk means values for Cu at $p < 0.05$. While the mean value of Cu in UHT milk was significantly higher than those of sheep's and buffalo's milk. In addition, the mean value of sheep's milk was significantly higher than that in cow milk.

On the other hand, the levels of Pb in the examined milk and cheese samples were very high and exceeded the permissible level of 0.1 mg/kg established by Egyptian Standard, (2012) table (2).

Table (2) showed that, only 5% of raw goat's milk samples recorded Cd content higher than the PL (0.05ppm) according to Egyptian Standard, (2012). The permissible limit of Cu was 0.4 ppm according to Anonymous, (1998), where 65% buffalo’s milk, 75% sheep’s milk, 65% goat’s milk, 75% of UHT milk, and 80% kariesh cheese exceeded the permissible limit, while no samples of cow's milk exceed the permissible limit.

The accepted daily intake (ADI) of Pb, Cd, and Cu in all examined samples and their calculated daily intake resulted from consumption of 200 ml of raw milk and UHT milk or 45 g kariesh cheese per day were illustrated in table (3). Where the highest calculated daily intake for Pb was 0.556 mg/day/person from consumption of raw sheep’s milk, while the least estimated value for it recorded 0.102 mg/day/person from consumption of kariesh cheese which represent about 111.2%, 20.4% of ADI recommended by Codex Alimentarius Commission, (2014) respectively.

Table (3) showed that the average concentration of Cd in the examined raw goat's milk, and kariesh cheese samples was 0.02, 0.02ppm for each type respectively that gave daily intake of about 0.004, 0.0009 mg /day/person from consumption of 200 ml of raw goat's milk, and 45 gm of kariesh cheese that contributed about 5.71%, 1.29% of ADI recommended by Codex Alimentarius Commission, (2014). Concerning daily intake of Cu, it could be concluded that the average daily intake of Cu from consumption of different examined samples were relatively low as was shown in table (3) and represents a low percentage of ADI recommended by FDA, (2013). Also, our results showed that milk and dairy products cannot contribute a great amount of the supply of Cu in the human diet.

As shown in table (4) THQ values of (Pb) >1 in raw cow's, buffalo's, sheep's, goat's milk, and UHT milk, while it was <1 in kariesh cheese. Regarding THQ values of Cd, they were <1 through the consumption of all the examined samples. On the other hand, THQ values of Cu were less than one through the consumption of all the examined samples.

Concerning the experimental part results which were represented in the figures (1.2). It was cleared that the adsorption percentage of Cu ions increased with increasing the resin concentration as the removal efficiency was 27.7% by using 0.05 g/L. resin dose, while it was 76.89% by using 0.8 g/L of it Figure (1A). There were no changes detected in the Ca content of the examined raw cow's milk samples with different resin concentration. Figure 1B, cleared that Cu ions adsorption increased with increasing the contact time with resin molecules till reach the maximum at the end of time (45 min.).

Table 1. Statistical analytical results of the examined residues of Pb, Cd and Cu in different raw milk and dairy product samples (No. = 20).

Samples Metal		Raw Cow's milk	Raw buffaloe's milk	Raw sheep's milk	Raw goat's milk	UHT milk	Kariesh cheese
Pb (ppm)	No.	20	19	20	20	20	18
	%	100%	95%	100%	100%	100%	90%
	Min.	0.21	0.12	0.59	0.06	0.03	0.33
	Max	6.32	4.69	5.90	4.21	3.64	4.17
	Mean ±SE	2.68±0. 41^{a}	2.04±0.34^{a}	2.78±0.35^{a}	1.85±0.29 ^{a}	1.94±0.26^{a}	2.26±0.35^{a}
Cd (ppm)	No.	0	0	0	7	0	7
	%	0%	0%	0%	35%	0%	35%
	Min.	0.00	0.00	0.00	0.01	0.00	0.01
	Max	0.00	0.00	0.00	3.64	0.00	4.21
	Mean ±SE	0.00	0.00	0.00	0.02±0.005^{d}	0.00	0.02±0.016^{d}
Cu (ppm)	No.	1	20	20	20	20	20
	%	5%	100%	100%	100%	100%	100%
	Min.	0.00	0.07	0.10	0.29	0.02	0.05
	Max	0.18	1.46	0.77	1.48	1.21	1.78
	Mean ±SE	0.009±0.008^{d}	0.58±0.07^{bc}	0.49±0.05^{c}	0.77±0.08^{ab}	0.62±0.08^{abc}	0.81±0.09^{a}

No. = Number of samples Results are represented as ppm.

Means in the same raw carrying different superscripts are significantly different at ($p< 0.05$). And the highest values were represented by the letter (a).

SE= Standard error

Table 2. Frequency distribution of Pb, Cd, and Cu in the examined different raw milk and dairy product samples (No. = 20).

Metal	P.L. (ppm)	Milk samples that exceed the permissible limit (P.L.)											
		Cow's milk		Buffalo's Milk		Sheep's Milk		Goat's milk		UHT Milk		Kariesh cheese	
		No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
Pb	0.1[a]	20	100 %	18	90%	20	100%	19	90%	18	90%	20	100%
Cd	0.05[a]	0	0%	0	0%	0	0%	1	5%	0	0%	0	0%
Cu	0.4[b]	0	0%	13	65%	15	75%	13	65%	15	75%	16	80%

a Egyptian Standard, (2012). b Anonymous, (1998).

No. = Number of samples. P.L. = permissible limit

Table 3. Comparison of Acceptable Daily Intake (ADI) values of Pb, Cd, and Cu with the calculated daily intake of the examined samples for adult (mg /day/person).

Metals	ADI mg /60kg person	Mean concentration of metals (ppm)		Calculated daily intake of metals (mg/day/ person) via consumption of milk and dairy products by adult [c]	
				(mg/day/person)	% [d]
Pb	0.5[a]	Raw Cow's milk	2.68	0.536	107.2%
		Raw buffalo's milk	2.04	0.408	81.6%
		Raw sheep's milk	2.78	0.556	111.2%
		Raw goat's milk	1.85	0.37	74%
		UHT milk	1.94	0.388	77.6%
		Kariesh cheese	2.26	0.102	20.4%
Cd	0.07[a]	Raw Cow's milk	0.00	0	0%
		Raw buffalo's milk	0.00	0	0%
		Raw sheep's milk	0.00	0	0%
		Raw goat's milk	0.02	0.004	5.71%
		UHT milk	0.00	0	0
		Kariesh cheese	0.02	0.0009	1.29%
Cu	*35*[b]	Raw Cow's milk	0.009	0.0018	0.005%
		Raw buffalo's milk	0.58	0.116	0.33%
		Raw sheep's milk	0.49	0.098	0.28%
		Raw goat's milk	0.77	0.154	0.44%
		UHT milk	0.62	0.124	0.35%
		Kariesh cheese	0.81	0.004	0.011%

a: Codex Alimentarius Commission (2014). b: FDA, (2013).

c: Daily consumption for adult person (60 kg b.w.) according to Nutrition Institute, Cairo, 2007.

D: Percentage calculated to ADI.

Table 4. Target hazard quotient (THQ) for daily exposure to Pb, Cd, and Cu through consumption of different raw milk and dairy product samples.

	Pb		Cd		Cu	
	EDI(mg/kg bw/day)	THQ	EDI(mg/kg bw/day)	THQ	EDI(mg/kg bw/day)	THQ
Raw Cow's milk	0.009	2.57	0	0	0.00003	0.00075
Raw buffalo's milk	0.007	2	0	0	0.002	0.05
Raw sheep's milk	0.009	2.57	0	0	0.002	0.05
Raw goat's milk	0.006	1.71	0.00007	0.07	0.003	0.075
UHT milk	0.006	1.71	0	0	0.002	0.05
Kariesh Cheese	0.002	0.57	0.00002	0.02	0.0006	0.015

EDI= Estimated daily intake (mg/kg bw/day)

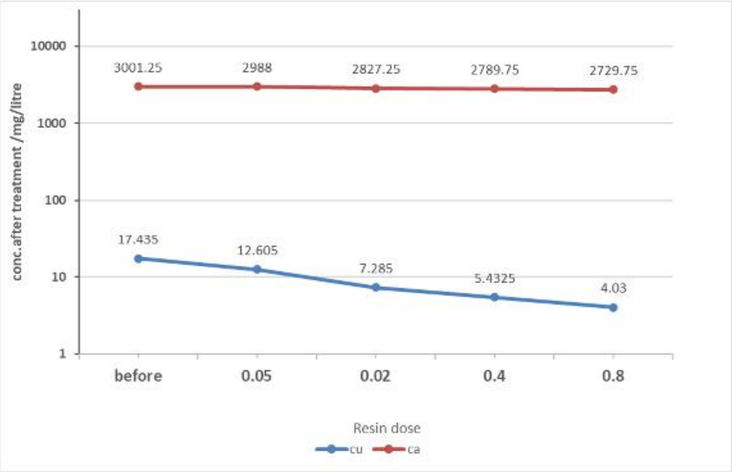

Fig.1A: Effectiveness of cation exchange with different concentration of resin on copper and calcium from fresh raw cow's milk.

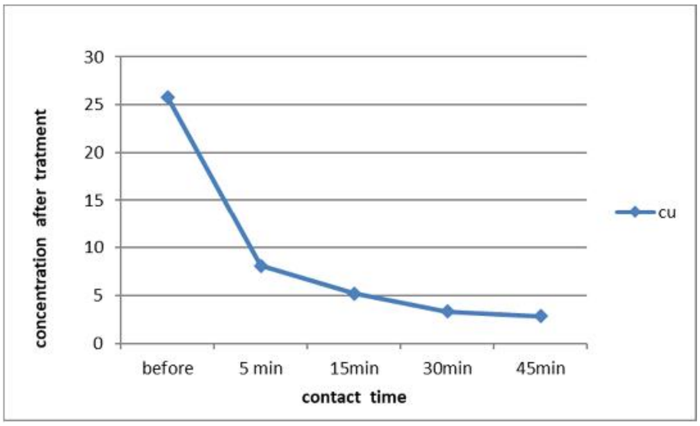

Fig.1B: Effectiveness of cation exchange of resin on copper from fresh raw cow's milk at different contact time.

4. DISCUSSION

Milk and other milk products are considered the most important components of the daily diet, especially for sensitive groups including, infants, children, and old age (Giri et al., 2011). Thus, the high exposure of these products to heavy metals has a negative effect on human health (Khan et al., 2013).

Lead is one of the nonessential elements that have a severe toxic cumulative effect.

The environmental sources are as disposal of wastes, atmospheric deposition, urban effluent, and vehicle exhausts may be considered the major resources for the presence of Pb in milk and milk products (Meshref et al., 2014). Pb could release into the air in the form of metal fumes or suspended particles (Ihedioha and Okoye, 2012). It is worth mentioning that Pb is a probable human teratogen, associated with hypertension and cardiovascular disease, causing neurotoxicity and affect the male fertility, memory deterioration (El-Sokkary et al., 2003).

Several authors have conducted researches on Pb, where lower results for milk samples were detected in different countries (Malhat et al., 2012, Temiz and Soylu, 2012, Rahimi, 2013, Ismail et al., 2015, Kim et al., 2016, and Castro-Gonzalez et al., 2017). For kariesh cheese, lower results were detected by (Ibrahim, 2004, Al-Ashmawy et al., 2008 and Deeb, 2010).

The higher levels of pb in the examined samples may be as a result of using contaminated water or sewerage water for agriculture purposes that may be directly accessed through drinking water, or through bioaccumulation of these metal residues in soil, fodder, and vegetables (Javed et al., 2009). Higher amount in kariesh cheese may be present because of the affinity of metals for the casein fraction, and also it was sold without a package (Fischer et al., 2011).

It is evident from the findings in Table (2) that mean concentrations of Pb in nearly all of samples were higher than standards set by the Egyptian Standard, (2012). Lower percentages were recorded by (El-Ansary, 2017 and Babu et al., 2018). These values can vary due to the sampling area and the time of year (Rahimi, 2013).

Cd is a toxic metal with extremely long biological half lifetime. Once contaminated food ingested, it can be absorbed via the alimentary tract, and may remain inside the body 15-20 years. It has many hazards on human health (Zhuang et al., 2009), such as renal damages, bone fractures, kidney dysfunction, and even cancer (Khan et al., 2013).

Concerning Cd results in our work, the results cleared the presence of Cd only in raw goat's milk and kariesh cheese, Cabrera et al. (1995) indicated that presence of low residues of Cd in raw or UHT milk and other milk products, except if dairy animals consumed polluted feed and water. Furthermore, Cd can be leached from food packages, or entered milk and other milk products during marketing, and storage. On the contrary, higher levels of Cd residues in raw milk and kariesh cheese were detected by (Javid et al., 2009, Deeb, 2010, Abd-El Aal et al., 2012, and Malhat et al., 2012).

Table (2) cleared that the mean concentrations of Cd only in 5% of raw goat's milk were higher than standards set by the EOSQ, (2012). Higher percentage was recorded by (El-Ansary, 2017 and Babu et al., 2018).

Cu is an essential microelement, necessary for adequate growth as it is responsible for many nutritional and biological functions in the body (Kazi et al., 2009). It is required only at low levels and if present in higher amounts, they can have some health hazards, and dairy technology problems (Lante et al., 2006).

The results in this work cleared that the concentration of Cu in different samples varied from 0.009 to 0.81 ppm. Lower results were detected by (Dobrzanski et al., 2005, Meshref et al., 2014, and Ahmad et al., 2017), while other authors recorded higher levels of Cu in cow milk samples (Yuet al., 2015, Issa et al., 2016 and Kabir et al., 2017) Regarding kareish cheese, higher level of Cu was reported by (Deeb, 2010). The presence of Cu residues in milk can occur from different sources as animal feed, water with high Cu content, or from Cu bearing and Cu alloys used in equipment (Mitchell, 1981).

Table (2) cleared that only raw cow's milk samples have no samples exceeded the standards for Cu according to Anonymous, (1998), while other samples exceeded it with different percentages varied from 65 - 80%. Nearly similar percentages were detected by (Babu et al., 218), while higher percentage were recorded by (Ismail et al., 2017). Other author detected lower results (Puls, 1994).

Regarding the results in Table (3), it was cleared that, Pb had the highest calculated daily intake from consumption of 200 ml raw sheep's milk per day (111.2%), while Cu had the least calculated value (0.005%) from consumption of 200 ml raw cow's milk per day. According to these results, milk could be represent a danger for human health because of the amount of Pb found in the examined samples, as these content exceeded the permissible values set by the Egyptian Standard, (2012), and also because of the high amount of milk consumed daily (Castro-González et al., 2017), On the contrary, in relation to the cheeses, it may represent no danger for human health, because of the low amount of cheese consumed daily (Moreno-Rojas et al., 2010).

The THQ has been identified as a complex guideline used for evaluation of risks caused by permenant exposure to various pollutant. It is not a quantitative measure about the probability of exposing population to health risks, but it only indicates the risk level due to exposure (US EPA, 2000). The THQ is a ratio of determined dose of a pollutant to a reference oral dose (RFDO) for that substance. The RFDO for Pb, is 0.0035 mg/kg bw/day according to US EPA, (2008), and for Cd, and Cu are 0.001, 0.04 mg/kg bw/day respectively according to USEPA, (2014).

According to the results of the present study, the consumers in Sharkia Governorate will be exposed to a potential health hazard from consuming these products because of the presence of Pb residues, as THQ values of (Pb) >1 through the consumption of in in all examined samples except, kariesh cheese. While THQ values for Cd, and Cu did not exceed any of the examined samples. These results were in agreement with those detected by (Meshref et al., 2014 and Ghafari and Sobhanardakani, 2017). Other authors found that none of the THQ values of Cd, Pb, and Cu were >1 through consumption of milk and dairy products (Arafa et al., 2014, and Kabir et al., 2017).

Ion exchange may be defined as the exchange of ions between the substrate and surrounding medium. Synthetic ion exchangers are generally polymeric materials that have been chemically treated to render them insoluble and to show the capacity of ion exchange, therefore these materials are used widely today (James and Medougall, 1996). Generally, resins are stable spherical, which resist physical degradation, high temperatures, and a wide pH range. They are completely insoluble in most aqueous and organic solutions (Sherrington, 1998). One of these resins is IMAC HP333, which is a weak acid cation exchange resin containing carboxylic groups on an acrylic matrix. It is designed for removing heavy metals from tap water for use in cooking and to improve the taste of water.

There are some parameters affect the quantitative uptake of metal ion by resin, including resin amount, pH, initial metal concentration and contact time. The amount of

Cu adsorption on resin was evaluated by using various concentration of IMAC HP resin (0.05–0.8 g), while the other parameters remained constant. It was apparent in (Figure, 1A) that the adsorption percentage of Cu ions increased with higher resin concentration and the removal efficiency of 76.89% was achieved by using 0.8 g/L. IMAC HP resin dose, and we used it as the optimum amount for the second part of the experiment. It can be explained as a result of availability of more adsorption sites and high surface area with increasing adsorbent dose. On the other hand, there is no noticeable change in Ca ion concentration using different amount of resin. Similar result was detected by (Nasef et al., 2002) as they concluded high removal percent for both Cd and Pb from fresh milk using 3% resin. While (Feng et al., 1995) found that only 11 to 19% of the Fe could be removed from milk.

In the contrary Lasheen et al. (2017) found that increasing the adsorbent dose above 0.5 g/L have a little or no change on metals removal, and explained this as a result of the aggregation on the adsorption sites, and so decreasing the surface area of the composite.
We used low pH values (6) in our work, as Cu ions could not be adsorbed easily at low pH < 3. The ions adsorption increased gradually with increasing pH till reaching 6, while at higher pH Cu ions precipitate due to formation of Cu hydroxides (Dinu and Dragan, 2008).

For analyzing effects of contact time during agitation on removal of Cu ions, using 0.8g/L resin at metal concentration of 100 mg/L and pH (6). Results in (Figure, 1B) showed that the removal efficiency of metal ions was increased with increasing time and the highest percentage of Cu ions adsorption was reached after 45 min. Similar results were recorded by (Pehlivan and Altun, 2006 and Alyüz and Veli, 2009) from using synthetic resin, but on aqueous solution.

5. Conclusion

It could be concluded that this survey confirmed the contamination of different types of raw milk and milk products with heavy metals.

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