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Contamination methods of milk with pesticides residues and veterinary drugs

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Abstract. The use of agricultural pesticides is very important in improving production, but the residue of these pesticides on crops have a serious health effect on humans. On the other hand, there is another type of pollutants resulting from the use of veterinary medicines, as well as heavy metals and mycotoxins that also result in health risks to humans due to their consumption of milk and dairy products. Milk is an important and necessary food for the body as it is consumed daily by many people because its contain fat, protein, vitamin, and minerals. In this work, we present a review of most scientific articles from 1964 until 2020, related to evaluating milk contamination with various chemicals, especially pesticides and veterinary drugs. We observe from many research papers at different country in the world Lingerling presence detectable values of chemical contaminate The maximum remainder, as a final result of this review paper we need to establish monitor program system for all chemical contaminate residue in milk and many food type to improve safety and reduce the risk for consumers in Iraq.

Keywords: Chemical contaminate, pesticide, veterinary drugs, milk.

1. Introduction

The essential need for the human body is a food because it's very important for human body growth and also perform the repair and reproduction process for all human activities [1]. Milk it is an integrated food because it contains all the important nutrients like , carbohydrates ,fats, proteins. and minerals Although the milk have high nutritional values, but it is an good Medium and suitable for the growth of microorganisms

So it is vulnerable to contamination and damage. Milk is a complex chemical compound. It is a mixture of fats, vitamins, proteins, carbohydrates, minerals and other compounds in small quantities [2]. For this reason, milk was considered a staple of a balanced healthy diet due to its formula rich in minerals like calcium and sodium and also rich in amino acids and free fatty acids [3]. Milk has a high chemical composition, conjugated linoleic acid, total elements and microelements see table 1 [4].

In order to protect agricultural crops from harmful and destructive pests and enhance food production, agricultural pesticides are using to control pests. The residues of these pesticides on agricultural yields and in food are contamination that poses a risk to the consumer's life. [5]. Consumption of food containing pesticide residues is not safe for humans. So pesticide residues in foods are considering dangerous for human health [6].

However, the ways in which milk is treated such as sterilization, pasteurization and fermentation cannot eliminate the remaining quantities of pesticides in milk and dairy products [4]. Spraying pesticides on field crops for the purpose of increasing production. However, the residues of these pesticides in the environment,



such as soil, water, and various vegetable parts, such as fruits and vegetables, are harmful to human health [7]. Pesticides are a major source of toxic and carcinogenic compounds that pose a threat to both animals and humans, as well as cause environmental pollution.

Veterinary medicines that are given to animals are part of the problem of contamination for animal products, the European Union has determined the maximum residual values (MRL) for a drugs such as 100 mg/kg for tetracycline and sulfonamide 50 mg/kg for macrolides and quinolones and also 100 mg/kg for pesticide. Several methods have also been developed to monitor and analyze the remaining substances in dairy products [8]. Milk is a complex food complex containing protein, fats, and other substances. Such a complex composition causes interference between its compounds during the analysis. During laboratory analysis, the sample must be prepared in practice by performing the extraction and purification process [9].

In Iraq, a few research deals with contamination of cow's milk with chemical materials resulting from agricultural pesticide residues that used to improve agricultural production, and also from the remnants of veterinary medicines used to treat animals.

Table 1. Milk composition [3].

Type of milk	Protein %	Lactose %	Fat %	Total solid %	Ash %	Moisture %
Human	1.25	6.95	3.20	11.8	0.21	88.25
Goat	3.30	4.40	3.90	12	0.7	88
Camel	2.90	4.30	3.60	11.7	0.75	88.35
Cow	3.40	4.80	3.75	12.8	0.71	87.23
Sheep	6.35	5.0	6.90	19.3	0.85	80.7
Buffalo	4.30	4.7	7.7	17.5	0.8	82.7

2. Origin of Milk Contaminants

2.1. Physical contaminants in milk

Milk is expose during the manufacturing process and also due to, handling, marketing, and storage to many physical contaminants such as animal hair, bush parts, dust, metal parts, udder peelings, dirt from the body of the cow, and unclean pots. Another source of contamination result from workers supervising , the milking and handling process, such as chewing tobacco, all previous sources physical contamination [2].

2.2. Chemical contaminants in milk

The milk and dairy products may be pollutant by chemical materials, the main source of which is from the pesticide residue, more than raw materials that are plant-based. Another source of chemical pollutants in milk and its product come from veterinary medicines such as antibiotics, sulfotamides, hormones, anti-worms, bush pesticides, and insects [10]. The major common chemical contaminants in milk and other products are worms antiseptics, insecticides, chlorine, nitrite, somatotropin and mycotoxins [11]. The chemical pollutants to which milk is exposed come from two main sources: the environment and the chemicals materials that are residue in milk. Where they are dangerous or cause other side effects that harm the health of the consumer [2].

2.3. Aflatoxins

Many molds can produce toxic metabolic products under appropriate conditions of temperature and humidity. These products are called aflatoxins, which cause a risk to human health and are found in animal milk that feeds on a bush containing fungi toxins of type B1. The toxin produced in milk M1 produced from metabolism of ruminants produces These molds toxins in wet feed that is not well dried or stored in a moist environment [2, 12 ,13].

2.4. Veterinary drugs (Antimicrobial Antibiotic residue drugs residue)

The common use of veterinary medicines by livestock breeders used to enhance the production of milk and its products. And also for the purpose of treating diseases such as mastitis and parasites and failure to observe the

adequate time period for disposal of these medicines by the animal, which leads to the exit of these medicines with milk and thus causes health risks to the consumer [14].

The human consumption of the remnants of veterinary medicines in milk is followed by many side effects that affect the health of the individual. The most important risks that accompany the consumption of milk containing antibiotics are the cancerous and genetic toxic response that often relates to chloramphenicol and sulfamethasin and others, see table 2.

It can also cause the creation of bacterial strains resistant to antibiotics as well as possible that the resistance move to other sensitive microorganisms, and the effect is not limited to the health aspect, but there are industrial effects, such as killing the starting bacteria, so fermentation does not occur [15,16].

Table 2. Represent the MRL of different drugs [2].

No.	Drugs	MRL Concentration $\mu\text{g}/\text{kg}$	Ref.
1	Amoxicillin	4	Codex
2	Ampicillin	4	EU
3	Cloxacillin	30	EU
4	Benzylpenicillin	4	MERCOSUR
5	Nafciline	30	EU
6	Tetracycline	100-200	EU
7	Oxytetracycline	100	EU
8	Chlortetracycline	100	EU
9	Trimethoprim	50	EU
10	Ceftiofur	100	EU
11	Striptomycine	200-1000	EU
12	Oxfendazole	10	EU
13	Sulphonamiduse	100	EU
14	Cephalexin	20	EU

2.5. Heavy metals residue

The definition of heavy metals are the materials that has density in standard state more than $5 \text{ g}/\text{cm}^3$. The presence of heavy metals in milk and dairy products results from consumption the animals to feed and water contain environmental pollution, and also the raw milk may be contaminates during manufacturing process. The existing of many toxic from heavy metals like cadmium, lead with low concentration produce disturbance in metabolic and health problems [17]. Other researchers also mentioned that the reason for the presence of heavy metals in dairy products is to eat lactating cows contaminated animal feed or the cause of pollution is contaminated manufacturing processes [18].

2.6. Hormone residue in milk

The reason for the contamination of dairy products with hormones is to give these hormones and veterinary medicines to animals in order to help expedite the production process and its quality, or it may give for a therapeutic purpose. During the incorrect treatment of animals, they cause pollution, part of which remains in the animal tissues, in undesirable proportions and not suitable for human consumption. An example of these materials is a natural and synthetic hormones [19, 20].

From an epidemiological point of view the contaminated milk can cause symptoms of allergic diseases for humans as well as there are some hormone dependent diseases and constitute a risk factor that stimulates many diseases for humans such as cancer and other diseases [21]. There should not be any hormone residues in the animal tissues. The highest permissible concentration according to European laboratories is 1 micrograms per kilogram for muscles and tissues to control hormone residues.

3. Pesticides and insecticides residue

In the agricultural sector, fruits, vegetables, and grains are sprayed with artificial chemicals that are known as pesticides, including rodenticides, herbicides, fungicides and pesticides. These pesticides are used before

harvest and during the storage period and these pesticides have the ability to transfer through the food chain from simple plants and animals to high-end animals which leads to the bioaccumulation of pesticides in animal products such as meat, milk, fats and eggs. The accumulation is caused by continuous exposure to the pesticide [11]. Chlorinated hydro carbonate is a highly effective and disturbing material for endocrine and bioaccumulative chemical toxins that spreads widely and enters the food chain by controlling animal and environmental pests. Contamination of fodder occurs in warehouses in the field due to the use of chlorinated insecticides such as Dichlorodiphenyltrichloroethane (DDT), Dichloro-dimethyl dichloroethane (DDD) and others. Dairy products are contaminated due to consumption of the contaminated cow feed.

The change that occurs in chlorine compounds in the environment is relatively slow over the years. It can be detected in meat, eggs, fish and dairy products, which are the main source of chlorine compounds reaching the human body [8]. The percentage of chlorinated hydro-carbon residues of milk is about 20%, which is mainly concentrated in the milk and butter fats which contain large quantities of pesticides [22]. Table 3 shows the residues of some chlorinated compounds in milk and its products. (DDT) is concentrated in animal fat tissue that is transferred to milk. That causes pollution by moving through the food chain.

Table 3. Average percentages of pesticides in raw milk and its products [11].

Pesticide Residue	Product type	Maximum residue limit mg per kg
HCB	milk	0.06
	Powder milk	0.0656
	Ras cheese	0.0037
	Damietta cheese	0.0045
	Spanish pasteurized milk	0.007
Aldrin-dieldrin	Cheese	0.2 ng/g
	milk	0.0074-0.0271
Dieldrin	Milk powder	0.0038
	Ras cheese	0.0039-0.0068
HCH	Damietta cheese	0.0025
	milk	0.094
	Milk pasteurized	0.015
	Milk powder	0.0149
	Ras cheese	0.00865
DDT	cheese	0.0115
	Butter	0.093
	Milk	0.159
DDT	Butter	0.049
	Milk powder	0.0546

HCB: Hexachlorobenzene; HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane

4. Pesticide Residues (PR) In Milk

The study of milk contamination and the ratios of pesticide residues in raw milk are very important because of their relationship to human health [4]. To study the residues of agricultural pesticides with raw milk, it is necessary to know the chemical composition of the milk components. Here two samples of raw milk were taken, one for bovine milk and the other for buffalo milk. And their chemical composition was studied to determine the percentages of agricultural pesticide residues in milk. Where the study showed that the buffalo milk sample showed higher levels of fats, total protein, total solid materials and whey than the cow's milk sample, while the lactose levels of the cow's milk sample were higher if compared to buffalo milk see table 4.

The presence of chlorine insecticides (OC) such as (HCB, Lindane, Aldrin and DDT) has been verified with values exceeding the MRL, according to the World Health Organization (WHO). Note that some pesticide residues that disappeared with skim milk and buttermilk during the production process. The yogurt has low level of pesticides due to heat treatment.

Table 4. pesticide residue of (mg/kg/fat basis) in milk samples %
(+) ve = percentage of positive sample [21].

Pesticide type	% (+) ve	Buffaloes milk Range of (+) ve	% (+) ve	Cow milk Range of (+) ve	MRL (WHO,FAO) 2008
HCB	41.7	0.081- 0.186	36.7	0.091-0.180	-
Lindane	50	0.021-0.082	43.3	0.012-0.046	0.01
Aldrin	33.3	0.040-0.080	26.7	0.030-0.072	0.006
Heptachlor	8.3	0.012-0.042	10	0.016-0.030	0.006
H epoxide	25	0.044-0.078	20	0.066-0.082	-
chlordan	16.7	0.010-0.036	20	0.010- 0.022	0.002
Endrin	20	0.016-0.020	16.7	0.010-0.016	0.0008

Commercial milk contamination is a very important topic, so many research and studies in this field has been reviewed, which relate to milk contamination with agricultural pesticide residues, including chlorine pesticides. This work provides us with an evaluation study of milk contamination of various types of organic pesticides in different parts of the world. From this work, note the existence of the chlorine pesticide in milk samples although it was banned since 1980s. Where in some samples exceeded the limits allowed by the World Health Organization, where it poses cause a large risk on human health due to its biological accumulation, causing many diseases [23].

The collected samples were examined by gas chromatography GC technique where used electron capture detector for detect the organochloride pesticide OCP residues using detector such as pulsed flame photometric. The dicofol at concentrations between 0.07±0.0007 remain at fodder sample while the organophosphorus like dimethoate exist in all milk samples at concentrations between 0.13 all the samples collected from Musi river. The results of test showed the fodder samples with residues of dicofol at concentration of 0.07±0.0007 (0.071-0.077) [11].

The milk contaminates by different organochlorine pesticides (OCPs) like (α HCH, β HCH, ϵ HCH) heptachlor, aldrin, heptachlor epoxide, γ chlordane, endosulfane, dieldrin, Endrin, p,p' -DDE, p,p' -DDD, and p,p' -DDT) was investigated and also the fat samples was extracted from milk to calculate pesticide residues. All the analysed samples contained detectable residues of organochloride pesticide. Also a high level of contamination with metabolites of DDT and HCH, p, p' -DDE, also another contaminant by p, p' -DDD. All the test samples showed acceptable values according to WHO [24].

Table 5. Average ratio of Recovery and RT for raw milk [24].

Pesticides	% *Recovery± SE	RT (min)	Limit of detection (ng g ⁻¹)	Fortification levels (ng g ⁻¹)
α HCH	833.35 ± 0.2998	6.02	0.03	0.5
β HCH	81.446 ± 0.8119	7.57	0.04	0.4
ϵ HCH	86.779 ± 1.2288	8.36	0.06	0.5
Heptachlor	84.91 ± 1.4453	8.92	0.05	0.1

Previous work provided a practical study to analyze level of organic chlorine pesticide residues and chemical composition in buffalo milk samples. Monitoring of the analyzed samples gives the research team information about the quantities and type of pesticides in the environment. The research team analyzed three types of pesticide residue like organochlorine pesticides, namely Hexachlorocyclohexane (HCH), Dichlorodiphenyltri- chloroethane (DDT) and Endosulfan while the Lindane Residues exceeded MRL values in 50% and cause the serious concern, the detected value of p,p'-DDT showed exist in 70% of the samples with p,p'-DDE (dichlorodiphenyldichloroethylene) in 80% from all tested milk samples. The DDD (Dichlorodiphenyldichloroethane) was detected in 65% of the milk samples. The results of study show that DDT is the major contaminants in different parts of Delhi state, due to statistical analysis shows no significant correlation between chemical compositions of the samples [25].

The study and analysed of 92 samples from raw milk taken from India's Ludhina province during the three years 1999, 2000 and 2001 and the results were 6 samples with a percentage of DDT of 4% and in two samples exceeding the maximum waste level (MRL). The remainder was fixed for DDT 0.05 mg / kg (MRL) For pesticide (HCH) was 0.01 mg / kg in whole milk, the collection of raw milk samples amounting to 49 samples exceeded the specified values, the study indicated that the milk was contaminated with pesticide residues despite the urban imposed by the agriculture and health programs on the use of pesticide (DDT) and (HCH) analysis of 40 samples of butter showed the presence of quantities of pesticide (DDT) in 28 samples.

And the presence of the pesticide (HCH) in 8 samples, however, none of the samples exceeded the value of the remaining (MRL) of (DDT), (HCH) .DDT residues from the P-DDE, P, P-TDE. HCH residues were present in 6 samples that are HCH and 2 samples revealed the presence of b-HCH the amount of MRL exceeded the acceptable value during daily consumption For tainted milk [26].

The study and analysis of milk samples was presented in [1] to clarify the ratios of pesticide residue in pasteurized and sterilized milk in Tehran province (Iran) such this pesticide OCP pesticides (such as α -HCH, γ -HCH, HCB, dieldrin, o. p- DDE, β -HCH p,p- DDE. p,p- DDD, p,p- DDT) and polychlorinated biphenyl (PCBs) congeners (28, 52, 101, 138, 153, 180) in containing 1.5%, 2.5%, and 3% fat from . The results clarify and indicated that is no direct correlation between fat percent and the concentration of PCBs and OC pesticides [1].

Experimental study from two different locations in Poland, one agriculture and the other industrial. were the levels of OPC evaluate such as DDT, the metabolites in cow's milk also study . All the samples, collected from different areas agricultural (n D 25) and industrial (n D 25) , the evaluation study was achieved by GC technique, DDT residue detected in all milk samples specially from agriculture sections where the concentration of DDT about 0.336 $\mu\text{g}/\text{Liter}$. While in the industrial samples found the concentration lower, at 0.131 $\mu\text{g}/\text{Liter}$ approach, 4, 4-DDT was the main metabolite, constituting 83% of total DDT metabolites.

The collected samples in some site exceeded the accepted ratios will cause health risk on human body [17]. The researcher presented a study to determine the quantities of pesticides such as organic phosphate pesticides in raw milk and also to detect residues of maloxone and malathion in cow's milk and buffalo consumed in Turkey. Therefore, we collected 75 samples of buffalo milk and 75 samples of cow's milk to determine the remaining concentration by using HPLC technology [21].

As review of past research introduce another study to determine the concentration of OPP pesticide and carbamates pesticide using GC technology and found the reminder ratios of pesticide in cow milk and also in feedstuff provided to diary cattle [27], the research team used HPLC method with .NH₂ column and also 97% acetonitrile elute to determine the insecticide cyromazine and metabolite melamine residues in pork and milk. The cyromazine and melamine was separated at 8 and 12 min retention time. We can get the linear calibration curves for cyromazine and melamine in range of concentration between 0.01–1.0 $\mu\text{g}/\text{mL}$ at with correlation coefficients of 0.9999 and 0.9997. The study presents a limit of detection for two compounds 0.2 $\mu\text{g}/\text{kg}$, and the limit of quantitation was 0.02 mg/kg.

The classic method based on HPLC was introduced to measurements the residue of twenty six veterinary and 187 pesticide residue samples in milk [28]. Moreover, many analytical methods used to study the pesticide residue in milk and fish. All or main of these results prove that the milk sample has own lower level of organochlorine pesticides than of fish sample [29].

Two fast methods were studied and evaluated. These methods used to prepare and analyze samples for fatty foods such as milk, eggs and avocado. The evaluation and comparison study was achieved for 32 samples to determine the agricultural pesticide residues because its represent a wide range of physical and chemical properties. One of them the method called the fast (quick), and easy to use also cheap and effective abbreviated as (Q,u,E,Ch,ER,S) method for pesticide residue analysis. Many researchers study the pesticide residue in milk and other dairy product but this work we take different five OCP pesticide such as hexachlorobenzene, methoxychlor alachlor, dieldrin, lindane and also other three OPP pesticide parathion-methyl chlorpyrifos, and malathion, all the analysis perform on milk samples [30].

We note from the results 44% from the samples have exist the lindane (HCH) pesticide and malathion residues with different concentrations exceeded not all time the levels set by the European union according code 2008. As a results of the work, the concentrations of residues for the methoxychlor, chlorpyrifos, and hexachlorobenzene exceeded the limit set by EU 2008 in 33%, 66%, and 88% of the examined samples. Also the other levels of residues for parathion-methyl alachlor, and dieldrin. Below the EU maximum residue limit in Egypt [31]. A develop reverse phase HPLC method, this method used to measure the melamine in milk with different process such as pasteurized and UHT milk and dairy products [32]. Using the fast method

QuEChERS (quick, easy, cheap, effective, rugged and safe) to extract the tetracyclines from the milk sample [33].

The main idea behind the work in reference [34] is to identify all the parameters affecting the quality of food as a result of pesticide residues. Due to direct impact of pesticides on the growth of microorganisms necessary for events of fermentation process such as bacteria and yeasts, as well as biological transformations of pesticides and their residues that may negatively affect the quality of sensory products (chemical and physical). Production of compounds responsible for flavoring fermented foods [34]. Present a experimental study to measure the residues of organic phosphorous pesticides, which included 13 types of pesticides that are frequently used to combat the external parasites of milk cows or in the feed used for feeding them.

Homogeneous samples were taken from homogenized pasteurized Mexican milk. 6% of the samples are on op residue. There were 8 samples that exceeded the permissible limit (MRL) of the pesticide. 5 samples contained dichlorvos, folate and one sample that contained chlorpyrifos, chlorine phenvinus. The remaining pesticide rate for 13 samples was less than the minimum permissible value ranging from 0.0015 to 0.0203 [35].

An experimental study was achieved to monitor the food treatments and the effect on reducing pesticide residue and their degradation of organic chlorine like HCH in milk samples. We note the concentration of residue for pesticide in milk will decay after heat process. The heat treatment will effect highly on the residue in milk sample and also the sterilization and boiling provide effective degradation of HCH isomers. Many chemical contaminants like heavy metals, veterinary drugs, pesticide residues, and, mycotoxins exist in milk and milk products [36, 37].

The analysis of pesticide residues in milk is a very important process to know the extent of their impact on human health, as pesticide residues are a major source of infection with many cancerous diseases and diseases of the nervous system. The MRLlimit proposed by EC for pesticides residue acceptable in different products. This work used Multiresidue LC-mass spectrometry methods (LC-MS) for testing food products [38].

Samples of buffalo milk were collected from different regions in Egypt to know the ratios of the pesticide residues in it. Then, the effect of the different process such as pasteurization, sterilization, fermentation, coagulation and temperature was studied on the pesticide residues in the milk. The main results of this study conclude all the treatment on milk will reduce the concentration of residue of pesticide [39].

Table 6. Effect of different milk process on pesticides [38].

Process	Concentration (mg/100 g)		Degradation (%)	
	dimethoate	malathion	dimethoate	malathion
Un treatment	3.852	1.695	-	-
Pasteurization	1.024	0.000	73.4	100
Sterilization	0.935	0.068	75.72	95.99
Fermentation	0.520	0.048	86.5	97.17
Coagulation curd	0.618	0.193	50.6	85.02
Whey	1.27	0.06	-	-

The use of chlorinated hydrocarbons as an insecticide remains in water, soil and biological materials and enters the food chain in many ways [40]. Here we note the effect of different heat process on pesticide residue in milk and diary products. The organochlorin pesticide reminder that detected in all test milk samples like DDE the found values in yoghurt reach to 2.7298 ± 0.1126 ppb, with a mean value of 1.9161 ± 0.0992 ppb., the residues detected in cottage cheese samples approach to zero. The main conclude results ,that the sterilization process of raw milk is the most effective method for reduction the pesticide residues to minimum value [41].

Milk samples were collected from different places in Romania, as well as studying the percentages of residual pesticides and knowing the extent of their impact on humans when consuming dairy products. Fifty-four samples of raw milk were collected, where proportions of the remaining pesticides were found of a type HCH while DDT not found all analysis achieved by using liquid chromatography. In this work, residual ratios of lindane were found ranging from 0.0042 to 0.2124 (mg / kg fat) in cow's milk samples, as well as ratios ranging from 0.0028 to 0.1408 (mg / kg fat) for pasteurized cow's milk. Also, the values ranged from 0.0042

to 0.2682 (mg / kg fat) for sour cream. The maximum values of detected OCP residues exceeded the maximum residue levels stipulated [42].

Table 7. Reminder ratio of concentration (mg kg⁻¹) of 7 OPP pesticides in milk. Cultured @ Lactobacillus spp. For 42 C [41].

Pesticide	Strain inoculated	Residual concentration at different times (h)							
		8	12	16	20	24			
Dimethoate	L. bulgaricus	1.100 0.025	± 0.987 0.047	± 0.909 0.046	± 0.876 0.013	± 0.808 0.039			
	L. paracasei	1.178 0.042	± 1.092 0.047	± 0.986 0.031	± 0.957 0.013	± 0.897 0.024			
	L. plantarum	0.990 0.017	± 0.861 0.029	± 0.841 0.048	± 0.798 0.026	± 0.735 0.032			
	Control	1.050 0.021	± 0.985 0.042	± 0.908 0.035	± 0.860 0.022	± 0.808 0.037			
Malathion	L. bulgaricus	0.987 0.026	± 0.907 0.022	± 0.853 0.042	± 0.760 0.043	± 0.677 0.046			
	L. paracasei	0.991 0.034	± 0.847 0.025	± 0.728 0.032	± 0.699 0.027	± 0.614 0.041			
	L. plantarum	0.912 0.044	± 0.854 0.027	± 0.663 0.036	± 0.565 0.014	± 0.484 0.033			
	Control	0.986 0.046	± 0.900 0.055	± 0.821 0.034	± 0.750 0.033	± 0.699 0.056			
Trichlorphon	L. bulgaricus	1.210 0.041	± 1.190 0.024	± 0.988 0.033	± 0.907 0.012	± 0.877 0.053			
	L. paracasei	1.136 0.025	± 0.987 0.033	± 0.900 0.011	± 0.830 0.046	± 0.778 0.019	± 0.		
	L. plantarum	1.230 0.033	± 1.160 0.019	± 0.990 0.014	± 0.930 0.021	± 0.847 0.012			
	Control	1.036 0.030	± 0.923 0.044	± 0.892 0.034	± 0.869 0.054	±	Not detected		

Continue to review the research that deals with calculating the remaining agricultural pesticides with milk and its products in this work it was studied adding seven types of pesticides such as trichlorphon methyl parathion fenthion monocrotophos dimethoate malathion phorate and were added to skimmed milk. We use one strain of Lactobacillus spp. including Lb. bulgaricus, Lb. paracasei and Lb. plantarum, to inoculated the milk at 42°C for 24 hours to check its impact on decay the OPPs. All the residue of pesticide in test samples were extracted by using extraction solvent And measured by GC technique after purification. Decay rate constant and half live periods of the OPPs were measured from a first-order reaction kinetics model. The main results indicate that the Lactobacillus spp. exhibited some speed up on Organo phosphorus degradation totally see table 7 [43].

Ectect organic phosphate residues in milk based on acetylcholine esterase inhibition. The study revealed that raw milk samples are stable for eight days if they are stored at a temperature of four degrees. Milk samples were extracted with acetonitrile prior to enzyme assay [44].

The effect of ultraviolet (UV) light on degradation of Chlorinated Hydrocarbon Pesticides in milk. The light was degrade organochlorine insecticides contaminating fluid whole milk or butter oil. The percentage of decomposition and decay depends on the thickness of the film and the depth of introduction of the rays into the sample when operating conditions are constant.

The effect of ultraviolet light on the degradation of chlorinated hydrocarbons in milk has been studied. Where the light analyzes the organic pesticides contaminated with chlorine in whole milk or butter oil. The degradation rate depends on thickness of the sample and also penetration depth. For the sample into the sample where the work was done under constant operating conditions. Decay of methoxychlor in butter oil was 96% after exposure for first time to UV light, little percentages insecticides were degraded also [45].

Thirty-five commercial samples taken from market for cow milk from the Iranian city of al-Ahwaz. Where seven types of insecticides of organic chlorine were discovered. All the identification and measurement process of the toxins were performed by using HPLC technique with an Ultra violet detector. The collected results noted the presence of lindane in ratios ranging from (0.042 mg/Kg) and DDT (0.28 mg/Kg) and the results above maximum limit ratio.by FAO and WHO [46].

The effect of fermentation, break down pesticide residues in milk. Seven samples of cow's milk were collected and added to them pesticides from organic phosphorous like, i.e., malathion, fenthion, methyl, parathion, dimethoate phorate, trichlorophon, monocrotophos and then fermented with 42°C. All the samples undergo to further process to extract pesticides by using organic solvent and tested by gas chromatography GC after purification process. The researchers noticed a significant degradation of the pesticide residues after supplementing the yoghurt with one of the initiators with the exception of the pesticide malathion [47].

The measurements of the OCPs pesticide in goat milk determined for seven OCPs. The researcher found the values in fat approximately 2.7%. If milk samples left at a temperature of 4°C for one week this will deceasing and cause decay the reminder of OCPs. OCPs were calculated and found that most were present with a mean of Heptachlor0.091695 while Dieldrin had a value of 0.034547 [46]. The effect of pesticides as Ivermectin and deltamethrin has been investigated. Because it used by farmers as an anti-parasite, and are very widely used for animals. The pesticides were detected by using liquid chromatography at wavelength of 233 nm. The QuEChERS method was used to extract pesticides from milk samples. All results confirmed that the recovery rate from bovine milk samples was 92.22-96.7% for ivermectin.and for deltamethrin average ratio recoveries from 92.56- 97.78%.

The minimum detection limits of ivermectin from 2 to 6 micrograms / kg and for deltamethrin from from 3 to 9 micrograms/kg. All results indicated that the ratios were 18.18, 28.57, 40, 100 and 60% of the samples for bovine milk containing residues of the type Ivermectin less than the maximum, while the rest of the samples contained 81.82, 71.43, 60, 0 and 40% of Ivermectin residues. All of them are above the maximum residue limit. While the deltamethrin cannot exist in 33 samples. The method indicated as good and reliable method for identification pesticide from type avermectin and deltamethrin in milk samples [48]. The veterinary medicines in milk from 2009 to 2011 were studied in Brazil and their effect on animals and what are the residual proportions of cow's milk for these drugs, where it was found that the proportions did not exceed the maximum permissible residue. The drugs were of the type of ivermectin that are given to dairy cows, especially quinolones and tetracyclines.

Table 8. Summary of literate review.

Researchers	Studied Samples	Country	Elements	Test methods	Year
J. E. Beam and D. J. tankinson	Milk	Italy	organophosphate	Acetyl cholinesterase inhibition	1964
B.J. Liska	Milk	China	chlorinated hydrocarbons	GC	1967
C, F. Li and R. L. Bradley	milk	USA	methoxychlor	UV	1968
Salwa M. Dogheim	Milk	Egypt	Pesticide	GC	1990
J. H. Salas	Milk	India	organophosphorus	gas chromatography	2003
R.S. Battu et al	Milk	India	DDT, HCH	Gc	2004
S.J. Lehotay	milk,	Egypt	Pesticide	QuEChERS, LC	2005

	eggs				
Nevein S. Ahmed and Eman M.S. Zaki	Milk	Egypt	α HCH, β HCH, ϵ HCH)	HPLC	2009
Ashnagar et al	Cow Milk	Iran	organochlorine	HPLC	2009
Ruicheng Wei et al	milk and pork	China	cyromazine and melamine	HPLC	2009
S. K. Nag	Milk	India	veterinary drugs, Pesticide	GC	2010
Li-Ying Bo et al	Bovine milk	china	dimethoate, fenthion, malathion	gas chromatograph (GC)	2010
A.M. Abo. Donia et al	Cow milk, Buffalo milk	Egypt	HCB, lindane, aldrin and DDT	GC	2010
Sara Bayat , Abbas Esmaili Sari	Milk	Australia	α -HCH, β -HCH, γ -HCH, HCB, dieldrin	GC	2010
Rafael Fagnani et al	Milk	Brazil	Organophosphorus, carbamate (CB)	GC	2011
Xin-Huai Zhao , Jing Wang	Milk	China	organophosphorus	gas chromatography (GC)	2011
Ayoub, M. M et al	Milk	Egypt	organochlorine	GC	2012
Filazi et al	Milk	Turkey	melamine	Reverse phase HPLC	2012
Julijana et al	Goat milk	India	organochlorine	gas chromatograph (GC)	2013
Jorge Regueiro	Milk	United kingdom	organochlorine	HPLC	2013
Mohd Aslam, Sumbul Rais, Masood Alam	buffalo milk	Egypt	Organochlorine (Hexachlorocyclohexane (HCH), Dichlorodiphenyltrichloroethane (DDT) and Endosulfan)alachlor, dield-rin, hexachlorobenzene, lindane , ,methoxychlor , organophosphorus pesticideschlorpyrifos, malathion , , parathion-methyl	HPLC	2013
Eman M. Shaker, Eman E. Elsharkawy	buffalo milk	Egypt	organophosphorus pesticideschlorpyrifos, malathion , , parathion-methyl	gas chromatography (GC)	2015
Anna Stachniuk and Emilia Fornal	Milk	Poland	Pesticide	Multiresidue liquid chromatography-mass spectrometry methods (LC-MS)	2015
J. Kuba et al	Milk	India	dichlorodiphenyltrichloroethane (DDT)	GC	2015
Korrapati et al	Milk	India	organochlorine	GC	2015
Husniye Imamoglu and Elmas Oktem Olgun	Milk	Turkey	veterinary drugs, pesticide	LC-MS/MS	2016
Fawzia Abd-Rabo et al	buffalo milk	Egypt	organophosphorus	GC	2016
L. RUSU et al	Milk	Romania	α -HCH, β -HCH and γ -	gas chromatography	2016

			HCH (GC)		
Hanan et al	Milk	Egypt	Deltamethrin Ivermectin	HPLC	2016
Stefani Faro et al	Cow milk	Brazil	tetracyclines	GC	2017
Sujatha Singh and Krishnaiah Nelapati	Milk	India	α , β , γ and δ hexachlorocyclohexane isomers (HCH))	HPLC	2017
E. Marinou et al	Milk	Greece	tetracyclines	QuEChERS	2019
Isabella C. Vasconcelos et al	Milk	Brazil	Organochlorine	-	2019

These drugs have been found in proportions, such as doxycycline (9%) and abamectin (1.6%), noting that these substances are not intended for use in milk-producing animals due to their effect on human consumption. Also the researcher note Norfloxacin drug at ratio 15% not exceed the allowed maximum ratio limit there is no residues for the treptomycin, chlortamphenicol, β -lactams were confirmed. As a final result, milk in Brazil contains low levels of veterinary medication so that it is not considered a risk as well as it does not contain toxicity risks related to milk consumption and does not raise public health concerns. All the previous research can be summarize as in table 8. whrer this table express about the briefly of review literatures.

5. Conclusions

We note from the review of previous research papers, the chemical contaminate of the milk especially pesticide residues remain the effective parameters in all the research papers because its relate directly to human health and dairy industry. There are many methods that lead to reducing the percentage of pesticide residues remaining in dairy products and these methods, such as thermal treatments, fermentation and radiation treatment. All fermentative microbiota in the reduction of the pesticide residues, during the fermentation time. A way in metabolomics to understand the common effects of pesticide residues on fermenting microorganisms (yeasts and bacteria) would be of essential, fundamental importance, together with on accounts in extraction methods and analytical mechanisms with the utilize of increasingly precise exposition tools mechanisms to estimate pesticide residues.

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