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Trace and Toxic Elements Concentration in Milk Before and After Zeolite Sorbent Filtration.

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ABSTRACT

In this paper the results of trace and toxic elements determination in the milk samples are presented. The milk samples are collected from the different regions of Semey city and filtrated through the zeolite sorbent. After the filtration the content of *Cr* reduced to 0.4 mg/l in comparison with control sample, which was 0.82 mg/l. Separately, the content of *Cr* after the filtration through the filter with 500g of zeolite was 0.42 mg/l; 300g of zeolite – 0.57 mg/l and through 100g of zeolite – 0.76 mg/l. The concentration of *Cd* after the filtration reduced until: 0.069 mg/l through 100 g; 0.051 mg/l through 300 g; 0.034 mg/l through 500 g in comparison with 0.079 mg/l before the filtration. *Ni* concentration reduced until 0.21 mg/l (500g of zeolite), which below the maximum allowable limit (for *Ni* is 0.23 mg/l).

Keywords: milk, filtration, zeolite, toxic element, installation

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INTRODUCTION

Large-scale industrial plants in East-Kazakhstan (Cement Plant, gravel-sand, coal mining enterprises) have been contaminated environment with heavy and toxic metals. Moreover, 40 years nuclear explosions at the former Soviet Union's Semipalatinsk Nuclear Test Site inflicted serious damage on people's health and contaminated environment (soil, water, vegetation, food) [1, 2].

At the same time, food raw materials and food products contain rather wide list of foreign substances (toxins of microorganisms, mycotoxins, heavy metals, antibiotics, hormonal preparations, regulators of plants height, pesticides, fertilizers, radionuclides, etc.). They strengthen chemical loading of food and can affect to the nutritious homeostasis [3].

Food specialists control those metals which are accumulated in the environment in high concentration and cause a serious biological and toxic danger to human body. Such toxic metals as cadmium, lead, zinc, copper pose biggest danger as they even at low concentration strongly expressed toxicological properties [4]. Food of vegetable and animal origin accumulates heavy metals through air, water and soil. Pollution of foodstuff is caused by the immediate sedimentation of aerosols from air on vegetation and vegetable foodstuff [5, 6].

From all the accumulated in human body heavy and toxic metals 1/3 part is entered through vegetable food, and 2/3 part – from the animal origin products. From here, one of the key problems facing the food experts is receiving ecologically safe milk products by blocking of migration of xenobiotics into the animal products. One of the methods for reducing the toxic elements concentration in animal origin products is to use of sorbents with high detoxicative activity in the animal fodders [7, 8].

It should be noted that in the food industry, during the food production there will not be the stage of food raw cleaning from pollutants. This kind of problem can be solved with the introduction to technological process of natural zeolites as efficient sorbents [9].

The aim of this paper is to study the content of mineral and toxic elements in milk before and after filtration through the zeolite sorbent.

MATERIALS AND METHODS

Milk samples are collected from the different regions of Semey city (Republic of Kazakhstan) from the local farmers and milk enterprises.

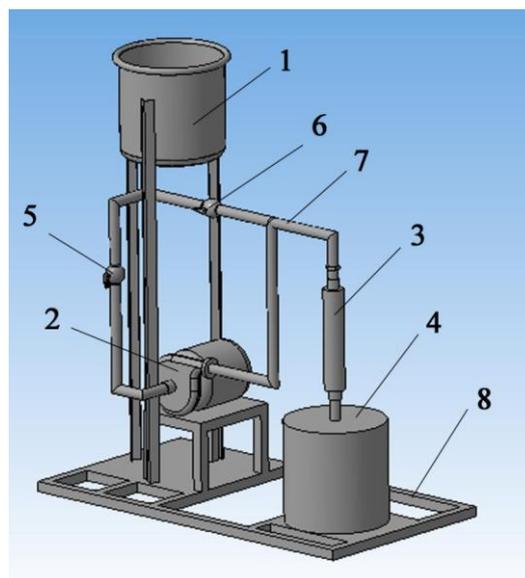


Fig. 1: Filtration installation design

Filtration process is carried out on the special designed installation, which allows controlling the quantities of zeolite in the filters. The pilot equipment for milk filtration consists of receiving hopper, pump, filters, drainage container and valves. Milk, from the hopper, flows through the three filters with different quantities of zeolite (100g, 150g and 200g). Determination of heavy and toxic metals investigated on ICP-MS mass-spectrometry.

Filtration installation consists of receiving tank 1, pump 2, filter 3, storage container 4, valves 5 and 6 (fig. 36). The milk from the receiving tank 1 through the valve 5 flows to the pump 2, at that the valve 6 must be closed. The pump transfers the milk to the filter 3 through the pipe 7. After filtration the milk is flowing to the storage container 4.

During the filtration the valve 5 must be closed and the valve 6 is opened. The milk through the valve 6 free-run to the filter 3 and after filtration flows to the storage container 4. All construction is installed on the frame 8. Receiving tank is made of stainless steel with cylindrical shape. For pipe are used the plastic water pipes with outside diameter of 50 mm. The storage container is made as a cylindrical container from stainless steel.

Determination of chemical elements by ICP-MS mass-spectrometry

One to two grams of the sample was placed in a high-pressure Teflon container. Each sample was combusted at 400°C for 4 h and then to 600°C for 2 h using a muffle furnace. A representative 1 g (dry weight) of ashes was digested by adding 3 cm³ HNO₃ and 2 cm³ of HF. This was placed in a microwave at 200 °C for 20 min (Berghof Speed Wave microwave system, Germany). After microwave digestion, the samples were diluted with 1% HNO₃ in a 10 cm³ vessel.

The content of elements in muscle samples was determined with an inductively coupled plasma–mass spectrometric method (ICP-MS, Varian-820 MS, Varian Company, Australia). The method was validated with certified reference materials. Calibration standards Var-TS-MS, IV-ICPMS-71A (Inorganic Ventures Company, USA) were used for calibrating the mass-spectrometer. The sensitivity of the mass-spectrometer was tuned up using a diluted calibration solution Var-TS-MS with concentration of Ba, Be, Ce, Co, B, Pb, Mg, Tl, Th of 10 µg/L. Three calibration solutions were used for the detector calibration. They were IV-ICPMS-71A of Cd, Pb, Cu, Zn elements diluted to 10, 50 and 100 µg/L. Discrepancies between the certified values and concentrations quantified were below 10 %. The operating parameters of the inductively coupled plasma mass spectrometer Varian ICP 820 –MS were as follows: plasma flow 17.5 L/min; auxiliary flow 1.7 L/min; sheath gas 0.2 L/min; nebulizer flow 1.0 L/min; sampling depth 6.5 mm; RF power 1.4 kW; pump rate 5.0 rpm; stabilization delay 10.0 s.

All analyses were performed in triplicates, and the results, given in mg/kg wet weight, are expressed as mean ± (SE).

RESULTS AND DISCUSSION

The results of chemical elements determination in the milk samples before and after filtration through the zeolite sorbent is presented in the table 1. According these findings, practically all the chemical elements tend to reduction (fig. 2, 3, 4).

Table 1: Chemical elements concentration before and after filtration, mg/l

Sample	Chemical elements, mg/l									
	Na	Mg	Al	P	Ca	Cr	Mn	Co	Ni	Cu
Milk	1,27	0,64	8,86	138,74	2,149	8,235	0,0190	0,0535	0,285	0,104
100g Z*	1,19	0,61	8,76	134,20	2,010	7,868	0,0189	0,0523	0,278	0,099
150g Z	1,17	0,60	9,07	131,296	2,017	7,826	0,0186	0,0519	0,275	0,098
200g Z	1,18	0,59	8,97	128,972	2,008	7,801	0,0187	0,0525	0,277	0,099

Table 1 (continued)

Sample	Chemical elements, mg/l						
	Zn	Rb	Sr	Ag	Cd	Cs 137	Ba 137
Milk	0,221	0,0210	0,0003091	0,0001892	0,00751	0,00154	0,0002284
100g Z	0,214	0,0209	0,0002966	0,0001809	0,00706	0,00146	0,000213
150g Z	0,213	0,0207	0,0002962	0,0001849	0,00705	0,00147	0,0002108
200g Z	0,214	0,0210	0,0003003	0,0001888	0,00712	0,00149	0,0002215

*Z - zeolite

Sodium content in the milk before filtration was 1.27 mg/l and after filtration it has reached 1.17 mg/l through 150g of zeolite; 1.18 mg/l through 200g of zeolite and 1.19 mg/l through 100g of zeolite sorbent (fig. 2).

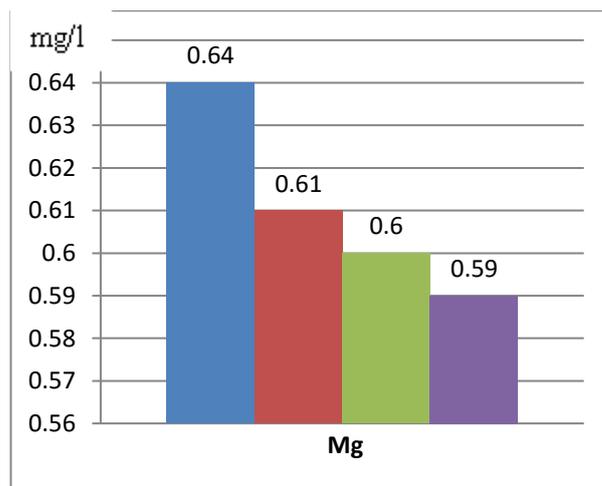
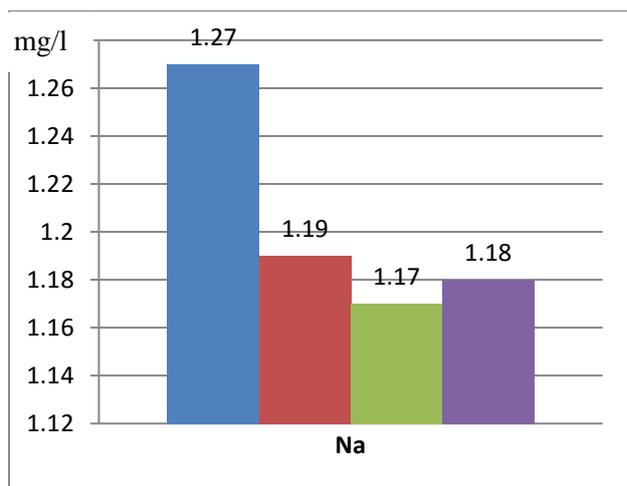
Mg has a tendency to decrease from 0.64 mg/l in control sample to 0.59 mg/l when filtrating through 200g of zeolite.

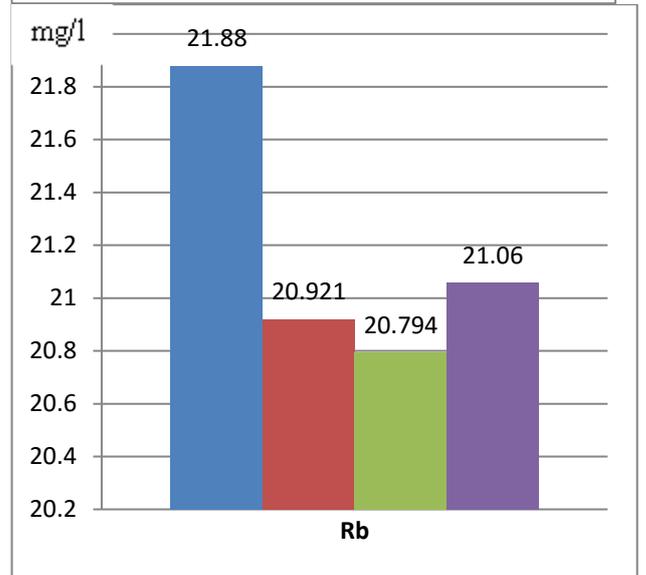
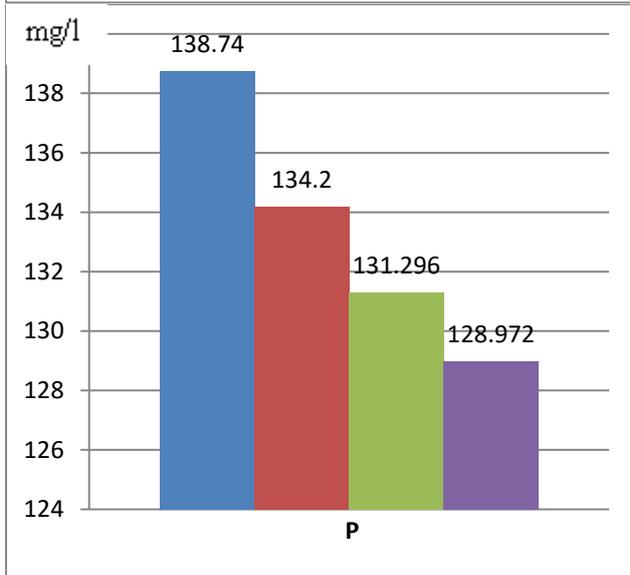
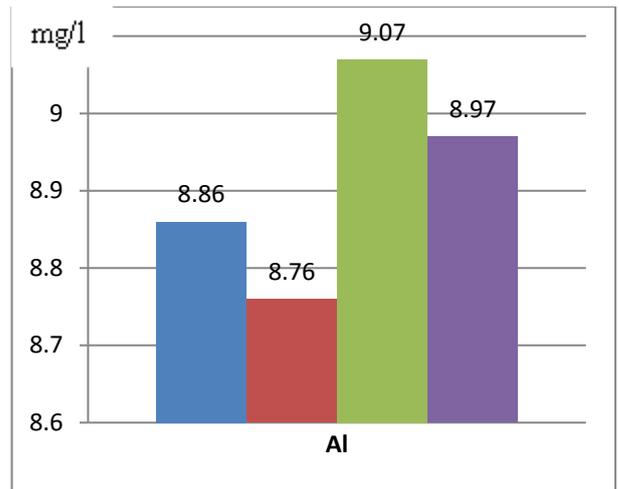
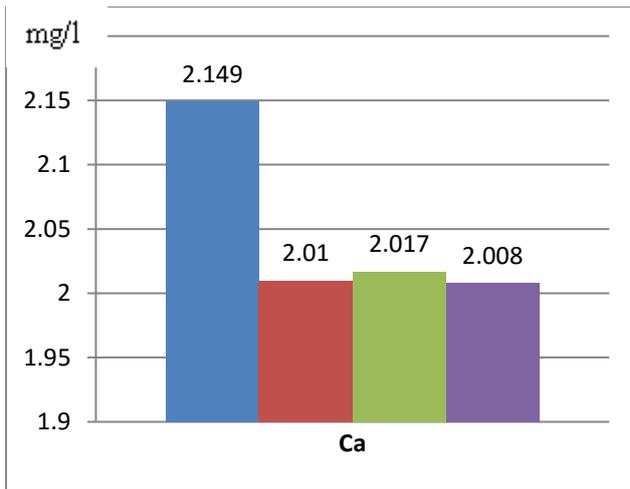
The most significant reducing of P concentration (to 7%) was observed in the milk sample filtrated through 200g of zeolite. Particularly, concentration of P in control sample was 138.74 mg/l and decreased until 128.97 mg/l. In the milk samples, after the filtration through 150g of zeolite, P concentration was 131.29 mg/l; and through 100g of zeolite – 134.2 mg/l.

Calcium concentration is reduced by 0.141 mg/l at filtration through 200g of zeolite comparing with the concentration of 2.149 mg/l in control milk sample. In other samples the obtained results as follows: through 150g of zeolite calcium content is 2.017 mg/l; through 100g – 2010 mg/l, respectively (fig. 2).

Based on the research findings the concentration of zinc before and after filtration is practically not changed. In the control milk sample the zinc concentration is 0.221 mg/l, after the filtration through 150g of zeolite zinc content is 0.213 mg/l, after 100g and 200g – 0.214 mg/l, respectively.

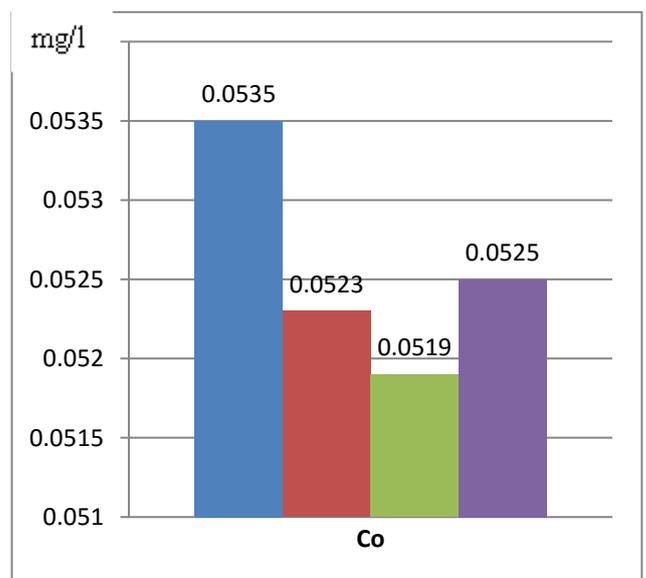
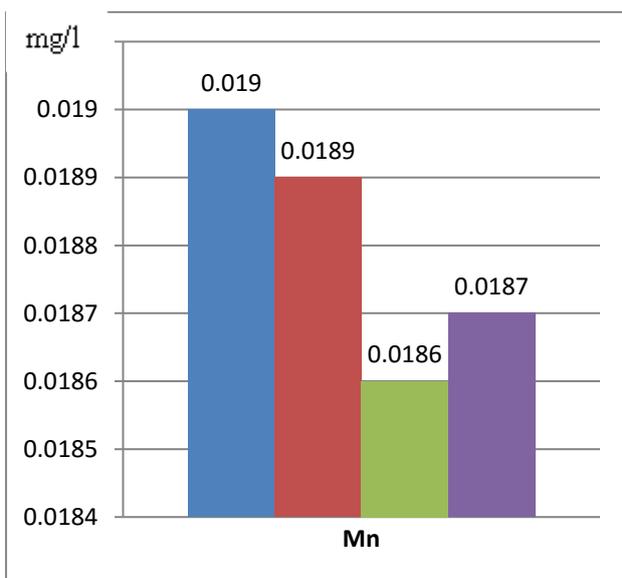
Content of Mn, Co before and after filtration not virtually changed. Content of Ni, after the 150g of zeolite filtration, was 0.275 mg/l, with comparison of 0.285 mg/l. Also, insignificant reducing of Cu: 0.098 mg/l after 150g of zeolite when in control sample it was 0.104 mg/l.

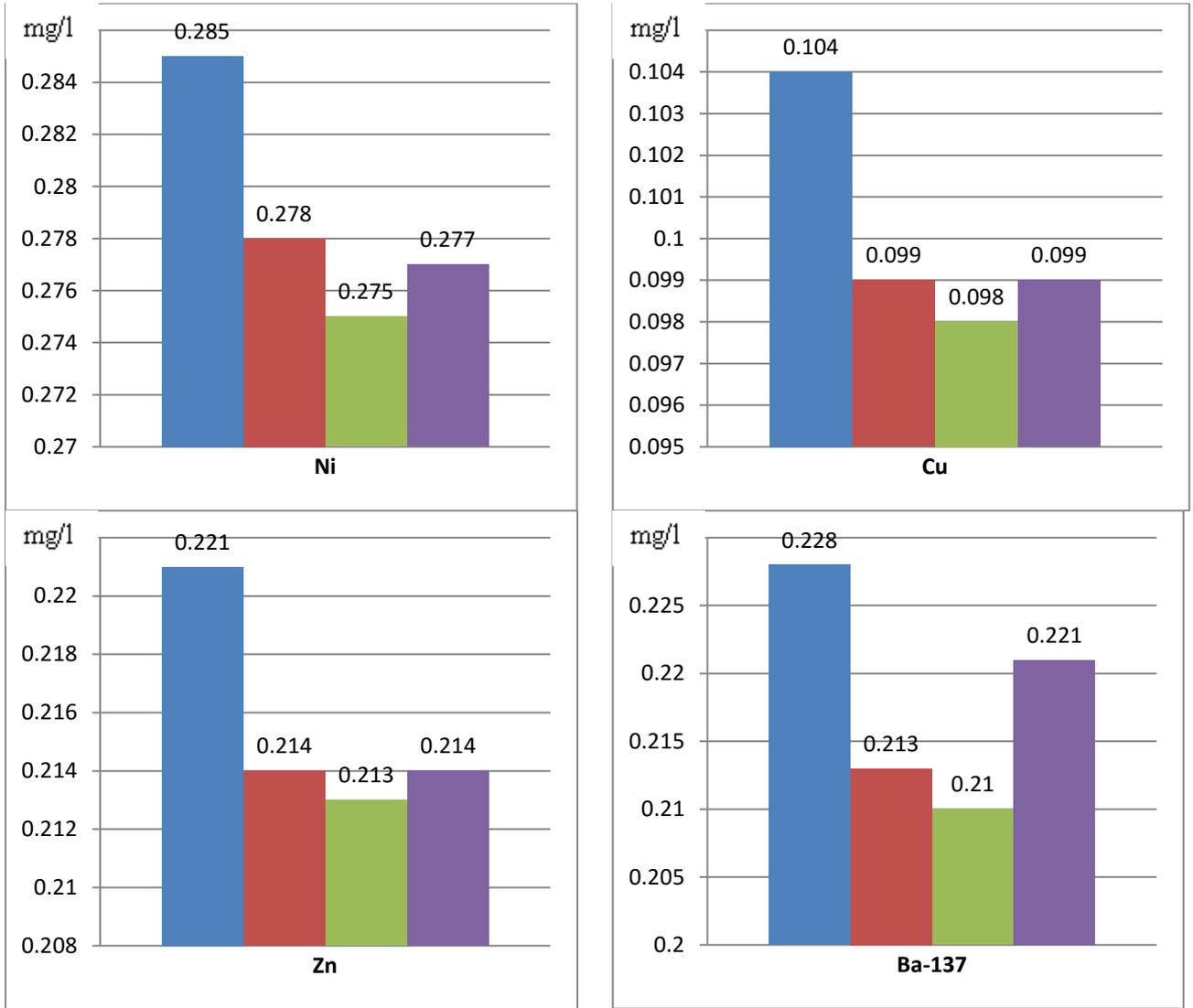




■ Milk (control) ■ 100 g Z ■ 150 g Z ■ 200 g Z

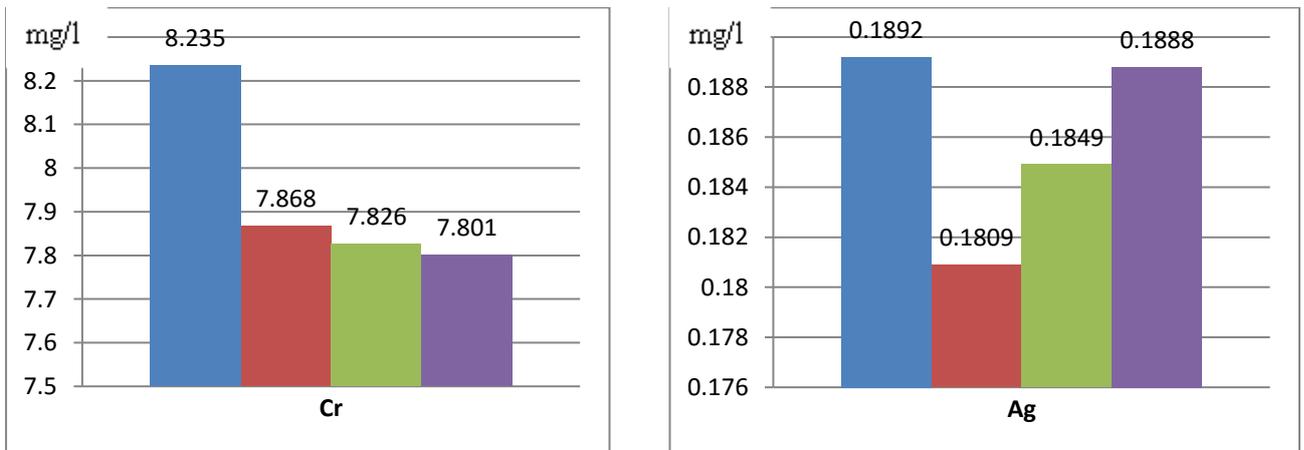
Fig. 2: Concentration of trace elements in milk before and after filtration





■ Milk (control) ■ 100 g Z ■ 150 g Z ■ 200 g Z

Fig. 3: Concentration of trace elements in milk before and after filtration



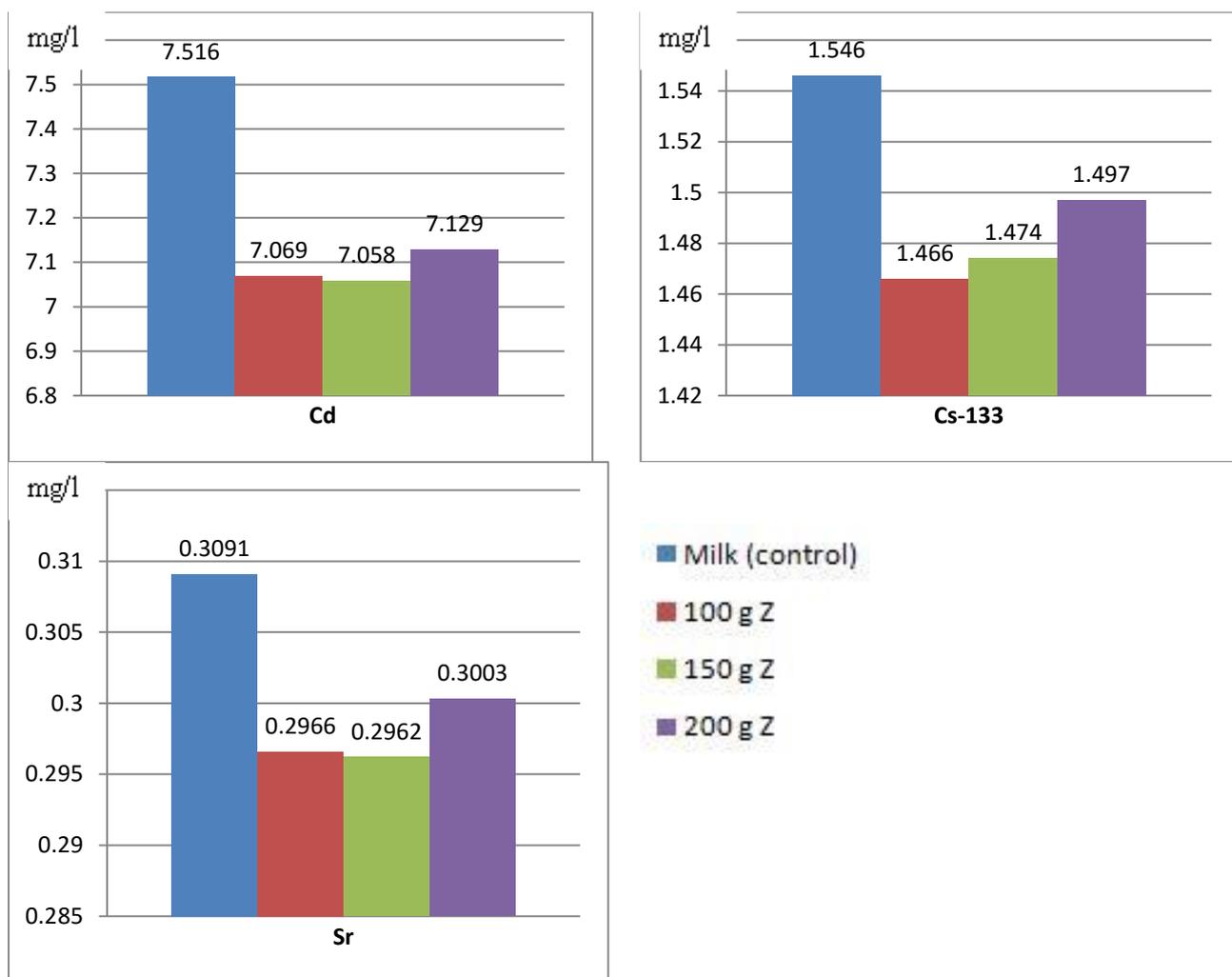


Fig. 4: Concentration of toxic elements in milk before and after filtration

The concentration of rubidium, strontium, silver and cadmium has remained practically constant (fig. 3, 4).

After the filtration the content of Cr reduced to 0.4 mg/l in comparison with control sample, which was 8.235 mg/l. Separately, the content of Cr after the filtration through the filter with 200g of zeolite was 7.801 mg/l; 150g of zeolite – 7.826 mg/l and through 100g of zeolite – 7.868 mg/l.

Cesium-133 concentration in the control milk sample is 1.54 mg/l and after filtration is reduced until 1.46 mg/l through 100g zeolite filtration; 1.47 mg/l – through 150 mg/l; and 1.49 mg/l – through 200 g of zeolite sorbent (fig. 4).

The smallest content of barium-137 is determined in the milk sample after filtration through 150g of zeolite sorbent – 0.210 mg/l. By the results, in the milk sample after filtration through 100g of zeolite the concentration of barium-137 is 0.213 mg/l, and through 200 g – 0.221 mg/l; in control sample – 0.228 mg/l.

By the results, it is concluded that the filtration of milk through the zeolite sorbent is significantly affect to the mineral and toxic elements concentration. Depending on the quantity of zeolite sorbent it is traced the downgrading dynamics of chemical elements content in the milk samples. Such method of milk filtration through the zeolite sorbent will allow obtaining clean milk from the environmentally unfriendly regions for further production of milk products for mass consumption.

CONCLUSION

Sum it up, utilizing of zeolite as a sorbent has an effect on the concentration of trace elements in milk. There was a tendency toward decreasing of trace elements in fact of the quantities of zeolite in filters (*Cd* from 0.079 to 0.034; *Cr* 0.82→0.42; *Ni* 0.31→0.21 mg/l). This method of reducing heavy metals in milk, sampled from different ecological unfavorable regions, allows getting pure raw milk for further production of milk products for human consumption.

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