Aspects of environmental safety improving of whole grain bakery products

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Abstract. Cereal grains, used as a whole for bread production, can be a source of potentially hazardous substances. The article presents averaged analytic data on the toxic elements content in 30 batches of wheat grown in the Orel region for 2015-2018. It is shown that in some cases grain contains lead, nickel and mercury in quantities exceeding permissible levels. The possibility of using enzyme preparations to reduce the pollution of grain by heavy metals in the technology of whole grain bread at the stage of grain steeping is investigated.

Whole grain bread is gaining popularity every year, it is recommended by nutritionists and followers of a healthy lifestyle. Research is actively carried out to develop and improve whole grain bread technologies, where all the nutrients of grain provided by nature are used rationally. Whole grain bread is the most important source of proteins, carbohydrates, amino acids, vitamins, minerals, dietary fiber and other nutrients. In terms of its nutritional and biological value, this bread is superior to all traditional breads, especially white bread. While being regularly used as food item, whole grain bread helps to normalize metabolism and blood composition, clear the body of toxins and carcinogens, lower cholesterol, improve cardiovascular system, decrease weight and improve intestinal motility.

Along with the listed advantages of whole grain bread, there is a problem of its safety, as grain can be a source and carrier of a large number of potentially dangerous, toxic substances [1]. The unfavorable environmental situation in a number of regions of the Russian Federation has led to the fact that the quality of grain products does not always meet the regulatory requirements (TR CU 021/2011 technical regulations of the Customs Union "About Food Safety"). In many cases, there is pollution of grain cereals by toxic elements. This is due to the high concentration of various industrial enterprises, the functioning of which contributes to the pollution of the environment by industrial emissions and, as a consequence, to the localization of toxic elements in the biosphere objects (soil, water bodies, etc.). In the future, penetrating into crops and moving along the biological chain, they can easily enter the human body and cause serious health disorders [2,3,4].

Getting into the human body, the compounds of many metals lead to poisoning and serious diseases. This applies primarily to those metals that under normal conditions are not contained in the body or are contained in extremely small quantities. Such metals-poisons (Pb, Cd, Ni and others) can cause severe intoxication of the body and even lead to death. Toxic effect can have even metals, which are characterized as "metals of life" (Cu, Zn, Fe), if their concentration exceeds the norms necessary for normal metabolism. The toxic effect of elements is manifested, as a rule, in the inactivation of certain groups of biological substrate due to the formation of complex compounds with a number of
functional groups on the surface or inside of cells, enzyme proteins, etc. Toxic metals can also interact with DNA and RNA, metalloproteins, phospholipids of membranes, etc.

Long-term studies have shown that grain products cultivated on the territory of the Orel region, in some cases, contain lead, nickel and mercury in quantities exceeding permissible levels (PL). Table 1 presents the averaged analytic data on the toxic elements content in 30 batches of wheat grown in the Orel region for 2015-2018.

| wheat grain  | Pb       | Ni       | Hg       | Cu       | Zn       | Cd       |
|--------------|----------|----------|----------|----------|----------|----------|
| 2015         | 0.125 ± 0.007 | 0.19 ± 0.005 | 0.007 ± 0.002 | 6.52 ± 0.01 | 21.9 ± 0.03 | 0.025 ± 0.002 |
| 2016         | 0.12 ± 0.004 | 0.59 ± 0.004 | 0.004 ± 0.001 | 5.7 ± 0.01  | 14.9 ± 0.02  | 0.02 ± 0.001  |
| 2017         | 0.28 ± 0.005 | 0.22 ± 0.004 | 0.007 ± 0.003 | 3.6 ± 0.005 | 15.1 ± 0.003 | 0.025 ± 0.002 |
| 2018         | 0.32 ± 0.006 | 0.66 ± 0.005 | 0.06 ± 0.003  | -         | -         | 0.01 ± 0.001  |

The results obtained confirm the data of a number of authors on the accumulation of pollutants by cereals. Scientists of the East Kazakhstan State University established regularities of toxic elements accumulation in grain and grain legume depending on their location (shell, core) and crop species. The tendency to accumulate lead, zinc and cadmium by larger grains is noted [5].

Shcheglova I. Yu., studied the distribution of heavy metals in wheat grain and dehulling products after processing with dehulling machine. It is found that the purest products are semolina and white flour, where heavy metals are either absent or contained in small quantities. The most polluted are by-products formed from the peripheral anatomical grain parts - it is grain kernel, where cadmium and lead exceed the permissible levels (PL), and bran, where quantity of heavy metal salts is within the PL. The obtained data indicate the predominant accumulation of heavy metal salts by the outer and inner grain shells and the grain kernel [2].

Insufficient attention is currently paid to the development of ways to reduce toxic elements content in grain raw materials, and the issue of environmental safety improving of whole grain bread, especially in areas with a high concentration of industrial enterprises, is relevant today. Researchers use only such technological methods as dehulling and washing of grain, allowing to slightly reduce the amount of toxic substances [6]. Kazakov E. D. notes that hydrothermal treatment leads to the migration of trace elements in grain. Some other scientists have found that dry dehulling of grain surface is one of the ways to reduce the harmful substances content [5-7].

"Classical" whole grain bread technology includes such technological operation as steeping of grain necessary for its softening and the subsequent crushing. Since heavy metals are mainly contained in the cell walls of grain shells in the form of complex compounds with non-starch polysaccharides, it is advisable to study the possibility of using enzyme preparations that promote partial hydrolysis of cellulose and hemicelluloses at this stage:

- Pentopan 500 BG (a set of cellulases represented mainly by xylanase);
- Celloviridin G 20X (proteinase, cellulase, β-glucanase and xylanase);
- Biobake 721 (set of hemicellulase enzymes: manases and xylanases);
- FungamylSuperAX (amylase and xylanase).

The introduction of these preparations during the steeping of grain was assumed to contribute to the destruction of intermolecular bonds and partial polymers fragmentation with the release and migration of toxic elements from the grain into the steep water. For successful use of the enzyme in the technological process, it is necessary to know the optimal parameters of its action and the influence nature of various factors on its stability. The main factors influencing the process of enzymatic hydrolysis are the dosage of the enzyme preparation, the duration of the process, the temperature and medium pH. We investigated the influence of the above factors on the enzymatic hydrolysis process of
wheat grain non-starch polysaccharides and determined the optimal conditions for the process (the effectiveness of enzyme preparations was judged by the accumulation of reducing sugars and changes in the fiber content in the grain):

- dosage of enzyme preparations (Pentopan 500 BG-0.004 %, Biobake 721-0.09 %, FungamillSuper AH-0.01 %, CelloviridinG 20X-0.08 % by weight of grain);
- process duration - 18 hours;
- temperature - 35-40 °C;
- pH - 4.5-5.0.

In subsequent experiments grain steeping was carried out under the above conditions for maximum effect of enzyme preparations. After the steeping time, the grain was washed with running water, was dried and the content of heavy metals salts in it was determined by high-performance liquid chromatography on the area of chromatographic peaks using the information processing program attached to the domestic chromatograph "MiLiChrome". The content of heavy metals salts was determined directly after steeping with enzyme preparations, as well as after steeping with subsequent washing with water, since the ionic forms of some of the studied elements (lead, copper, zinc) are very mobile. Table 2 shows the average values of the heavy metals content in the grain after steeping with enzyme preparations.

**Table 2.- Effect of enzyme preparations on the heavy metals content in grain during steeping and washing.**

| enzyme preparations      | Pb     | Ni     | Zn     | Cu     |
|--------------------------|--------|--------|--------|--------|
|                          | Without washing |        |        |        |
| Control sample *         | 0.256 ± 0.003   | 0.254 ± 0.002 | 3.76 ± 0.03 | 0.584 ± 0.005 |
| CelloviridinG 20X        | 0.162 ± 0.003   | 0.133 ± 0.004 | 2.81 ± 0.04 | 0.474 ± 0.002 |
| Biobake 721              | 0.196 ± 0.004   | 0.164 ± 0.001 | 2.56 ± 0.04 | 0.531 ± 0.004 |
| Pentopan500 BG           | 0.238 ± 0.006   | 0.203 ± 0.003 | 3.65 ± 0.01 | 0.581 ± 0.004 |
| Fungamill Super AX       | 0.236 ± 0.002   | 0.216 ± 0.003 | 3.13 ± 0.03 | 0.499 ± 0.003 |
|                          | After washing   |        |        |        |
| Control sample *         | 0.187 ± 0.002   | 0.119 ± 0.002 | 2.82 ± 0.04 | 0.534 ± 0.005 |
| CelloviridinG 20X        | 0.059 ± 0.003   | 0.101 ± 0.002 | 2.02 ± 0.02 | 0.429 ± 0.002 |
| Biobake 721              | 0.112 ± 0.002   | 0.066 ± 0.004 | 1.89 ± 0.05 | 0.432 ± 0.002 |
| Pentopan500 BG           | 0.212 ± 0.004   | 0.115 ± 0.002 | 3.06 ± 0.05 | 0.517 ± 0.004 |
| Fungamill Super AX       | 0.201 ± 0.001   | 0.113 ± 0.003 | 2.48 ± 0.03 | 0.436 ± 0.003 |

* - Control sample was the untreated wheat grain

It was found that while steeping the grain with all enzyme preparations, the heavy metals content in the grain decreases compared to the control sample, and the greatest decrease is noted when steeping with subsequent washing with water. While steeping grain without enzyme preparations, there is also a slight decrease in the heavy metals content due to their leaching. At the same time, only metal ions in the free state migrate. When using enzyme preparations at the grain steeping stage, there is a much greater migration of heavy metals into the steep water, since in this case, not only free, but also (trapped) heavy metal ions that are in complexes with non-starch polysaccharides migrate.

The most effective of all enzyme preparations used was the preparation Celloviridin G 20X. When steeping the grain with the preparation, the content of lead is reduced by 36.7 %, nickel-by 47.6 %, zinc-by 25.3 %, copper-by 18.0 %, respectively, compared with untreated grain. Grain steeping with Celloviridin G 20X followed by washing with running water leads to a decrease in lead content by 68.4 %, nickel-by 99 %, zinc-by 28.4 %, copper-by 14.1 %, respectively, compared with the control sample.
The effectiveness of this preparation, containing a complex of enzymes, is explained by a deeper destruction of the fruit and seed shells structure of grain, as a result of which the cellulose microfibrils are released from connection with the cell wall matrix, contributing to the release of heavy metals and their migration into the liquid phase.

Thus, as a result of the conducted research it was established that using enzyme preparations of cellulolytic action while grain steeping allows to reduce pollution of grain by heavy metals. There is a migration of heavy metals into steep water, as in this case, not only free, but also (trapped) heavy metal ions in complexes with non-starch polysaccharides migrate. The efficiency of grain washing after steeping to remove toxic elements ions released from the complexes was noted.

References

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