Heavy metal sorption by native shells of pea grain

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Abstract. One of the current problems of the agricultural and industrial complex is the increase in the volume of waste generated, with a low level of recycling. A promising way to recycle waste from enterprises engaged in grain processing is to produce sorbents for purification of polluted water. The aim of this work was to study the degree of sorption of heavy metal ions, which are one of the main pollutants of surface and industrial wastewater, native shells of pea grains. The raw materials investigated were crushed and infused in distilled water. Then solutions of heavy metals in a certain concentration were added, followed by filtration, mineralisation of the obtained samples, and determination of the residual concentration of heavy metal ions by inversion voltammetry. It was found that the sorption activity of pea grain shells varies depending on the variety of this crop and the type of heavy metals. The lowest residual concentration of cadmium in the model solutions after exposure indicates the highest sorption capacity of the native shells of the pea grains in relation to the ions of this metal. The best ability to bind heavy metal ions were the shells of pea variety Temp. However, native shells of pea grains are not able to fully extract heavy metal ions from aqueous solutions. Modification of pea grain shells will increase their sorption activity.

1 Introduction

Grain processing generates fodder grain products, crushed fodder, chaff, flours, bran, shells (husk, aril), aspiration dust and fine grain. Among the grain processing industry companies, cereal production is characterised by the lowest degree of utilisation of secondary raw material resources, with annual volumes of husk and flours of up to 850 thousand tons.

At the same time, the waste products of grain processing have a high energy and biological value, they are harmless, hypoallergenic, easily amenable to bioconversion, as well as various types of processing. The predominant components in the composition of grain shells are hard hydrolysable polysaccharides, including cellulose, hemicellulose, pentosans, and lignin [1], which determine their ability to physical sorption. The advantages of using grain wastes as sorption materials are their availability, low cost, comparative efficiency, and ease of processing technology, as well as the possibility of regeneration [2]. Factors that significantly affect the sorption capacity of materials from waste grain processing are the

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concentration of sorbate and time of interaction with it, particle size, dosage, initial humidity of raw materials [3, 4].

2 Materials and methods

Native grain membranes of pea varieties Amio r and Temp selected by Federal Scientific Research Center of Grain Legumes and Cereals (Orel, Russia) were used as the material for the study (Fig. 1). Pea shells consist of epidermis covered with cuticle, hypodermic layer and several layers of parenchyma. The predominant component in their composition is cellulose, with small amounts of other polysaccharides, proteins, lipids, ash elements.

Fig. 1. Appearance of pea grain shells.

The casings were first cleaned of mechanical impurities and then milled to a particle size of not more than 1 mm.

The sorption activity of the grain shells against zinc, cadmium, lead and copper ions was determined as follows. Grinded shells were dissolved in distilled water heated to 90°C, obtaining a 1.0% solution. The suspension was infused for 3 h. After completion of exposure the test solution was mixed with a heavy metal solution with a concentration of 100.0 mg/l. The resulting solution was incubated for 3 h, followed by filtration. The resulting filtrate was used to determine the residual amount of heavy metal ions in solution. To obtain heavy metal solutions we used standard samples of solutions of determined ions - zinc, cadmium, lead and copper.

Preliminary preparation of samples for determination of heavy metal concentration was made by a combination of "wet" and "dry" mineralisation. The filtrate from the shells was placed in quartz beakers, evaporated and then ozolised in a programmable dual-chamber PDP-Lab oven.

Residual amounts of heavy metal ions were determined on a TA-Lab analyzer (SPE Tomanalit, Russia) by inverse voltammetry. The precipitate obtained after ashing was prepared for analysis according to the method developed by SPE Tomanalit Ltd. Then mass concentration of zinc, cadmium, lead and copper ions was measured in corresponding analysed samples using method of addition of certified mixtures of elements. The studies were carried out in triplicate, followed by mathematical processing of the data obtained.

3 Results and discussion

The results of the sorption activity of native pea grain shells with respect to heavy metal ions are shown in Tables 1 and 2.
Table 1. Sorption activity of native shells from grain of pea variety Temp.

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<tr>
<th>Element name</th>
<th>Measurement unit</th>
<th>Element concentration</th>
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<td></td>
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<td>Initial</td>
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<tr>
<td>lead</td>
<td>mg/l</td>
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<tr>
<td>cadmium</td>
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<tr>
<td>copper</td>
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<tr>
<td>zinc</td>
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The data presented in Table 1 show that the shells of Temp pea grains sorbed cadmium ions to the greatest extent. At the same time, 36.5 mg/l of the total amount of ions of this metal remained in the sample. The lowest ability to bind grain envelopes of this variety showed the lowest ability to zinc ions.

Table 2. Sorption activity of native shells from grain of pea variety Amior.

<table>
<thead>
<tr>
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<tr>
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The grain coatings of the Amior pea cultivar also had the highest sorption activity toward cadmium ions (Table 2). To a lesser extent, they bound copper and zinc ions.

Thus, both pea Temp and Amior varieties of grain shells most actively sorbed cadmium and lead ions. Cellulose contained in the grain shells, due to its structure, detained in the greatest amount of cadmium and lead cations [5]. The sorption activity of aqueous solutions obtained from native shells of pea grains was also due to the formation of complex compounds of amino acids contained in the proteins of the grain shells with heavy metal ions. These complexes have been found to be insoluble in water and highly stable [6].

Figure 2 shows the data on the degree of sorption of heavy metals by native shells of pea grain varieties.
Fig. 2. Sorption of heavy metal ions by native shells of pea grains.

It was noted that the highest degree of sorption of cadmium and lead ions was distinguished by native shells isolated from Temp pea varieties. The value of this indicator was 8.1 and 7.7%, respectively, higher than that of the pea variety Amior grain shells.

It was found that the pea variety Temp grain shells sample bound copper ions more actively than the pea variety Amior grain shells sample. Sorption activity of the analyzed samples of pea grain shells in relation to zinc ions was the lowest.

Thus, the ability of pea grain shells to absorb in the model solutions to the greatest extent of cadmium ions and lead was revealed. The data obtained indicate a relatively low sorption activity of native shells of pea grains in relation to zinc and copper ions.

In a number of studies it is mentioned that the modification of grain wastes, including shells, is an effective way to increase the sorption properties. Pre-treatment of grain wastes causes breakdown of polysaccharide molecules, dissolution and washout of low molecular weight components and proteins, which leads to the formation of new pore spaces.

Currently, chemical, physical, physicochemical, and other methods are used to modify the waste products of grain processing. Chemical modification is carried out with solutions of inorganic and organic acids, alkalis, inorganic salts, organic solvents etc. [7, 8, 9]. A promising method of grain waste modification is low-temperature treatment with alkali solution [10]. By adjusting its parameters, it is possible to obtain materials with different sorption capacity and selectivity. Activation of grain wastes with inorganic acids followed by treatment with organic salts also considerably increases the degree of pollutants extraction [3].

By polymerisation of grain waste, highly effective grafted copolymers with high sorption capacity and easy separability after wastewater treatment can be obtained [3]. Sorbents obtained from husks by pyrolysis are characterised by large volumes of micropores and mesopores, because they actively sorb heavy metal ions [11, 12]. Microwave irradiation [13] and ultrasound [14] have also been suggested to reduce the time required to prepare grain processing waste for modification.

Thus, further research should aim to find the optimal method to modify native shells of pea grains, which will significantly increase their sorption activity in relation to heavy metal ions.

4 Conclusion
Research on the sorption activity of native pea grain shells has shown that their ability to bind heavy metal ions depends on the variety of the crop and the type of element. The sorption properties of pea grain shells are primarily due to their composition of high-molecular weight biopolymers, carbohydrates and proteins. It was found that native pea grain shells show the greatest sorption activity toward cadmium and lead ions. However, they are not able to fully extract heavy metal ions from aqueous solutions. Modification of native pea grain shells can significantly increase their sorption activity.

References