A Study of Zn\textsuperscript{2+} ions adsorption by native and chemically modified pea (Pisum sativum) pods

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Abstract. The paper deals with a study of Zn\textsuperscript{2+} ions adsorption by native and modified fine-cut pea (Pisum sativum) pod shells. The sorption material under study was treated using 1%, 2% and 3% NaOH or H\textsubscript{2}SO\textsubscript{4} solutions. Isotherms of Zn\textsuperscript{2+} ions adsorption by native and treated pea pod shells were plotted and calculated using the Langmuir, Freundlich, Tyomkin, and Dubinin-Radushkevich models. It was determined that the isotherm of zinc ions adsorption by native shells of pea pods is most accurately described by the Langmuir model, by modified shells – by the Freundlich model. According to the values of the adsorption energy and the Gibbs energy, the adsorption is a physical process. The paper provides data on the degree of crystallinity, elemental analysis, and IR spectra of native and treated pea pods.

Environmental pollution by various pollutants is becoming increasingly threatening [1, 2]. One of the most severe pollutants are heavy metal ions that enter water bodies with production wastewater. Zinc ions are often present in the wastewater of machinery production, ore dressing plants, chemical, pharmaceutical, and other industries. Getting into natural water sources, zinc ions can subsequently enter living organisms, including humans, through water supply systems.

If ingested in large quantities for a long time, all zinc salts, especially sulfates and chlorides, can cause poisoning due to the ions toxicity. Ingestion of zinc ions leads to anemia, growth retardation, infertility. Upon entering the body, zinc is concentrated in liver, gradually spreading to organs and tissues. In the intestine, zinc forms compounds with proteins and other ligands [3].

As a rule, at existing production facilities heavy metal ions are removed using chemical methods [4]. The disadvantages of these methods are constant consumption of reagents, sludge formation, and the challenging separation of the target products from the latter.

One of the most effective ways to remove metal ions from various aqueous media is the adsorption method based on extended surface absorption [5, 6]. However, activated carbon used in industry for organic compounds removal are not very effective for heavy metal ions extraction. The drawbacks also include the high cost of activated carbon, which makes the process economically unviable. In addition, certain difficulties are caused by metal ions desorption from activated carbon pores. This circumstance contributes to the increase in the cost of the process.

The solution to this situation is the use of cheap sorption materials from industrial and agricultural production waste as reagents for removal of various pollutants from natural and wastewater [7-9]. By-
products of agricultural raw materials are very promising as adsorption materials for heavy metal ions extraction [10-16].

By-products of legumes are very promising as sorption materials to remove heavy metal ions from water [17, 18]. The latter contain proteins that are known to form complex compounds with metal ions, which increases their sorption capacity. In connection with the above, this work was devoted to Zn\(^{2+}\) adsorption by native and chemically treated shells of pea (*Pisum sativum*) pods.

Initially, pea pods were treated with 1, 2, and 3% sulfuric acid and sodium hydroxide solutions. To this end, the pea pods were finely cut (to a size of 1 to 10mm), washed with distilled water and placed in an acid or alkali solution for 5 hours at 20°C. After the above period, the sorption material was extracted, washed with distilled water to a neutral pH, and dried at room temperature.

The effect of treating pea pods with solutions of sulfuric acid and sodium hydroxide on the chemical composition and structure of the material was studied using the elemental analysis, X-ray diffraction analysis, and IR spectroscopy methods.

The results of the elemental analysis for studying the physico-chemical properties of pea pods as a sorbent are shown in Table 1 (N, C, H, O), and oxygen is calculated with the assumption that the pea pods biomass contains no other chemical elements.

**Table 1. Results of elemental analysis of pea pods**

| Treatment       | N, %  | C, %  | H, %  | O, %  |
|-----------------|-------|-------|-------|-------|
| Before treatment| 2.645 | 40.69 | 6.13  | 50.535|
| 1% H\(_2\)SO\(_4\) | 2.205 | 40.185| 5.86  | 51.75 |
| 2% H\(_2\)SO\(_4\) | 1.925 | 38.44 | 5.915 | 53.72 |
| 3% H\(_2\)SO\(_4\) | 1.8   | 36.75 | 5.69  | 55.76 |
| 1% NaOH        | 1.575 | 40.225| 6.345 | 51.855|
| 2% NaOH        | 0.945 | 38.67 | 5.475 | 54.91 |
| 3% NaOH        | 0.72  | 38.045| 5.46  | 55.775|

Based on the results of the elemental analysis, it can be concluded that an increase in oxygen in the sorbent composition results in an increase in the sorption capacity of pea pods. This means that the chemisorption process is more intensive since one of the possible mechanisms for metal ions sorption by cellulose-containing materials is ion exchange involving all the oxygen atoms of cellulose building block.

The degree of crystallinity of a polymer, including natural polymers, affects the transport characteristics. In this regard, X-ray diffraction analysis of pea pods before and after treatment was carried out, which provided diffraction patterns (Fig. 1) with the corresponding crystallinity degrees.

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The hydroscopic capacity of cellulose and other polysaccharides of pea pods is due to the large number of hydroxyl groups in macromolecules. In this case, the sorption capacity of cellulose depends on the density of the package and decreases as the degree of crystallinity increases. Hence, spatial absorption occurs in amorphous sections only. The pea pods membranes' degree of crystallinity (Fig. 1) before treatment was \(\gamma_1 = 0.293\), after treatment with 1%, 2%, 3% H\(_2\)SO\(_4\), respectively, \(\gamma_2 = 0.276\), \(\gamma_3 = 0.250\) kg, \(\gamma_4 = 0.283\), after treatment with 1%, 2%, 3% NaOH \(\gamma_5 = 0.200\), \(\gamma_6 = 0.190\), \(\gamma_7 = 0.180\). Consequently, treating pea pods with sulfuric acid and sodium hydroxide solutions leads to a decrease in the degree of crystallinity of the materials.
This sorption material shows a high sorption capacity of amorphous sections since in them there is no strict three-dimensional order, the general longitudinal orientation of macromolecules is preserved, and an unstable short-range order in the arrangement of chains is observed. The intermolecular interaction energy in amorphous sections is less than that in the crystalline section and they are more accessible to solvents as well as to chemical reagents.

The main chemical components of pea pods (% dry weight) were: cellulose - 43.6, hemicellulose - 13.4, lignin - 30.1, and protein - 3.3. This composition indicates the probable presence of phenolic (lignin), carboxylic (hemicellulose, lignin), hydroxyl (cellulose, hemicellulose, lignin), and carbonyl
groups (lignin). To determine which functional groups and chemical bonds in pea pods are involved in Zn(II) ions adsorption, an IR spectroscopic study was performed on the sorbent composition.

The peaks appearing in IR spectra were assigned to various functional groups, as well as to chemical bonds, according to their respective wave numbers (vibrations) using relevant literature. A wide and strong peak was observed at a height of ~ 3.428 cm\(^{-1}\) indicating the presence of –OH groups (alcohols, phenols, carboxylic acids) as in lignin and cellulose, while a mild peak at ~ 2.923 cm\(^{-1}\) indicates a C–H bond from the CH\(_2\) group present in lignin. The peak at ~ 1.737 cm\(^{-1}\) corresponds to the C=O group. A symmetrical stretchable peak of the carboxylic groups (–COO\(^-\)) appeared at 1.636 cm\(^{-1}\). Vibrations at 1.454 cm\(^{-1}\) showed the presence of aromatic structures in lignin. The peak is also observed at the level of 1.062 cm\(^{-1}\), presumably it can be assigned as C–OH alcohol groups and carboxylic acids vibration [61] and 1.111 cm\(^{-1}\) corresponds to the C-O group. The content of approximately 52% of raw fiber consisting of cellulose, hemicellulose and lignin indicates the presence of many –OH and –C(\(\text{O}\))OH groups in the lignocellulosic complexes. The hydrogen of these groups is capable of ion exchange with metal cations.

The protein content of pea pods after acid and alkali treatment is less than 5%, which is advantageous compared to the protein-rich algal and fungal biomass predicted as metallic biological sorbents, since the protein materials are likely to decompose in wet conditions.

![Figure 2](image)

**Figure 2.** Isotherms of Zn\(^{2+}\) ions adsorption:

a) 1 – by native pea pods and those treated with sulfuric acid solutions having the following concentrations: 2 – 1%, 3 – 2%, 4 – 3%; b) 1 – by native pea pods and those treated with sodium hydroxide solutions having the following concentrations: 2 – 1%, 3 – 2%, 4 – 3%.

To determine the sorption characteristics of native and treated pea pods under static conditions, ZnSO\(_4\) solutions were prepared using zinc (II) ions with the following Zn\(^{2+}\) concentrations: 0; 5; 10; 30; 50; 100; 250; 500; 1 000 and 1 500 mg/dm\(^3\). 100 cm\(^3\) of the solution of the pre-defined concentration was measured using a measuring flask and placed in a 250 cm\(^3\) conical flask. Next, 1g of the sorption material was added to the flask, the flask was tightly closed with a cork and shaken on a shaker for 5 hours. After that, the solution was filtered through a paper filter and the equilibrium concentrations of Zn (II) ions were determined in the filtrates by titrimetric method. Based on the resulting values of the equilibrium concentrations of zinc ions in solutions after sorption (Ce, mg/dm\(^3\)) and the initial concentrations of zinc ions in solutions before sorption (Cs, mg/dm\(^3\)), the sorption capacity of the materials (A, mg/g) was calculated according to Formula 1 and isotherms of the adsorption of zinc (II) ions by native and treated pea pods were plotted (Fig. 2).

The adsorption isotherms (Fig. 2) show that pea pods treatment with sulfuric acid and sodium hydroxide solutions with concentrations from 1 to 3% results in an increase in the sorption capacity of the material with respect to Zn(II) ions under static conditions from 33 mg/g (for native sorption material) to 38 mg/g (for pea pods treated with 2% sulfuric acid) and to 36 mg/g (for pea pods treated with 2% sodium hydroxide solution).
In order to determine the adsorption mechanism and the thermodynamic parameters of the studied processes, the adsorption isotherms were processed within the framework of the four most common monomolecular sorption models: those of Langmuir, Freundlich, Dubinin-Radushkevich, and Tyomkin (Table. 2), that is, linearized in coordinates: $1/A = f(1/Ce)$, $\log A = f(\log Ce)$, $\ln A = f(\ln (Cs/Ce)^{2})$, $A = f(\ln Ce)$, respectively [19].

**Table 2.** Results of processing isotherms of Zn$^{2+}$ ion sorption with native and treated pea pods in the framework of monomolecular sorption models

| Sorptionmaterial | Langmuir | Freundlich | Dubinin-Radushkevich | Tyomkin |
|------------------|----------|------------|-----------------------|---------|
| Native peas pods | y = 9.294x+0.032 R² = 0.999 | y = 0.832x−1.067 R² = 0.948 | y = 2.936x−0.990 R² = 0.287 | y = 0.094x+0.216 R² = 0.898 |
| Peapods + 1% H$_2$SO$_4$ | y = 9.135x+1.184 R² = 0.868 | y = 0.891x−1.151 R² = 0.975 | y = 1.264x−0.703 R² = 0.259 | y = 0.101x+0.205 R² = 0.830 |
| Peapods + 2% H$_2$SO$_4$ | y = 3.638x+9.732 R² = 0.872 | y = 0.772x−0.915 R² = 0.942 | y = 1.189x−0.729 R² = 0.339 | y = 0.104x+0.276 R² = 0.894 |
| Peapods + 3% H$_2$SO$_4$ | y = 1.613x+13.64 R² = 0.904 | y = 0.914x−1.240 R² = 0.982 | y = 0.872x−1.071 R² = 0.214 | y = 0.097x+0.184 R² = 0.800 |
| Peapods + 1% NaOH | y = 6.963x+11.39 R² = 0.948 | y = 0.816x−1.161 R² = 0.977 | y = 1.176x−0.656 R² = 0.556 | y = 0.084x+0.185 R² = 0.841 |
| Peapods + 2% NaOH | y = 2.741x+7.705 R² = 0.948 | y = 0.805x−0.947 R² = 0.977 | y = 0.914x−2.139 R² = 0.019 | y = 0.103x+0.264 R² = 0.936 |
| Peapods + 3% NaOH | y = 3.198x+9.105 R² = 0.971 | y = 0.828x−1.167 R² = 0.973 | y = 0.887x−0.308 R² = 0.57 | y = 0.085x+0.184 R² = 0.847 |

Table 2 shows that when zinc (II) ions are adsorbed by treated pea pods, adsorption occurs on the surface of the sorption material with active centers of varying intensity (Freundlich model), and when zinc (II) ions are adsorbed by native pea pods, adsorption occurs on the surface of the sorption material with active centers of equal intensity (Langmuir model). Therefore, we can conclude that pea pods treatment with 1-3% solutions of sulfuric acid and sodium hydroxide results in the formation of active centers with a greater sorption capacity for Zn$^{2+}$ ions.

The thermodynamic parameters of the adsorption processes (sorption energy and Gibbs energy) were calculated using the constants of the Langmuir and Dubinin-Radushkevich equations (formulae 1 and 2) for the processes under study obtained through linearization in the corresponding coordinates and presented in Table 2.

\[
\Delta G = -R \cdot T \cdot \ln K_L
\]

\[
E = \frac{R \cdot T}{\sqrt{(R \cdot T \cdot E)^2}}
\]

where $(R \cdot T \cdot E)^2$ is the slope of straight line in the linearized Dubinin-Radushkevich equation.

**Table 3.** Thermodynamic parameters of Zn$^{2+}$ ion sorption by native and treated pea pods

| Sorptionmaterial | $E$, kJ/mol | $\Delta G$, kJ/mol |
|------------------|-------------|------------------|
| Native peas pods | 1.422       | - 0.048          |
| Peapods + 1% H$_2$SO$_4$ | 2.167 | - 0.632 |
| Peapods + 2% H$_2$SO$_4$ | 2.234 | - 2.397 |
| Peapods + 3% H$_2$SO$_4$ | 2.609 | - 5.201 |
| Peapods + 1% NaOH | 2.246 | - 1.252 |
| Peapods + 2% NaOH | 2.548 | - 2.518 |
| Peapods + 3% NaOH | 2.586 | - 2.549 |
Table 3 shows that the values of both sorption energy (E) and Gibbs energy to modulo (ΔG) of zinc (II) ions sorption by treated pea pods are higher compared to similar values for sorption by native pea pods. This phenomenon means that Zn$^{2+}$ ion adsorption by treated pea pods is more preferable compared to native pea pods.

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