Studies on the Sorption Mechanism of Removing Nickel Ions from Model Waters by Cereal Grain Husks

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Abstract. The study discusses the possibility of using cereal husks (barley, wheat and oats) as a sorption material for removing Ni²⁺ ions from model waters. The article shows that the adsorption capacity at initial concentration of Ni²⁺ ions of 17 mmol/dm³ reaches 1.1 mmol/g, and at concentration of 68 mmol/dm³ reaches 1.4 mmol/g. The built isotherms of Ni²⁺ ions adsorption by cereal husks from model waters at a large correlation coefficient are described using the Langmuir model, but the same is observed (within the range from 0.83 to 0.98) in the Freundlich and Temkin models, which can also indicate multilayer sorption and intermolecular linear interaction between adsorbate molecules.

1. Introduction

Problems associated with purification of surface and waste waters are becoming more urgent with rapid positive dynamics in the development of industrial production. Wastewater from industrial enterprises contains a large amount of heavy metal ions [1]. The ability of heavy metals to bioaccumulate and the toxicity of their ionic forms are associated with their high physical and chemical activity (the formation of complex compounds with organic substances) and biological activity (participation in metabolic processes). Nickel is one of the hazardous elements, the entry of which into water bodies must be strictly controlled [2, 3]. According to the Country report on state of the environment over the past 25 years, the amount of nickel discharged with wastewater into surface natural water bodies in Russia has decreased by more than 12 times due to the introduction of relevant legislation and new treatment technologies, while in 2018 the amount of nickel discharged remains quite high and amounts to 30,248 kg [4,5].

Various methods, including sorption ones are used to remove heavy metal ions from wastewater. Sorbents based on activated carbons, zeolites, natural minerals, etc. are used. These materials are often expensive and require use of natural resources. In this case, research aimed at obtaining and studying the adsorption properties of inexpensive and readily available materials, such as plant waste, is of particular relevance [6, 7]. The use of vegetable waste from agricultural production, such as the husk of cereals, for the treatment of waste water from heavy metal ions is a promising area. Their advantage lies in their low cost and relatively simple processing technology. Currently, there is a large number of studies on plant materials (leaves and bark of various types of trees, husks and straw of cereals, legumes, etc.) as sorption materials for the removal of various pollutants (metal ions, oil, phenols, etc.)
[7-10]. The work sets out to study the sorption process of nickel ions (Ni\(^{2+}\)) with materials based on plant waste from harvesting cereals. To achieve the research goal, the following tasks have been set:
- study of the sorption capacity of samples of plant sorption materials (SM) in relation to nickel ions in an aqueous medium;
- determination of the mechanism and model of nickel ions sorption with plant sorption material samples.

2. Material and methods
The samples of barley grain husks (BGH), wheat (WGH), and oats (OGH), which are formed in large quantities in the middle and lower Volga region as a result of agricultural works, were used as sorption material.

To simulate contaminated wastewater, a solution of NiCl\(_2\)·6H\(_2\)O salt with a concentration of Ni\(^{2+}\) ions from 0.34 mmol/L to 68 mmol/L was prepared. Weighed portions of salt were taken according to crystallization water.

The wastewater treatment process was carried out in flat-bottomed flasks with volume of 250 cm\(^3\), where 200 cm\(^3\) of solutions containing Ni\(^{2+}\) ions with a concentration of 0.34 mmol/L to 68 mmol/L were poured, and samples of the studied sorption material (SM), namely BGH, WGH, OGH weighing 1 g, were placed. The experiment was carried out for three hours with constant stirring. Then the SM was filtered off, and the residual content of Ni\(^{2+}\) ions in the filtrates was determined by the photometric method. [11].

The amount of pollutant ions, sorbed by 1 g of SM was calculated by the formula:

\[ A = (C_i - C_f) \cdot \frac{V}{m}, \]

where \( C_i \) is the initial concentration of the metal in the solution, mmol/dm\(^3\);
\( C_f \) is the final concentration of metal in solution, mmol/dm\(^3\);
\( V \) is the volume of the solution, cm\(^3\);
\( m \) is the mass of sorption material, g

3. Results
According to the methods described above, the following results of nickel ions removal from model water at various initial concentrations of the pollutant were obtained. The data on the sorption capacity of native samples (BGH, WGH, OGH) are shown in Figure 1.

![Figure 1. Isotherm of Ni\(^{2+}\) ions sorption by initial samples of sorption materials.](image-url)
Figure 1 shows that BGH samples have the highest adsorption capacity with respect to Ni\textsuperscript{2+} ions. The isotherms shown in Figure 1 are almost identical; therefore, the Langmuir, Freundlich, BET, Temkin equations were used to study the nature of the process and calculate the adsorption parameters. Within the framework of these models, the experimental sorption isotherms for the BGH, WGH and OGH samples were processed by the least squares method using data approximation. The processing data is presented in Table 1.

Table 1. Parameters of the equations for describing the adsorption of Ni\textsuperscript{2+} by native samples of CGH.

| Model   | Sample | Equation (correlation coefficient R\textsuperscript{2}) | Constants |
|---------|--------|-----------------------------------------------------|-----------|
| Langmuir | BGH    | \( y = 10.753x + 1.2131 \) \( R^2 = 0.951 \) \( A_\infty \) | 0.113 \( A_\infty \) 0.824 |
|         | WGH    | \( y = 15.322x + 0.331 \) \( R^2 = 0.9994 \) \( A_\infty \) | 0.002 \( A_\infty \) 3.021 |
|         | OGH    | \( y = 1.0673x + 4.2703 \) \( R^2 = 0.681 \) \( A_\infty \) | 0.001 \( A_\infty \) 0.234 |
| Freundlich | BGH   | \( y = 0.9093x - 1.0188 \) \( R^2 = 0.987 \) \( n \) | 0.096 \( n \) 1.099 |
|          | WGH    | \( y = 0.914x - 1.0565 \) \( R^2 = 0.874 \) \( n \) | 0.087 \( n \) 1.094 |
|          | OGH    | \( y = 0.6715x - 0.6715 \) \( R^2 = 0.867 \) \( n \) | 0.213 \( n \) 1.550 |
| BET     | BGH    | \( y = -12.461x + 35.121 \) \( R^2 = 0.001 \) \( A_\infty \) | 1.355 \( A_\infty \) 0.021 |
|         | WGH    | \( y = 61.953x - 13.75 \) \( R^2 = 0.067 \) \( \alpha \) | 3.504 \( \alpha \) 2.011 |
|         | OGH    | \( y = -0.9033x + 3.6664 \) \( R^2 = 0.002 \) \( \alpha \) | 0.754 \( \alpha \) 0.362 |
| Temkin  | BGH    | \( y = 0.3405x + 0.2398 \) \( R^2 = 0.841 \) \( b_{TE} \) | 2.022 \( b_{TE} \) 7276.262 |
|          | WGH    | \( y = 0.314x + 0.2158 \) \( R^2 = 0.868 \) \( b_{TE} \) | 1.988 \( b_{TE} \) 7890.341 |
|          | OGH    | \( y = 0.2672x + 0.4625 \) \( R^2 = 0.844 \) \( b_{TE} \) | 5.646 \( b_{TE} \) 9272.332 |

The data presented in Table 1 shows that the coefficient of approximation of the samples within each model is approximately equivalent (within the margin of error). The largest coefficient of approximation is obtained within the Langmuir model, which indicates the occurrence of monomolecular adsorption on the surface of the samples. In this case, adsorption occurs in active spots that always exist on the adsorbent surface, and the spots are able to adsorb only one molecule each [12-14]. As a rule, in the case of this type of adsorption, the adsorbate is retained on the surface of the adsorbent for some time and then desorbed. Quite high correlation coefficients (ranging from 0.83-0.98) are detected in the Freundlich and Temkin models, which may also indicate multilayer sorption and intermolecular linear interaction between adsorbate molecules. The above studies indicate that the isotherm of the nickel ions sorption with CGH samples does not reflect a clear understanding of the adsorption process. It may be assumed that mixed adsorption occurs, which is described by different models. Figure 1 shows that at a concentration of Ni\textsuperscript{2+} ions 0 to 17 mmol/dm\textsuperscript{3}, the saturation of the samples occurs actively, while in the case of 17 to 68 mmol/dm\textsuperscript{3}, the curve passes into a horizontal position, which may indicate an insignificant desorption. In doing so, the graph does not reach a
plateau; therefore, complete pores saturation of the SM samples does not occur. According to the classification of the Gils and Smith’s isotherms, this type of curve can be attributed to the C class isotherm, which is characteristic to adsorption on microporous adsorbents. The number of free adsorption spots remains constant over a wide range of solution concentrations in this process. As some centers are filled, new ones appear and the surface available for adsorption increases in proportion to the amount of substance adsorbed from the solution.

In the conclusion, it is possible to say the following:
- the use of agricultural waste, namely the cereal grain husks, as sorption materials for removal of Ni\(^{2+}\) ions from wastewater is potentially acceptable;
- the constructed sorption isotherms are ambiguous, as they meet several adsorption models with a high degree of convergence, which may indicate mixed adsorption.

4 References

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