Protection of water objects against pollution with the use of sunflower growing waste

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Abstract. Phenols are among the most common contaminants which enter a water objects with a sewage from various enterprises: oil refineries, coke-chemical, wood-chemical, aniline dyes, etc. Phenols are very toxic compounds. They can cause not only poisoning of organisms, but also significantly change the regime of biogenic elements and gases dissolved in water and first of all oxygen and carbon dioxide.

1. Introduction and Background
One of the most effective methods of water purification from phenols is a sorption which allows reaching the concentrations for discharge into fisheries. However, often the use of this method is limited by the high cost of the used adsorbents and the need of the thorough preliminary water preparation. In this regard a promising avenue for improving phenol-containing wastewater treatment systems is to replace traditional sorbents with a more affordable which can be obtained from various raw materials including crop production waste. Such approach allows involving of the secondary material resources which also characterized by a high degree of environmental safety.

Such materials can be used both in the native form and also modified to increase the sorption efficiency. In particular rice husks and straw were used by the authors [1] as an adsorbent for water purification from phenol. Sunflower and buckwheat husks were cultivated by various solutions of mineral acids and alkalis [2, 3], authors [4] were activating wheat straw by pyrolysis with a coal ash addition. Pyrolysis modified rice husk with a subsequent treatment by potassium hydroxide solution can be used to adsorb phenol from water in a wide range of concentrations [5, 6]. The authors [7] proposed a magnetically processed chitosan-based sorbent. Carbon nanotubes materials synthesized with the use of various catalysts can be attributed to the one of the latest generations of sorbents [8, 9].

2. Materials and Methods
At the Altai Technical University there are studies being conducted to obtain sorbents for water purification from various compounds [8, 9]. For the phenol extraction it has been proposed to use sunflower stalks that are not used in agriculture and also are widespread waste. In order to increase their sorption capacity they were subjected to various types of modifications such as carbonization at the temperature of 200 °C, treatment with sodium hydroxide (500 mg / l) and ammonium oxalate (0.5 n).

To determine a static sorption capacity 1 g of materials was placed in solutions with a phenol concentration from 10 to 1500 mg / l. The phenols content analysis of the solutions was carried out by the photocolorimetric method according to the method [10] and for the determination of the phenol...
high concentrations solutions were previously diluted. For comparison the static capacity of the widely used granular activated carbon adsorbent (AC-3) has been studied.

3. Experimental section

Initially the physico-chemical properties of the starting and obtained materials were determined. Two components have been isolated from the stalks for this: outer shell and inner spongy tissue. So that the proportion of the outer sheath was about 88% of the stalk weight and spongy tissue was 12%. The results are shown in Table 1.

| Table 1. Physico-chemical properties of sunflower stalks materials. |
|---------------------------------------------------------------|
| Physico-chemical indicator | Stalk shell | Inner spongy fabric |
|                            | native      | modified solution of sodium hydroxide | native | carbonized |
| Bulk density tapped, kg / m$^3$ | 96          | 95 | 68 | 20 | 16 |
| Mechanical strength, %    | 99          | 99 | 99 | 98 | - |
| Humidity, %               | 6           | 40 | 6 | 10 | 8 |
| Ash content, %            | 3.1         | 2.8 | 2.9 | 1.5 | 1.3 |
| Total pore volume, g / g  | 6.4         | 7.8 | 4.5 | 21.2 | - |

During the research it was found that for the carbonized spongy tissue it is impossible to determine the mechanical strength parameters and total pore volume due to the very loose state of the material which is disintegrating into small fractions even with a slight mechanical effect. All other samples of sorbents have high mechanical strength (98-99)%. The maximum total pore volume has been noted for native spongy tissue - 21.2 g / g, while for the outer shell of the stalk it is in the range of 4.5-7.8 g / g. The ash native husk content is slightly higher compared to the modified materials (it is 2.8%), which is probably due to leaching of soluble compounds during chemical activation and their transition into the gaseous phase during pyrolysis.

The moisture content of all materials turned out to be almost the same - ranging from 6% to 10%, the exception is of the stalk membranes modified with the sodium hydroxide solution. Also the significant difference of the bulk density of materials has been recorded - the inner part was lighter than the outer shell more than 5 times.

At the next stage the phenol sorption kinetics of native sunflower stalks was studied. For this model solutions with the phenol concentration of 150 mg / l were used to which there was 1 g of a sorbent added. After stirring during a specified time samples were taken for the analysis and diluted for the phenol content. The results are show in the Figure 1.

![Figure 1. The kinetic dependence of the phenol sorption by the sunflower stalks.](image_url)
From the Figure 1 it can be seen that the equilibrium in the solution is established in about 5 minutes while the sorption capacity reaches 6 mg / g.

The results of static capacity studies of materials are shown in Figure 2, which shows that the stalks in the native form reach a sufficiently high capacity (70 mg / g), comparable to the capacity of an activated carbon. If the modification is provided by the method of carbonization and treatment with ammonium oxalate it will not lead to the increase of the sorption capacity, conversely, it decreases slightly (to 66.7 mg / g and 61.6 mg / g respectively). Sorption isotherms for all the above materials can be attributed to the L1 type according to Guils’s classification which suggests the presence of a large number of micropores in their structure [11].

The maximum capacity values were noted for stalks modified with sodium hydroxide (104.4 mg / g), the sorption isotherm is L3 according to Guils's classification which indicates the mesopores presence along with micropores. The adsorbent AC-3 showed a maximum capacity which is a bit less than the capacity of stalks (64.8 mg / g).

![Figure 2. Dependence of the sorption capacity (A) of the spongy tissue from the equilibrium concentration (Equal) of the phenol.](image)

4. Results and discussion

Thus, we can conclude that the sunflower stalks can be used to remove phenol from water, while their treatment with sodium hydroxide solution is expedient. So that we can conclude that the sunflower stalks can be used to remove phenol from water and it is expedient to treat them with sodium hydroxide solution.

The study of the sorption capacity under dynamic conditions in the process of studying the sorption characteristics of sorbents is necessary not only to determine their capacity with relative to the extracted substance, but also to evaluate the possibility of their practical application.

For the research of the dynamic capacity the phenol solution was initially diluted with an initial concentration of 5 mg / l. Native sunflower stalks (20 g) modified with sodium hydroxide solution were used as loading. After the sorbent had reached its full dynamic capacity it was regenerated with
the sodium hydroxide solution with the concentration of 100 mg / l. The results of the dynamic capacity studies are presented in Figure 3.

![Figure 3](image-url)

*Figure 3.* The dependence of extraction efficiency (E) of phenol from the solution by native stalks of sunflower (a) and modified NaOH (b) on the specific filtrate volume (V).

As it can be seen from Figure 3 the water dephenolation efficiency under the dynamic conditions is higher when it is used as a load in the native form and reaches 84%. With the use of the modified stalks only 69% of phenol was recovered. After the regeneration, the maximum cleaning efficiency for the native stalks decreased to 50 %, for the modified ones - to 34 %.

5. Summary and Conclusion

Thus, on the basis of the conducted research the following conclusions can be made: the materials based on the native sunflower stalks can be used to purify water from phenol and for the regeneration, the selection of other solutions is necessary.

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