Studying the sorption of heavy metal ions by materials based on food industry waste

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Abstract. The present study treats on cleaning wastewater originated from industrial buildings using sorption materials. As sorption materials for the recovery of heavy metal ions, industry wastes were used: threshing millet, cotton fiber, chitosan. The basic sorption characteristics such as purification efficiency, sorption capacity, specific surface and sorption capacity on water were considered. Conditions and modes of heat treatment of sorption materials (temperature and time) are described. A combined use of materials in the form of a layer-by-layer filter and granules is proposed. The efficiency of cleaning materials is 93 to 99.9%, the sorption capacity is from 6.9 to 50 mg/g.

Introduction

Competent design of the sewerage system from industrial enterprises allows one to extend the service life of sewer facilities. Sewerage network, pumping stations and facilities for cleaning shop floor drains that are placed at the industrial site, refer to the system on-site sewage enterprises. Wastewater discharge from the territory of industrial enterprises is often carried out on a separate sewerage system, i.e. rainwater and industrial fused separately. For some enterprises with appropriate technical and economic justification the combined sewage system can be accepted [1].

In those enterprises where the production waste water in composition and nature of contamination close to domestic waters, satisfied with the overall sewer network to share their leads. Rainwater is discharged by drains. If you have conditionally-net production of water, they come in a water recycling or diverted watercourses. In this case, the separate sewerage system has two networks: a network of polluted industrial and domestic waters and a network of conditionally clean industrial and rainwater. If industrial wastewater is not take together with household due to the fact that they contain specific pollution (fats, oil products, heavy metal ions, etc.), which can cause irregularities in the sewer, arrange for local treatment facilities (e.g., girolomoni, septic tanks, filter for wool, neutralization installations, etc.), having them in the shops or near them.

In modern conditions, when water shortage is acute in many regions of the country, the urgent task is to create closed water supply systems with utilization of all water treatment products.
It is possible to prevent pollutants from entering the General sewage system by means of local wastewater treatment systems based on different methods: chemical, physico-chemical and biological [2-4]. One of the most effective methods is the sorption method of wastewater treatment, which allows to remove ions of heavy metals. Various materials (activated carbons, zeolite, silica gel, peat) are used as sorbents and find application in various technological solutions [5-7]. Ash is used for effective removal of lead, cadmium, copper and zinc from polluted water [8].

In recent years, much attention has been paid to the use of low-cost adsorbents from plant waste to remove Cu (II) and Zn (II) from polluted waters. In article [9] sorption characteristics of two types of the wastes received as a result of agriculture are studied: soy bran and mustard husk. The influence of contact time, initial concentration of metal ions, pH, sorbent mass and temperature on the adsorption capacity of materials as sorbents is investigated. Article [10] describes the use of olive seeds for extraction of iron, lead, copper.

This papers [11-12] presents the first results concerning the possible use of cotton stalks and apricot seeds as biosorbents of heavy metals. These materials were chosen due to its high availability and basic cellulose structure. The heavy metals selected as sorbates were Cu and Pb. The purpose of this paper was to study adsorption. The use of various agricultural wastes to remove heavy metal ions of these from aqueous solution under various experimental conditions. The influence of various operating parameters on biosorption, such as initial pH and metal concentration, adsorbent amount and adsorbent particle size, was studied and optimal experimental conditions were determined. Another purpose of this study was to test the toxic effect of heavy metals on the soil bacterium Pseudomonas aeruginosa ATCC 10145 before and after biosorption with agricultural waste.

For the treatment of wastewater from organic and inorganic dyes are used disaccharides [13]. The authors [14-15] show the possibility of using barley grain shells for sorption from water surfaces of oil and oil products. It was found that the modification of the shells with weak sulfuric acid solutions leads to the removal of the hydrophilic component from the material, which helps to reduce water absorption by 16.5% and thus increase the sorption capacity in relation to oil and petroleum products by 30%.

The aim of this work was to develop sorption materials that allow highly efficient extraction of heavy metal ions from sewage effluents of industrial enterprises.

**Methods**

The objects of the study were agricultural waste i.e. carbonized waste of millet (CWM); cotton fiber (CF) - waste of weaving cotton fabrics; chitosan (waste from processed crustaceans).

As method for obtaining sorption materials, heat treatment is used in a muffle furnace (SNOL brand) in a special unit with limited oxygen access.

The thermal treatment modes for the threshing millet waste was a temperature of 300°C for 20 minutes, and for the weaving cotton fabrics wastes a 450°C temperature during 8 minutes (TCF).

The layer filter was made as follows: the materials were placed in a special polymeric housing in such a way that the outer layers contained TCF, and the inner layer - (CWM) sorbent.

The granular materials made of chitosan and CWM were prepared according to the following procedure:

Sample 1 - A mixture is prepared for the preparation of the granules. 40 g of chitosan was added to 960 g of acetic acid 3%. The mixture is stirred for 4-5 hours until the chitosan is completely dissolved. The obtained gel-like mixture is the poured through a syringe into a 5% solution of sodium hydroxide (NaOH). The formed granules are held for 24 hours in an alkali solution (NaOH), followed by washing with water of a 7.0-7.5 pH.

Sample 2- A CWM additive in an amount of 20% by weight is added to the resulting mixture of chitosan in acetic acid (described above for Sample 1). The mixture is thoroughly mixed and poured through a syringe into a 5% solution of sodium hydroxide (NaOH).

The content of heavy metal ions in the sample wastewater was monitored voltammetrically using the analyzer of the voltammetric model AKV-07 MK.
**Results and Discussion**

In [16-19], the authors selected the optimal conditions for the thermal treatment of agricultural waste. As a result of heat treatment, a carbonized waste of grind mill (CWM). The initial threshing of millet contains a large amount of organic substances (cellulose, lignin, cellulose, etc.), with heat treatment, a porous material containing carbon, which determines sorption properties of sorbents. For a given sorption material, the specific surface area is: \( S = 188 \text{ m}^2/\text{g} \), the total pore volume in water is \( V = 0.3 \text{ cm}^3/\text{g} \) [20].

To determine the efficiency of wastewater purification from IHM (Ions of heavy metals) (Pb(II), Cd(II), Zn(II), Cu(II) \( C_{\text{initial}} = 10 \text{ mg/dm}^3 \)) using (CWM), 20 grams per liter of model wastewater solution were added to wastewater and static sorption was carried out for 20 minutes at constant stirring. (CWM) was separated from the water by filtration. Based on the final concentrations found in the solution, the wastewater purification efficiency and the CWM sorption capacity were determined (Table 1).

| IHM   | C final, mg/l | E, % | A, mg/g |
|-------|---------------|------|---------|
| Pb(II)| 0.68          | 93.0 | 15      |
| Cd(II)| 0.57          | 94.0 | 16      |
| Zn(II)| 0.19          | 98.0 | 18      |
| Cu(II)| 0.12          | 98.0 | 14      |

| IHM   | C final, mg/l | E, % | A, mg/g |
|-------|---------------|------|---------|
| Pb(II)| 0.54          | 94.5 | 6.9     |
| Cd(II)| 0.17          | 98.3 | 14.4    |
| Zn(II)| 0.39          | 96.0 | 13.2    |
| Cu(II)| 0.01          | 99.9 | 15.1    |

The next object of research as a sorption material (SM) for wastewater treatment from heavy metal ions was cotton fiber waste of weaving cotton fabrics. It is formed during the mill process while weaving the thread of the weft with the warp thread. In the article, the optimal conditions for the heat treatment for cotton fibres were established.

Treatment was carried out in a special cell without air access. Under these conditions, heat-treated cotton fiber (TCF) is formed which forms a high sorption characteristics, due to mechanical sorption. The main characteristics for cotton fibre: the specific surface area is - \( S_{sp} = 50.8 \text{ m}^2/\text{g} \), the total pore volume in water is \( V_{pore} = 0.8 \text{ cm}^3/\text{g} \), for TCF: the specific surface is - \( S_{sp} = 1700 \text{ m}^2/\text{g} \), the total pore volume by water \( V_{por} = 1.4 \text{ cm}^3/\text{g} \).

The obtained TCF was investigated for the purification of wastewater from the IHM in the static regime (Table 1). The time for achieving the sorption equilibrium was 30 min, during which the
sorbent was kept at the optimum ratio of 1g/dm³. Based on the final concentrations found in the solution, the purification efficiency of wastewater and the sorption capacity of TCF were determined (Table 1). Morphology of the surface is shown in the figure 1.

When using powdered CWM as a sorbent, fine particles of CWM are carried away with the water flow and further pollutes the water. For convenient use of powdered CWM, sorption materials of CWM and TCF are proposed to be laid in layers [19].

The article [19] studied the ratio of fibrous and cellulose-containing waste (20: 80% by weight). External fibrous layers play the role of a framework for lose, powdery sorbents, and when the wastewater is filtered. The filter was analyzed for its ability to absorb the IHM dynamically. It turned out that the efficiency of purification from IHM is up to 93%. It has been established that the calculated values of the total sorption capacity (A, mg/g) for IHM increase in the series: Zn(II) (A = 13.6) < Cd(II) (A = 12.8) < Pb(II) (A = 12.4) (Fig. 2).

![Figure 2. Dependence of the efficiency of IHM purification from the volume of the filtered wastewater through the filter (m = 5 g)](image)

The next technical solution of the powdered material is its granulation. For the production of granules as a binder, proposed to use chitosan, which also has sorption properties. The paper [20] shows that powdered chitosan is used to purify wastewater from IHM. The obtained granular sorption composite materials (granules) of the following composition: 1 - chitosan; 2 - chitosan + CWM;

To study the sorption properties of graphs in an amount of 20 g/l, the addition of lead ions with initial concentration of 30 mg/l to model solutions containing lead ions and the sorption process carried out for 60 min under static conditions. Then, the model solutions were filtered, and the residual content of lead ions was analyzed. At the final and initial concentrations, the efficiency and sorption capacity of cleaning model solutions are calculated. The results are shown in Table 2.

| Granules composition | C initial, mg/l | C final, mg/l | E, % | A, mg/g |
|----------------------|----------------|--------------|------|---------|
| Sample 1 (chitosan)  | 30             | 6.34         | 78.0 | 43      |
| Sample 2 (chitosan + CWM) | 30         | 0.41         | 98.6 | 50      |

From Table 2, it can be seen that the addition of CWM to chitosan granules makes it possible to increase the purification efficiency from 78 to 98% and the sorption capacity from 43 to 50 mg/g.
When studying the morphology of the surface of sample 2 with a CWM content of 20% (Figure 3), it can be seen that sample have an inhomogeneous structure, with a portion of the porous surface. With CWM content, the granule surface has pores with dimensions of 4-12 nm and 20-24 nm (Figure 3). The porous surface structure explains the high efficiency of the sample 2, in which the extraction of the IHM occurs due to physical adsorption into the pores.

![Figure 3](image-url)

**Figure 3. Morphology of the surface of granulated samples x 100; A-sample 1 (chitosan), sample 2 (chitosan-CWM)**

**Conclusion**

All the above SM have their advantages and disadvantages: CWM and TCF are cheap materials with high sorption characteristics, but additional modifications are required for practical application. The design of the layer-by-layer filter makes it possible to clean the wastewater in a dynamic mode.

Granulated SM also have a high purification efficiency and CWM additive allows to reduce the cost of a material based on chitosan and to provide convenience of use.

As a result of the study, the following conclusions were drawn

1. Methods for obtaining SM from wastes and the possibility of cleaning industrial sewage with the use of obtained SM has been shown.
2. The main parameters of the SM were determined:
   - CWM in relation to the IHM: sorption equilibrium time (20 min), optimum mass ratio of SM to the volume of model wastewater (20 g/dm³), purification efficiency of wastewater (from 93 to 98%) and maximum sorption capacity (14-18 mg/g).
   - TCF in relation to IHM: sorption equilibrium time (20 min), optimum mass ratio of SM to the volume of model wastewater (20 g/dm³), purification efficiency of wastewater (from 94.5 to 99.9%) and maximum sorption capacity (6, 9-15.1 mg/g).
   - Filter based on CWM and TCF in relation to IHM: sorption equilibrium time (20 min), optimal mass ratio of SM to volume of model wastewater (20 g/dm³), purification efficiency of wastewater (up to 93%) and maximum sorption capacity (12.4 -13.6 mg/g).
   - Granulated SM based on chitosan and chitosan with additive CWM in relation to IHM: sorption equilibrium time (20 min), optimal mass ratio of CM to volume of model wastewater (20 g/dm³), purification efficiency of wastewater (from 78 to 98.6%) and maximum sorption capacity (43-50 mg/g).

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