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Research paper

Composite Granulated Adsorbents Based on Chitosan and Agricultural Processing Waste for Sewage Treatment

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Abstract

To minimize the impact of industrial enterprises on water objects, a wide variety of adsorbents (based on activated carbon, natural materials, nanomaterials, vegetable waste of agro-industrial complex, etc.) is used. Recently, chitin and chitosan have attracted the attention of scientists due to a number of unique physico-chemical and biological properties (adsorption, antioxidant, radioprotective, immunomodulating, lamina-forming). We have improved the method of obtaining powdered chitosan and established the basic physical and chemical parameters (bulk density, humidity). The method of obtaining chitosan granules and composite materials based on chitosan and modified sunflower husks (MSH) has been further developed by the "drip method". The adsorption properties of powder chitosan, chitosan granules and MSH were studied. It is set that a granular adsorbent has a high adsorbtivity in comparing to the original chitosan. Efficiency of wastewater treatment with the use of chitosan granules and MSH is equally high (up to 98%). The optimum amount of adsorbent for effective cleaning of contaminated water is 1% of its volume. The use of the results of the conducted research allows us to obtain an effective adsorbent for the treatment of industrial waste water.

Keywords*: chitosan, composite adsorbent, sewage, treatment, waste.*

1. Introduction

According to UNESCO, the most widespread and dangerous pollutants of the environment (including the hydrosphere) are metal ions and petroleum products. The main sources of the formation of ecological danger [1] are enterprises mining industry, the system of transfer and transportation, oil terminals and petroleum storage facilities, petroleum storage facilities, transport, refueling complexes and stations [2]. Therefore, the search for new methods, materials and technologies that will minimize the inflow of heavy metal ions, oil and products of its processing into the hydrosphere is relevant.

To reduce the impact of industrial enterprises on water objects use a variety of adsorption materials. Adsorbents are obtained on the basis of activated carbon, natural materials, nanomaterials, vegetable waste of the agro-industrial complex, and others [3]. The promising use of waste from the agro-industrial complex for the production of efficient and inexpensive adsorbents is due to the fact that their main chemical components are cellulose, lignin, hemicellulose and extractive substances [4].

Recently, chitin and chitosan have attracted the attention of scientists due to a number of unique physico-chemical and biological properties (adsorption, antioxidant, radioprotective, immunomodulating, antitumor, fiber and lamina forming). Chitin (poly-N-acetyl-D-glucose-2-amine) is a nitrogen-containing polysaccharide that has a chemical similarity to cellulose, but instead of the hydroxide (-OH), on each ring (monomer) of 6 Carbon atoms there is an amino group in which one of two atoms of the Hydrogen is replaced by an acetyl group. Chitin was first isolated from outer shells of tarantulas. With prolonged heating of chitin with concentrated alkaline solutions N-deacetylation occurs and chitosan is formed. Trans-location in the elementary chain of the macromolecule of chitin substitutes (acetamide and hydroxyl groups) causes a significant hydrolytic stability of acetamide groups, including in alkaline hydrolysis conditions. Therefore, cleavage of acetamide groups can only be carried out under relatively strict conditions - as a result of treatment with a concentrated aqueous solution of NaOH at a temperature of 110-140 ° C for 4-6 hours. However, in these conditions, the degree of deacetylation (the proportion of acetamide groups that were split off, per unit element) does not reach the unit (that is, quantitative removal of these groups is not ensured) [5].

Chitosan is an amino sacocor, a derivative of linear polysaccharide. Its macromolecules consist of randomly linked β- (1-4) D-glucosamine units and N-acetyl-D-glucosamine. This explains the ability of chitosan to heavy ions of various metals firmly. It can bind a significant amount of organic water-soluble substances.

Chitosan is one of the powerful natural biosorbents of a broad but selective action, the only natural polysaccharide containing nitrogen atoms in its molecule. Due to this, it possesses unique adsorption properties - it binds and removes toxins and heavy metals, but does not remove the main nutrient elements (potassium, calcium, sodium, magnesium, etc.), amino acids and sugars; that is, does not violate the mineral exchange. The presence of reactive functional groups provides the obtaining of various chemically-modified derivatives of chitosan (sulfate, carboxyl, fluorine, etc.), which are widely used in medicine, ecology, biotechnology, agriculture. These properties are determined by the chemical structure of the chitosan molecules, namely, the molecular weight, the degree of deacetylation, and the uniform distribution of the deacetylated units along the length of the polymer molecule. The strong hydrogen bond of chitin chains interferes with its dissolution in acids and meadows.

The cleavage of chitin and chitosan to N-acetyl-D-glucosamine and D-glucosamine can be effected by microbial enzymes such as chitinase and chitobiaze. Due to this, chitosan is completely biodegradable, while it does not pollute the environment [6].

Characteristic features of chitosan, which are decisive for its application in various industries, are solubility in the aquatic environment, high viscosity of solutions, the ability to form *laminans* and granules, biocompatibility, low toxicity, and the ability to biodegradate in the natural environment. The chitosan molecule contains a significant amount of free amino groups, which allows binding of hydrogen ions and obtaining an excessive positive charge. This explains the ability of chitosan to contain ions of heavy metals [7].

The main source of chitin is a product isolated from crustacean shells. Despite the high values of the degree of deacetylation (80-90%), there is also a significant destruction of chitosan, which is accompanied by a decrease in the molecular weight of the polymer to oligomers, and a high concentration of alkaline solutions negatively affects the adsorption properties. More and more researchers are attracted by a raw material source such as fungi that could be grown industrially [8].

Studies aimed at obtaining composite adsorbents (on the basis of chitosan using waste from the agro-industrial complex) for the treatment of waste water from heavy metals and petroleum ions are relevant scientific and practical tasks.

2. The Main Part

To obtain chitin-containing materials with high consumer qualities, we analyzed various types of higher fungi for the content of chitin in cell walls and the detection of physico-mechanical properties of micelle fibers. The choice of tinder fungus (Fomes fomentarius), the use of which allows to get chitosan with a high degree of deacetylation, is substantiated. The chitin in the cell wall of the fungi has a microfibrillar structure (Fig. 1 and 2), a thickness of microfibrils of 15-25 nm and a length of 1-2 microns. Chitin microfibrils form a spatial network in the cell wall. Due to the microfibrillary structure, fungal chitin has a rather high specific surface (over 1000 m^2/g) [6].

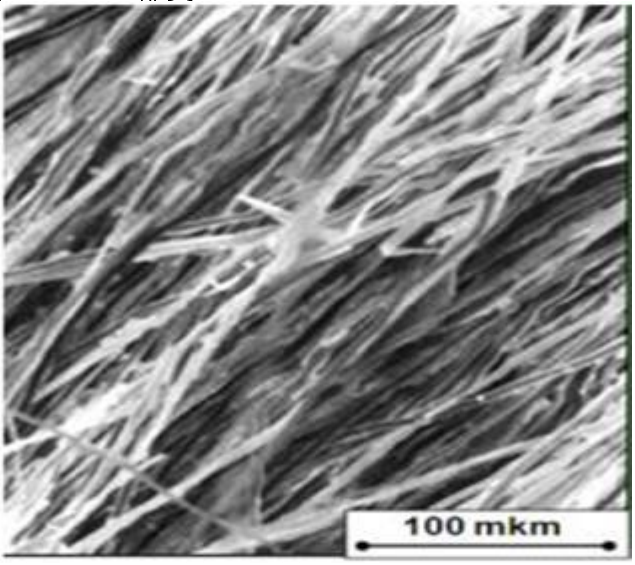


Fig. 1: Microfibrillary structure of chitin in the cell wall

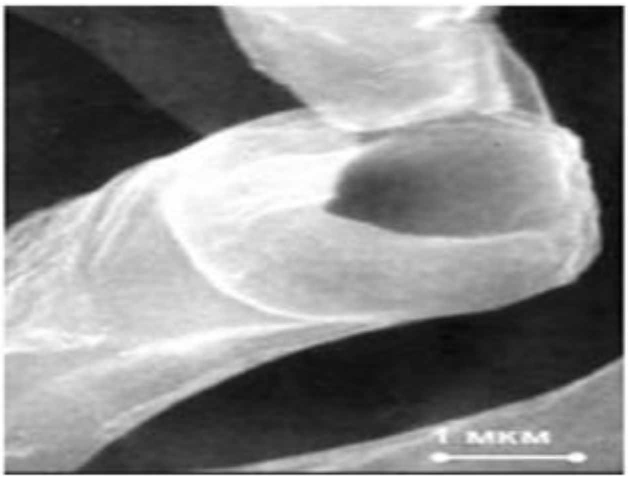


Fig. 2: Cell wall of fungus hypha

In the process of obtaining chitin, live protoplast and other soluble components of the cell wall were removed. The insoluble part of the cell wall is a complex consisting of three biopolymers: chitin, glucans and melanins, each having practical value by itself. In order to study the content of chitin in the fetal bodies, in the development process, samples of tinder of different ages (from one to four years) were selected, which were previously divided into trama (inner) and dermis (crust) (Table 1) [9].

Table 1: Chitin content in the Tinder fruit bodies

Part of the fetal body	Chitin content,%			
	Age of the fetal body, years			
	1	2	3	4
Trama	7.7	8.7	9.6	10.5
Derma	8.4	9.1	9.8	10.7

The process of obtaining chitosan includes the following stages:

– allocation of chitin (deproteinization, purification from mineral components of raw materials);

– formation of chitosan from chitin (deacetylation and final purification of chitosan).

The following research methodology is used. Fungi purified from mechanical impurities and washed with distilled water, were subjected to deproteinization (crushed, placed in a glass flask, poured into a 0.1n solution of NaOH in a ratio of 1:10). The solution was treated with alkaline solution on a magnetic stirrer at constant stirring for 4 hours at a temperature of 20°C. Upon completion of the process, the raw material was filtered, washed with distilled water to a neutral medium (pH = 7). Purification from the mineral components of the raw material was performed using a 0.6N solution of chloride acid, whereupon the deproteinized raw material was placed in a glass flask, poured into an acid solution (in the ratio of 1:10) and held for 4 hours. The solution was separated from the precipitate by filtration and washed with distilled water to pH = 7. The resulting chitin was discolored with 3% Hydrogen peroxide solution for 3 hours, washed with distilled water and ethanol and dried at 20°C.

Chitosan was prepared from chitin as follows. The dry crushed chitin was filled into a flask, a 1:10 40% NaOH solution having a temperature of 80°C was poured into the flask, stirred in a magnetic stirrer for 10 minutes, the contents of the flask were heated to 130°C for 2 hours. The system was then cooled down quickly. The resulting chitosan was washed with ethanol and ether for final purification and dried at 20°C.

The yield of chitosan (by chitin) is 78% of the theoretically possible. The main advantages of the method are the availability of raw materials, the ease of utilization of mineral and protein waste, the possibility of multiple use of 40% NaOH solution. The resulting chitosan is a mixture of polydisperse flakes of milky color. The physical and chemical parameters of chitosan, which are presented in Table 2, are determined.

Table 2: Physico-chemical parameters of chitosan

Parameters	Value
Bulk density, g / dm^3	0.2734
Humidity,%	13.8
Degree of deacetylation,%	78

The degree of deacetylation is a qualitative characteristic of chitosan, which reflects the efficiency of substituting acetyl groups for amino groups in the amino-polysaccharide molecule. The granular form of chitosan has advantages, since the granules are characterized by a higher bulk density, can be obtained with a given particle size distribution, and with a sufficiently high dispersion, with a much larger specific surface area, which, in combination with high amorphous granules, positively affects the adsorption capacity.

The use of granulated chitosan is not economically profitable. Therefore, we proposed to obtain composite adsorbents based on chitosan and modified waste from the agro-industrial complex, which have high adsorption properties.

To obtain adsorbent from sunflower husk, a laboratory plant was used (Fig. 3). Glass Ceramic (1) with a capacity of 1 dm^3 was placed on an electric tile (4). The cover (2) has a mixer (6), a thermometer (5) and an outlet for the output of SO_2 and H_2O.

After shredding, the resulting raw material was dried to a constant mass at 105°C. In this case, physically bound water is completely removed. The dried raw material was then weighed and transferred to a reaction glass. A certain amount of sulphate acid was added at a concentration of 65% by weight. The ratio of plant material - sulfate acid is 1: 1.5. The reaction mass was heated at constant stirring for 1.5 hours at a temperature of 130 ° C. in the drawer, with steam, water, CO_2 and SO_2 isolated. The resulting carbonaceous product was dried at 105 ° C., washed with distilled water to pH 7 and transferred to a desiccator for storage [10].

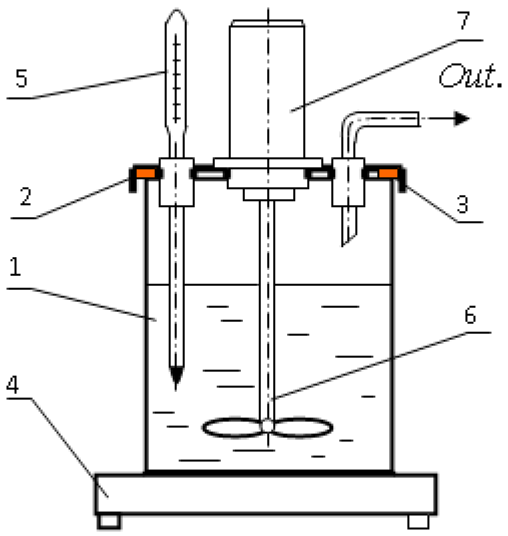


Fig. 3: Laboratory setting for adsorbent preparation: 1 - glass; 2 - cover; 3 - sealant; 4 - heater; 5 - thermometer; 6 - mixer; 7 - electric motor of the mixer.

The physical and chemical parameters of the received adsorbent from sunflower husk (Table 3) are determined.

Table 3: Physicochemical parameters of adsorbent

Parameters of adsorbent	Value
Bulk density, g/cm^3	0.66
Humidity,%	1.5
Granulometric composition, mm	0.03 – 0.1
Dispersion, nm	10
Pore size, nm	0.5 – 50

Humidity and bulk density of the adsorbent are important indicators that affect the speed and efficiency of wastewater treatment and adsorbent water adsorption. Increasing the bulk density reduces the amount of adsorbent used to clean water from petroleum products, which affects production costs.

The results of electron microscopy (Figure 4) showed that the adsorbent particles are varied in size and shape.

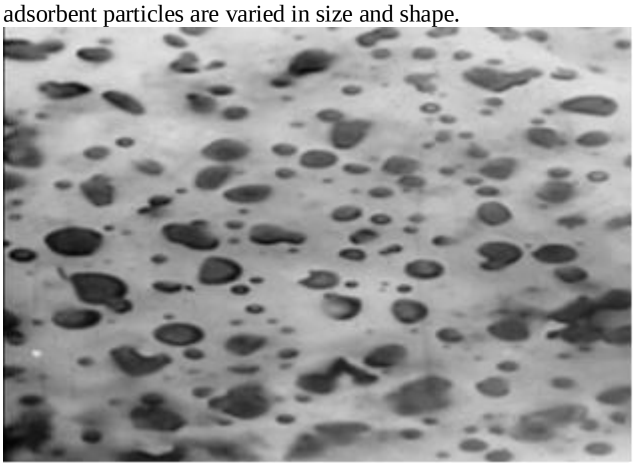


Fig.4: Microstructure of adsorbent from a sunflower husk

The study of the microstructure of the surface of the adsorbent allowed to detect micropores with a diameter of about 0.5 nm, transition pores, smaller than 5 nm in size and macropores, the size of which varies in the range of 5-50 nm. The intervals between the particles in the aggregates form a system of channels in the size of 1-2 nm. The dispersion of the adsorbent is 10 nm [9].

The granulation process consists of the following: a 2% solution of chitosan with ethanic acid and a mixture of chitosan with ethanic acid and a powder of crushed sunflower husk adsorbent in a quantity of 20% is injected through syringes. The droplets are made in an air gap between the needle with a hole diameter of 240 microns and a sedimentation bath with 1 n NaOH solution (Fig. 5). Visualization of modifications of chitosan granules is shown in Fig. 5.

The use of granulated chitosan is economically not profitable. Therefore, we proposed to obtain composite adsorbents on the basis of chitosan and modified waste from the agro-industrial complex. The combination of chitosan reduces the cost of adsorbent, improves the adsorption properties and allows the recycling of plant waste. Composite adsorbents can be widely used for sewage industrial waste water treatment.

The microscopic test of the granules was carried out on a microscope XS - 3330 MICROMED (optical magnification - 65). The results are shown in Fig. 6, where it is observed more loose structure of composite granules based on chitosan and sunflower husk adsorbent. Pores and defects of the structure (fig. 6, b) occur, which determine the physical adsorption of pollutants from waste water.

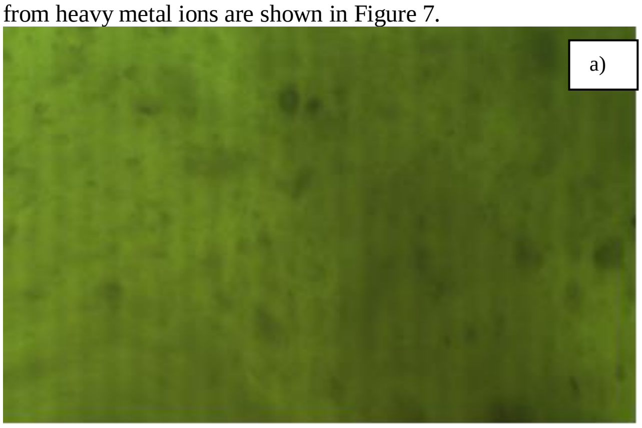
Fig. 5: Characteristics of the granulation process: a) - chitosan granules; b) - composite granules of chitosan with modified sunflower husk

As a result of the analysis of the dependence of the granulometric capacity of chitosan solutions of different concentrations, it has been established that the formation of granules from low viscosity solutions of chitosan (with a concentration of less than 2%) leads to the deposition of flakes. At the same time, when trying to precipitate chitosan in the form of spherical particles by slowly adding its viscous solutions (the concentration of chitosan was more than 6-8%), the difficulty of separating the drop from the tip of the needle and strain (flattening) the drop when entering the sediment bath.

It was established that according to the proposed conditions for the formation of spherical granulated material in 5% sodium hydroxide solution, the optimal concentration range providing spherical granules was 2-6%. The formation of chitosan granules from weakly viscous or high viscosity solutions leads to the deposition of irregularly formed granules.

In the dissolved form, chitosan has a better adsorption effect than in the insoluble one. Due to the effect of molecular sieve and hydrophobic interactions, chitosan is capable of adsorbing ions of heavy metals, petroleum products, fats and fat-soluble compounds. Also, the efficiency of chitosan is determined by the degree of deacetylation.

The obtained granules were investigated on the ability to bind heavy metal ions from model drains. The prepared model solutions contain ions of heavy metals Fe^{2+}, Zn^{2+}, at a concentration of 1 g/dm^3. Up to 100 cm^3 of model solutions, 1 g of "pure" chitosan granules and chitosan granules with modified sunflower husks were added. The adsorption process was carried out in static conditions in a magnetic stirrer for 40 minutes (time of achievement of adsorption equilibrium) with constant mixing. For comparison, a similar experiment was conducted with an initial powder chitosan. Calculated values of the efficiency of wastewater treatment from heavy metal ions are shown in Figure 7.



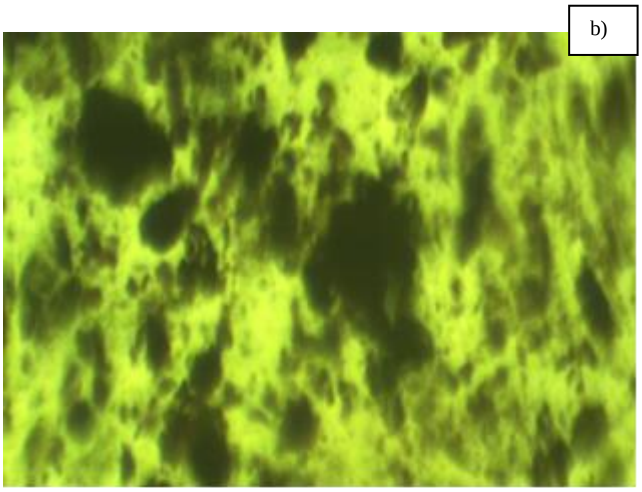


Fig.6: Microstructure of chitosan granules (a) and chitosan granules with modified sunflower husks (b).

As a result of the analysis of the obtained results, we note that the granulation adsorbent has a higher purification efficiency compared to the initial chitosan. Efficiency of wastewater treatment with the use of granules of "pure" chitosan and composite granules of chitosan with sunflower husk, is equally high (up to 98%).

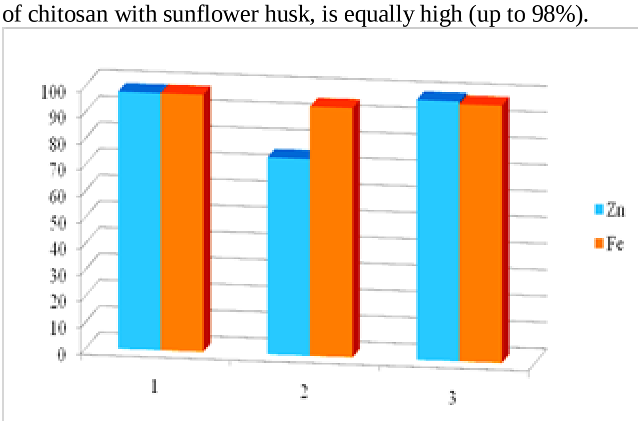


Fig. 7: Dependence of the efficiency of cleaning (E) sewage from heavy metal ions by different materials: 1 - chitosan granules; 2 - powder chitosan; 3 - chitosan granules with modified sunflower husk

Efficiency of purification of waste water from oil products (namely technological lubricants) with chitosan granules with modified sunflower husk has been investigated. In the model runoff with a concentration of lubricant of 100 mg/dm^3, composite chitosan granules were added in the amount of 1, 2 and 3 grams. Adsorption was carried out in static conditions for vigorous mixing for 40 minutes. The results are presented in Figure 8.

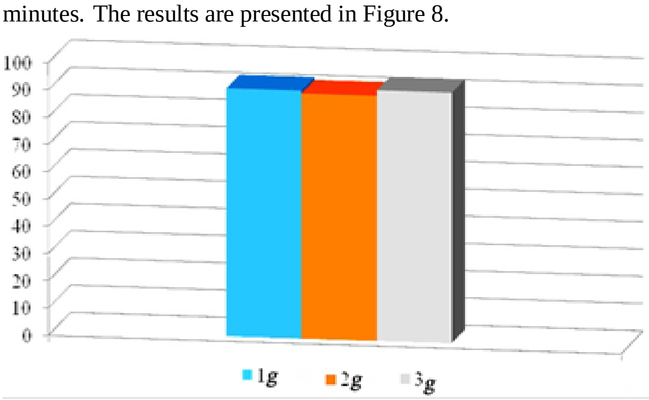
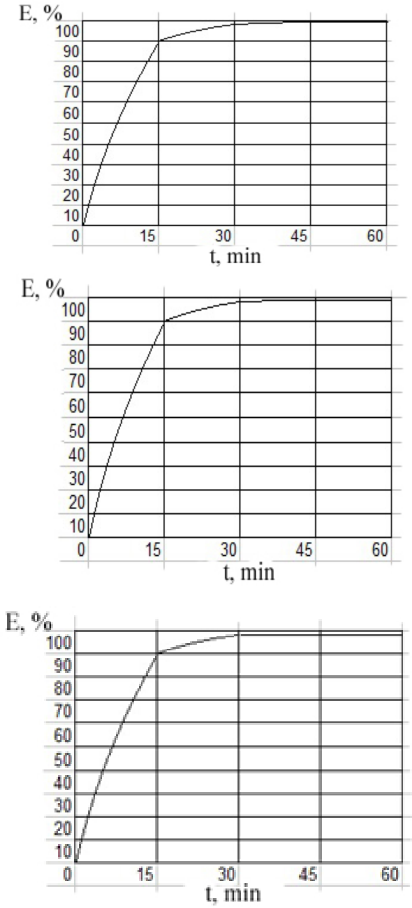


Fig. 8: Efficiency of cleaning (E) of contaminated water from technological lubrication

As a result of the experiment, it was found that the optimum amount of adsorbent required for efficient cleaning of contaminated water is 1 g. Further increase in the amount of composite adsorbent is inappropriate.

The efficiency of wastewater treatment from petroleum products, namely technological lubrication, depending on the granulometric composition of the composite adsorbent is investigated. During the purification we used an adsorbent with a different granulometric composition, namely: 0.03-0.01 mm; 0.1-1 mm; more than 1 mm. Adsorption was carried out by a volumetric method for an hour. The amount of adsorbent required for efficient cleaning of contaminated water is 1% of the volume of cleaned water.
Efficiency of removal of technological lubricants from contaminated water by a composite adsorbent with different granulometric composition is shown in Fig. 9.



a) b) c)

Fig. 9: Results of the purification of contaminated water from the technological lubricant by a compositional adsorbent, the granulometric composition of which: a) 0.03 - 0,1 mm; b) 0.1 - 1 mm; c) more than 1 mm.

As a result of the experiments, it was established that the granulometric composition of the adsorption material affects the efficiency of wastewater treatment from petroleum products. The finer granulometric composition has an adsorbent, the purity efficiency is higher.

3. Conclusions

As a result of the conducted studies, the relevant scientific and practical task of improving the method of obtaining chitosan and studying its adsorption properties to minimize the level of environmental danger of water objects, namely, for wastewater treatment of industrial enterprises from heavy metals and petroleum products, is solved. Specifying the following:
- it was established that tinder (Fomes fomentarius) contains a sufficiently high amount of chitin and chitosan;
- the method for obtaining chitosan with deacetylation degree of 78% was improved with the use of 40% NaOH solution;
- the basic physicochemical parameters of the obtained chitosan were established (namely: bulk density - 0.27 g/dm^3, humidity - 13.8%, degree of deacetylation - 80%);
- an improved method of obtaining granules of chitosan and granulated materials on the basis of chitosan and modified sunflower husk "drip method", namely by filtration of 2-6% solution of chitosan in a 5% solution of NaOH;
- adsorption properties of chitosan, chitosan granules and composite materials based on chitosan modified sunflower husk were studied. It has been established that the best purification efficiency (up to 98%) has a granular adsorbent with an optimal amount of 1% of the volume of contaminated water.

Thus, the introduction of the results of the conducted studies allows us to obtain an effective adsorbent for treatment of industrial waste water.

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