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ГРАНУЛИРОВАННЫЕ СОРБЦИОННЫЕ МАТЕРИАЛЫ ДЛЯ ОЧИСТКИ СТОЧНЫХ ВОД ОТ ИОНОВ ЦИНКА (Zn^{2+})

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В статье описаны основные области применения биополимера – хитозана, наиболее важными из которых являются медицина и пищевая промышленность. В последнее время много работ посвящено применению хитозана для очистки стоков, т.к. он обладает флокуляционными и сорбционными свойствами. Стоимость на рынке хитозана высока, поэтому в статье предложено создавать гранулированные композиционные сорбционные материалы на основе хитозана и отходов сельхозпереработки, которые позволят снизить себестоимость и повысить сорбционные свойства. В качестве отходов сельхозпереработки предложено использовать термообработанный обмолот проса, который обладает высокими сорбционными свойствами. Получены композиты, где в качестве связующего используется хитозан, а в качестве наполнителя - термообработанный обмолот проса с различным содержанием (10 %; 20 %; 30 %; 40 % от общей массы). Построены изотермы адсорбции ионов цинка на полученных композиционных сорбционных материалах с различным содержанием наполнителя и рассчитаны значения максимальной сорбционной емкости. Определены механические свойства (истираемость и измельчаемость) полученных композиционных сорбционных материалов и показано, что лучшими характеристиками обладает сорбционный композиционный материал с добавкой наполнителя в количестве 30%. Разработана технологическая схема получения композиционных материалов из термообработанного обмолота проса и хитозана для очистки сточных вод. Проведены микроструктурные исследования полученных материалов, которые показали, что добавка термообработанного обмолота проса увеличивает пористость материала и, как следствие, сорбционную емкость. Рассчитаны экономические показатели производства композиционных сорбционных материалов и рассмотрены их способы утилизации.

Ключевые слова: сорбенты, сточные воды, хитозан, ионы цинка, шелуха проса

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GRANULATED SORPTION MATERIALS FOR WASTE WATERS PURUFUCATION FROM ZINK IONS (Zn^{2+})

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The article describes the main applications of biopolymer – chitosan, the most important of which are medicine and food industry. In recent times, many works devoted to the application of chitosan for wastewater treatment because it has a flocculation and sorption properties. The market price of chitosan is high, so it is proposed to create a granular composite sorption materials based on chitosan and waste of agricultural processing, which will reduce the cost and improve the sorption properties. As waste agricultural processing is proposed to use heat-treated threshing of millet which has high sorption properties. The composites, where the binder is chitosan and the filler - heat-treated threshing millet with different content (10 %; 20 %; 30 %; 40 % of the total weight) were obtained. The adsorption isotherms of zinc ions on the composite adsorbent materials with different content of filler were constructed and the values of maximum sorption capacity were calculated. The mechanical properties (abrasion and grindability) of the obtained composite sorption materials were determined and it was shown that the best sorption characteristics of composite material with the addition of the filler for 30%. The technological scheme of production of composite materials of the heat-treated millet threshing and chitosan for wastewater treatment was developed. The microstructural study of the obtained materials showed that heat-treated additive threshing of millet increases. The economic indicators of production of composite sorption materials were calculated and the methods of disposal were examined.

Key words: sorption materials, wastewater, chitosan, zinc ions, millet husk

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INTRODUCTION

As early as XIX century, French scientists separated chitin from acyl and got chitosan in substance. Since then, a lot of chitosan fundamental research is have been conducted and tree Nobel Prize winners' academic works appeared on the subject – 1903, 1929 and 1939. This natural polymer is still of interest nowadays and its unique properties attract attention of different experts with various specialties [1-5]. At present, we have many ways to use chitosan in different branches of industry where the most important ones are medicine, food industry and water purification. The main advantage of chitosan is its safety for a man and environment. In nature, chitosan fully decays. As it is ecological, its usage has good prospects for achieving ecological goals. Chitosan is also known for its great sorption and coagulation properties, might be used as a flocculant, antibacterial properties make it possible to use chitosan for water purification in production process [6-9]. It is not justified to use chitosan in substance for waste waters purification because of its high cost price starting from 2000 rub/kg. Obtaining composites on basis of chitosan as binding and cheaper raw materials as filling will reduce the cost and help use these materials more extensively. It makes the research aimed at production long-range and economically sound sorbents using secondary raw materials and chitosan relevant and scientifically and practically important.

Purpose of the research: development of technologies to obtain composite sorption materials on basis of chitosan and cellulose agricultural processing waste – millet threshing for wastewaters purification of zinc nuclei.

METHOD AND DISCUSSION OF THE EXPERIMENT

To increase sorption capacity and reduce chitosan cost production it is offered to produce composite sorption materials where chitosan is used as binding and heat-treated millet threshing as filling. In Russian Federation most regions are agricultural ones where a great quantity of lignine and cellulose agricultural processing wastes is generated (sunflower husk, wheat husk, millet husk etc.) which when modified acquire high sorption properties [10, 11]. Vast areas are needed for the waste storage. Using them as secondary materials will solve two problems at a time – water purification and waste utilization. It makes combining of chitosan and heat-treated millet threshing (HTMT) rational and cost-effective. The authors [10] describe in details sorption properties of HTMT at 300 ºC within 20 min. The thermal treatment and burning result in formation of a porous structure with the pores size ranged between ~0.8 and 4-5 nm. The obtained sorbate possesses rather high sorption properties: A ≈ 17 mg/g, specific surface S = 188 m^2/g, the total volume of pores by water V = 0.3 sm^3/g.

To get composite sorption materials was chosen 6% chitosan solution in 3% acetic acid solution [12] with addition of HTMT powder (composite material chitosan-millet (CMCM)) with quantity 10%; 20%; 30%; 40% of a total mass and without HTMT addition and (composite material chitosan (CMC)). The resultant mixture is stirred homogeneously for 1 h. The resultant mixtures are poured with syringes in 5% solution of sodium hydroxide (NaOH) with the following water washing to the value pH 7.0-7.5 and drying at room temperature within 24 h.

The Granules obtained were analyzed for ability to recover zinc ions (Zn^{2+}) from simulated wastewaters with initial concentration from 5 to 100 mg/l with a step of 5 mg/l. The granules were added to simulated solutions with quantity of 20 g per 1 l and sorption process was conducted under static conditions within 20 min (time for sorption equilibrium) [12] with stirring and thermostating in the temperature range of 293+2 K. For comparison, the same sorption process was conducted with granulated chitosan without HTMT. After wastewater purification process, the sorbate was filtered and the final concentration of heavy metals ions was determined by means of voltamperometric analysis.

By initial and final concentrations sorption capacity Ap was determined and adsorption isotherms was built (Fig. 1).

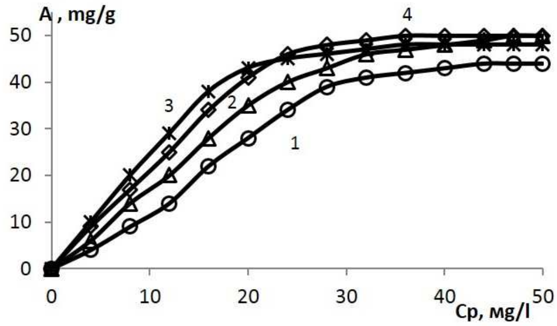


Fig. 1. Adsorption isotherms of Zn^{2+} for CMCM with different proportions of HTMT: 1 – 10%, 2 – 20%, 3 – 30%, 4 – 40%
Рис. 1. Изотермы адсорбции Zn^{2+} на КМХП при различном содержании ТОП: 1 – 10%, 2 – 20%, 3 – 30%, 4 – 40%

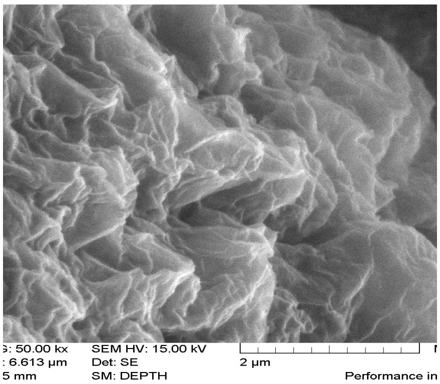
Adsorption isotherms of Zn^{2+} for CMCM with different proportions of HTMT were used to determine values of maximum volume capacity (Table). Comparing sorption capacity of modified materials with different content of heat-treated threshed millet showed that maximum sorption capacity (50 mg/g) is for CMCM with HTMT40 and 20%. With HTMT additive of 40% granules mechanical strength is much lower than with additive of 20%. Granules with additives of 40% and 30% are not of accurate form and decay during purification process.

Table

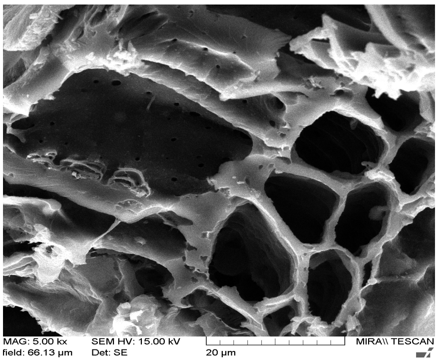
Physical-mechanical and sorption properties of CMCM depending on the composition

Таблица. **Физико-механические и сорбционные характеристики КМХП в зависимости от состава**

Millet husk quantity for CMCM, %	Abradability	Grindability	Sorption capacity, A Zn^{2+}, mg/g
0	0.3	3	36
10	0.3	3	44
20	0.3	3	48
30	0.9	6	50
40	1.2	10	50



a



b

Fig. 2. Microphotography of the granules surface: a – CMC; б – CMCM (20%)

Рис. 2. Микрофотография поверхности гранул: а – КМХ; б – КМХП (20 %)

Physical-mechanical properties (abradability and grindability) of the obtained composite materials (CMCM) were studied. The properties were determined using method [13] (Table). As shown in Table, CMCM with HTMT of 10 and 20% and CMC without HTMT comply with requirements of GOST P 51641-2000 (abradability is no more than 0.5%, grindability is no more than 4%).

Analyzing the data, it might be concluded that HTMT additive increases sorption capacity. CMCM with HTMT additive of 20% shows the best parameters: high sorption capacity (50 mg/g), abradability 3%, grindability 0.3%. That is why this composed material is supposed to be used for drains purification from HMI. Granules without HTMT additive are mechanically strong but have low sorption capacity, A = 36 mg/g.

Surface morphology analysis of CMCM containing HTMT of 20% and without it revealed that with HTMT additive appears porous surface area. Porous structure of the surface results from the increase in CMCM sorption capacity with HTMT additive.

To obtain CMCM a process flowsheet has been elaborated (Fig. 3). The chitosan flakes from the chitosan container (3) go through the doser (4) to the mixer (5). At the same time 3% solution of the acetic acid goes through the doser (6) to the mixer (5).

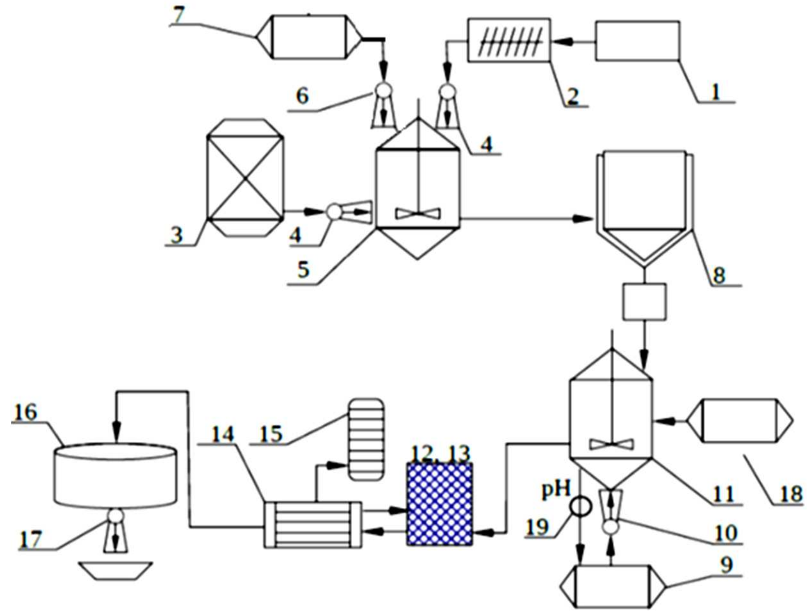


Fig. 3. A scheme of CMCM obtaining: 1 – container for millet husk storage; 2 – stove for millet husk heat treatment; 3 – container for chitosan storage; 4 – chitosan doser; 5 – mixer; 6 – acetic acid doser; 7 – container for acetic acid storage; 8 – doser; 9 – container for alkali storage; 10 – alkali doser; 11 – granules settling chamber; 12, 13 – mesh filters; 14 – drying chamber; 15 – absorber; 16 – container for granules storage; 17 – doser of the obtained granules; 18 – water tank; 19 – pH tester

Рис. 3. Схема получения КМХП: 1 – емкость для хранения шелухи проса; 2 – печь для термообработки шелухи проса; 3 – емкость для хранения хитозана; 4 – дозатор хитозана; 5 – смеситель; 6 – дозатор уксусной кислоты; 7 – емкость для хранения уксусной кислоты; 8 – дозирующее устройство; 9 – емкость для хранения щелочи; 10 – дозатор щелочи; 11 – камера осаждения гранул; 12,13 – сетчатые фильтры; 14 – сушильная шкаф; 15 – абсорбер; 16 – емкость для хранения гранул; 17 – дозирующее устройство полученных гранул; 18 – бак с водой; 19 – рН- метр

The acid goes from the container (7). A composition is formed as a result of 24 h chitosan and acetic acid mixing in the mixer (5). Millet threshing previously goes to the stove (2) from the container (1) where it goes through the heat treatment (T = 300 ºC, t = 20 min). By the use of the doser (4) HTMT goes to the mixer (5) where the solution of chitosan and acetic acid is ready and being mixed for 1 h. Prepared mixture by the use of the doser (8) drop by drop goes to the granules settling chamber, which is already filled with 5% solution of alkali. The alkali goes from the container (9) by the use of the doser (10). Granules of black colour are formed in the granules settling chamber. Size of the granules might be varied depending on the volume of the solution dropped through the doser. Water from the tank (18) is used for washing the granules. The water goes to the alkali tank (9) until the value pH reaches 7-7.5. Measuring of the pH is done with the pH tester (19). The alkali is supplied to the tank (9) until the concentration of the solution of NaOH equals to 5%. To separate the obtained granules from the solution a mesh filter made of inert material (stainless steel, chemically persistent polymer materials) is used (12) with mesh size less than granules size (1-2 mm). The filter with the granules is moved to the drying box (14) and is used for drying within 4 h. To clean air from alkali vapour an absorber (15) is used. To make the process for granules obtaining continuing two replacing mesh filters (12), (13) are used. After drying, the granules are poured into the container for granules storage. An empty filter is replaced by the filter with newly obtained granules. The obtained granules from the container (17) by use of the doser are packaged (5 to 50 kg sacks on terms of the customer).

In the article [14] it is offered to utilize waste sorption materials on basis of chitosan as soil fertilizers if they were used to purify heavy metals ions – microelements (Cu^{2+}; Zn^{2+}). It is proved that CMCM used as soil fertilizer results in significant increase in germinating capacity (12%) and plants growing.

Calculation of economic indexes was made for CMCM production with quantity of 150 tons of sorbate per year. The selling price was 117.3 rub/kg. Initial chitosan price is 2 thousand rub/kg. Investments to produce CMCM were 867027 rub with the payback period more than two years.

SUMMARY

It was proved that high sorption composite materials might be obtained on basis of chitosan and HTMT. It was established that sorption capacity, abradability, grindability CMCM depend on the percentage of HTMT. It was established that CMCM with HTMT of 20% is of high sorption capacity (50 mg/g) and optimal mechanical properties.

Microstructure study revealed that HTMT additive causes the formation of a porous CMCM surface structure with possible physical adsorption during HMI recovering process.

A technology for obtaining and using CMCM for the wastewaters purification process was elaborated.

Calculation of economic indexes for CMCM production showed that HTMT additive significantly reduces the cost of sorption materials on basis of chitosan (CMCM – 117.3 rub/kg, chitosan as substance – 2 thousand rub/kg).

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