

Technology of Obtaining Composite Sorbents for Water Purification

Politaeva Natalia Anatolievna, Taranovskaya Elena Aleksandrovna*, Slugin Vladimir Valentinovich and Prokhorov Vladislav Vladimirovich

Peter The Great St. Petersburg Polytechnic University, 194021, Polytechnic Street-29, Saint Petersburg, Russia

Abstract

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.

Keywords: Sorption materials; Wastewater; Chitosan; Zinc ions; Millet husk

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 has 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 rubles/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.

Materials and Methods

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°C within 20 minutes. 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: $A \approx 17$ mg/g, specific surface $S = 188$ M²/g, the total volume of pores by water, $V = 0.3$ CM³/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 one hour. 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 hours.

The Granules obtained were analyzed for ability to recover zinc ions (Zn²⁺) from simulated wastewaters with initial concentration from 5 to

***Corresponding author:** Taranovskaya Elena Aleksandrovna, Peter The Great St. Petersburg Polytechnic University, 194021, Polytechnic Street-29, Saint Petersburg, Russia, Tel: 89379753775; E-mail: conata07@list.ru

Received April 11, 2017; Accepted May 12, 2017; Published May 20, 2017

Citation: Anatolievna PN, Aleksandrovna TE, Valentinovich SV, Vladimirovich PV (2017) Technology of Obtaining Composite Sorbents for Water Purification. J Chem Eng Process Technol 8: 338. doi: [10.4172/2157-7048.1000338](https://doi.org/10.4172/2157-7048.1000338)

Copyright: © 2017 Anatolievna PN, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

100 mg/l with a step 5 mg/l. The granules were added to simulated solutions with quantity 20 g per 1 liter and sorption process was conducted under static conditions within 20 minutes (time for sorption equilibrium) [12] with stirring and thermo stating in the temperature range 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.

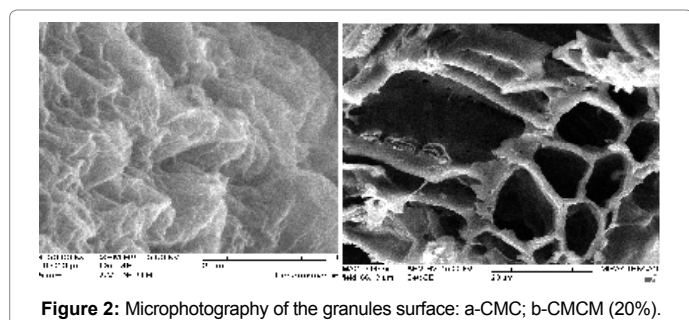
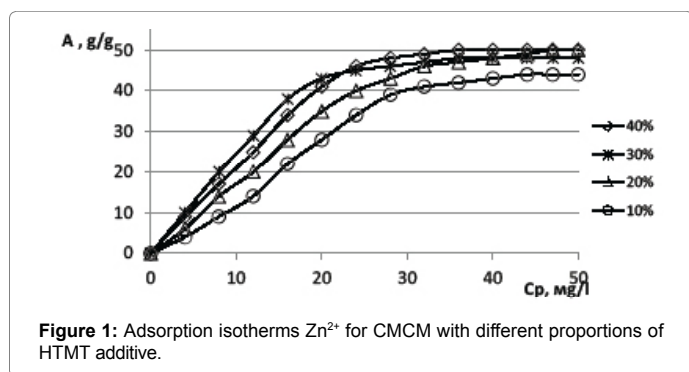
Results and Discussion

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

Adsorption isotherms Zn^{2+} for CMCM with different proportions of HTMT were used to determine values of maximum volume capacity (Table 1). Comparing sorption capacity of modified materials with different content of heat-treated threshed millet showed that maximum sorption capacity (50 g/g) is for CMCM with HTMT40 and 20%. With HTMT additive 40% granules mechanical strength is much lower than with additive 20%. Granules with additives 40% and 30% are not of accurate form and decay during purification process (Figure 2).

Physical-mechanical properties (abradability and grindability) of the obtained composite materials (CMCM) were studied. The properties were determined using method [13] (Table 1). As shown in Table 1, CMCM with HTMT 10 and 20% and CMC without HTMT comply with requirements of GOST P 51641-2000 (abradability no more than 0.5%, grindability no more than 4%).

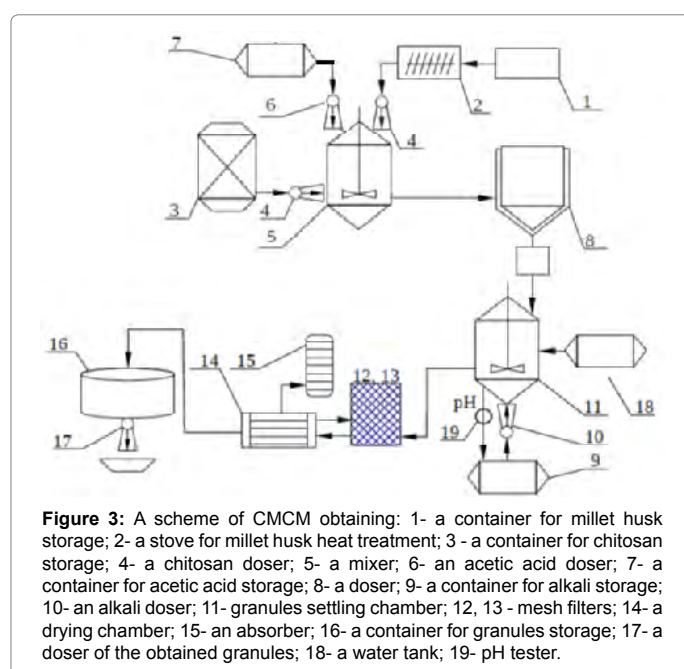
Analyzing the data, it might be concluded that HTMT additive increases sorption capacity. CMCM with HTMT additive 20% shows the best parameters: high sorption capacity (50 g/g), abradability 3%, grindability 0.3%. That is why this composed material is supposed to be used for drains purification from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



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

To obtain CMCM a process flowsheet has been elaborated (Figure 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). The acid goes from the container (7). A composition is formed as a result of 24 hours 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 ($T=300^{\circ}C$, $t=20$ мин.). 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 hour. 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 NaOH equal 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 hours. To clean air of alkali vapor 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 replaces 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



Millet husk quantity for CMCM %	Abradability	Grindability	Sorption Capacity A Zn ²⁺ , mg/
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

Table 1: Physical-mechanical and sorption properties of CMCM depending on the composition.

metals ions- microelements (Cu²⁺; Zn²⁺). It is proved that CMCM used as soil fertilizer results in significant increase of germinating capacity (12%) and plants growing.

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 (Cu²⁺; Zn²⁺). It is proved that CMCM used as soil fertilizer results in significant increase of germinating capacity (12%) and plants growing.

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

Conclusions

It is proved that high sorption composite materials might be obtained on basis of chitosan and HTMT. It is established that sorption capacity, abrasibility, grindability CMCM depends on the percentage of HTMT. It is established that CMCM with HTMT 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).

References

1. Skryabin KG, Vihoreva GA, Varlamov VP, Nauka M (2002) Obtaining, properties and use /under the editorship. Chitin and Chitosan, p: 368.
2. Galbraih LC (2001) Chitin and chitosan: Structure, properties. Sorovsky Educational Magazine 7: 51-56.
3. Bikova VM, Krivosheina LI, Glazunov OI, Ezhova EA (2003) Chitosan use in medical cosmetics. New achievements in chitin and chitosan study: Materials of the 7th International Conference, pp: 231-233.
4. Safronova TM (2002) Chitosan use in food Obtaining, properties and use. pp: 346-359.
5. Dubinskaya AM (1989) Chitin and its derivatives use in pharmacy (review). A chemical and pharmaceutical magazine 23: 623-628.
6. Seliverstov AF (1997) Composite materials on the basis of chitin for metals ions sorption from water solutions. Applied chemistry magazine 70: 148.
7. Gorovoi LF (2002) Chitin and its derivatives sorption properties M. Nauka, pp: 217-246.
8. Bikova VM (2004) Some aspects of chitin and chitosan use as flocculants. Agricultural Russia 5: 30-31.
9. Gil G (2004) Selective antimicrobial activity of chitosan on beer spoilage bacteria and brewing yeasts. Biotechnology Letters 26: 576-574.
10. Sobgaida NA (2010) Influence of the modified wheat husk on its sorption properties to ions Pb²⁺, Cd²⁺, Zn²⁺ and Cu²⁺. Higher Institutions bulletin. Sec Chemistry and Chemical Technology 53: 36-40.
11. Chikina C (2008) Use of Sorbent on the basis of polyurethane foam and buckwheat husk to reduce environmental load for the water area. Environment protection in the oil and gas complex 10: 53-57.
12. Taranovskaya EA (2016) Technology of obtaining and use of granulate sorbents on the chitosan basis. Chemical and Oil and Gas Machine Industry 5: 42-44.
13. Gost P (2000) Filter granular materials. General specifications. M. Standartinform, p: 14.
14. Politaeva NA (2016) Utilization of waste sorption materials on basis of chitosan. Technological University Bulletin 19: 25-28.