E3S Web of Conferences 434, 02033 (2023) https://doi.org/10.1051/e3sconf/202343402033
ICECAE 2023

Development of a sorbent based on chitosan and vermiculite for purification of textile wastewater

Gulnora Ikhtiyarova[1], *Nailya* Valeeva[1,*], *Munira* Aripdzhanova[1], *Mukhabbat* Ayupova[1] and *Gulnoza* Usmanova[1]

[1]Tashkent State Technical University, Tashkent, 100095, Uzbekistan

Abstract. The study detailed in the article has led to the creation of a novel botanical adsorbent. This adsorbent is formulated using a combination of chitosan, which is sourced from Apis mellifera (honeybees), and vermiculite. The primary application of this adsorbent is targeted towards the treatment of wastewater generated by the textile industry. The article also presents a comparative analysis of two distinct procedures: one involving organovermiculite and the other involving vermiculite that has been modified using hydrochloric acid. The objective of this research is to explore the potential of this newly developed adsorbent as an effective solution for treating wastewater generated by the textile sector. The inclusion of chitosan derived from Apis mellifera enhances the adsorption capabilities of the material. Additionally, vermiculite, a naturally occurring mineral with adsorption properties, is incorporated to further augment the adsorbent's efficiency. The article systematically compares two methodologies for preparing the adsorbent: one involves the utilization of organovermiculite, while the other involves the modification of vermiculite through treatment with hydrochloric acid. This comparison delves into the nuances of each approach, assessing their respective effectiveness and potential advantages for textile wastewater treatment. This study underscores the innovative strides being taken in the field of wastewater treatment, utilizing unique combinations of natural materials to address environmental challenges posed by industries like textiles. The development of this botanical adsorbent demonstrates a promising approach to tackling wastewater issues and promoting sustainable practices within the textile sector.

1. Introduction

Despite the many physical and chemical processes currently used in the practice of wastewater treatment, the most effective and promising for removing the bulk of pollutants are sorption processes using natural adsorbents [1]. Along with traditional sorption materials, activated carbons, such natural aluminosilicates as clays and with an expanding (montmorillonite, vermiculite) or rigid structural cell (kaolinite, hydromica, and hydroxide) are widely used for these purposes. Taking into account the fact that the composition and properties of clays are individual for each deposit, it is important to obtain new cheap and versatile sorbents based on vermiculites and mineral clays [2, 3], to study the mechanisms of interaction between dye pollutants and the obtained organosorbents, and to develop cleaning technologies. Wastewater allows to create a closed water circulation system and reduce the burden on the environment [4].

The primary objective of this scientific endeavor is to develop an innovative sorbent and subsequently employ an organosorbent for the treatment of wastewater generated by the textile industry [5, 6]. The foundation of this sorbent is based on locally sourced vermiculite, which is then modified using chitosan synthesized from deceased honeybees. This synthesis process takes place at the Department of General Chemistry within the Tashkent State Technical University.

The significance of this development stems from the escalating interest in formulating novel and environmentally sustainable sorbents. These sorbents are crafted from naturally occurring hydromicas and aluminosilicates [7, 8]. However, it is pertinent to acknowledge that the broader application of organovermiculites for treating textile wastewater is impeded by a significant challenge: the lack of effective granulation technologies. This is due to the inherent tendency of these sorbents to disperse when exposed to aqueous environments [9-11].

* Corresponding author: valeevang2017@list.ru

The research is propelled by the growing demand for environmentally friendly solutions in wastewater treatment. The utilization of locally available resources like vermiculite, coupled with chitosan derived from bees, underpins the focus on sustainability. Addressing the granulation issue holds the key to expanding the practical application of these novel sorbents, potentially transforming wastewater treatment processes in the textile industry.
This scientific endeavor exemplifies a concerted effort to merge innovation, sustainable practices, and environmental consciousness to create effective solutions for a pressing industrial challenge.

2. Materials and methods

Based on the data obtained and on the basis of complex experimental studies, scientific and methodological principles for the creation of modified vermiculites with organic reagents were developed:
Expanded Vermiculite (Tibinbulok deposits in the Karakalpak region) was chosen for research. The hydromica modifier was hydrochloric acid and chitosan *A pis Mellifera* (KhZ) [5, 6]. The developed organosorbent is provisionally named organovermiculite OV. Chitosan from dead bees *Apis mellifera* was synthesized according to the following procedure: 10 g dead bees *Apis mellifera* were crushed in liquid nitrogen, then washed with distilled water and dried. Further, 8 g of the purified and dried substance was added to 80 ml of an aqueous solution of 0.1 M. HCl, at room temperature for 24 h, filtered, washed to a neutral medium and dried. The demineralized substance for deproteinization was added with 100 ml of an aqueous solution of 0,1 N NaOH alkali and heated at 70-80 ºC for 1 hour, filtered, washed to a neutral medium to remove the protein and dried. At the next stage, to the crude product (1.2 g) by adding 30% solution of H_2O_2 with a volume of 20 ml was kept for a day, then heated and then filtered, washed several times with water. As a result, chitin plates of beige color were obtained with a yield of 15 %. To obtain chitosan with a certain molecular weight, chitin (1.0 g) was heated with 10 ml of 35% NaOH aqueous solution for 2 hours at 80-90 ºC. Molecular Weight of the Obtained Chitosan The obtained chitosan was used as a modifier for expanded vermiculite.
Chitosan has a molecular weight of no more than 165000 D, its carbon content is 41.8%, nitrogen –8.3%, water 8.8%; the degree of deacetylation is 88.0%; the viscosity of a 1% solution in a 2% aqueous solution of acetic acid is 73.0 mmg/s. Gross formula of natural polysaccharide: $(C_6O_4H_7NH_2)n$. The modification of vermiculite with hydrochloric acid was carried out as follows: 100 g of vermiculite heated to constant weight at a temperature of 120-150 °C with a grain size of 0.10-0.05 mm was mixed in 200 ml of 5 (7, 15, 20) % hydrochloric acid solution in within two days. Then the suspension was filtered and washed with distilled water until neutral. The resulting vermiculite was dried to a constant weight and analyzed for the content of the main elements, and then organovermiculite was obtained from the modified vermiculite. The greatest number of acid sites is obtained by the action of 15 % hydrochloric acid.

3. Results and discussion

IR spectra of sorbents were obtained in two forms: based on vermiculite modified with 7 % hydrochloric acid, and also with chitosan (Fig. 1).

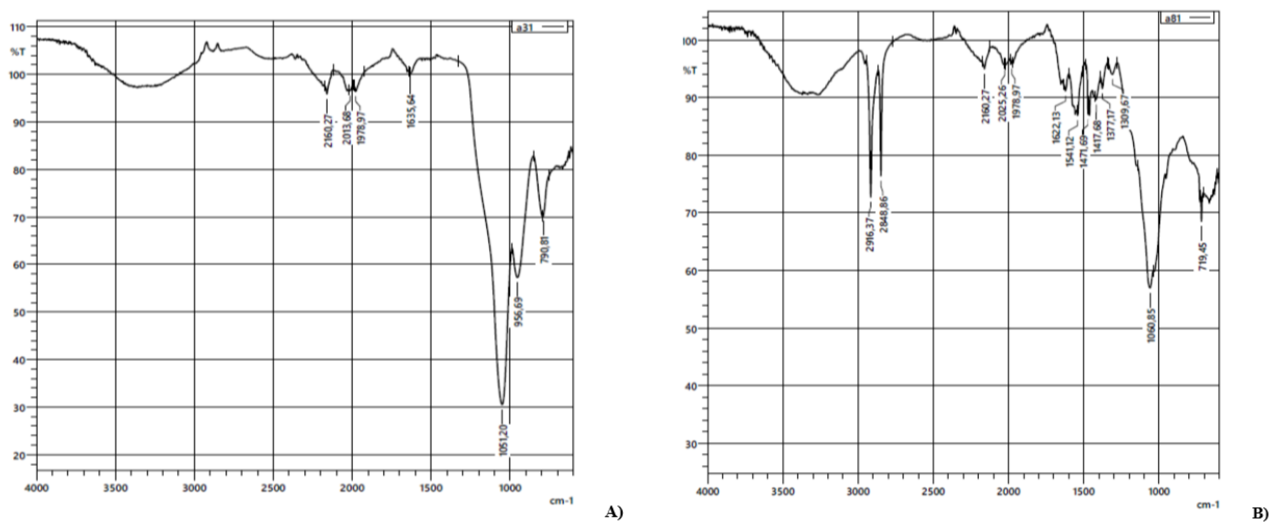


Fig. 1. IR Fourier spectra: a) Vermiculite, b) modified Vermiculite with HCl with chitosan.

Fig. 1 shows that the absorption band at 1643 cm^{-1} belongs to the bending vibrations of adsorbed water molecules and the absorption band at 3459 cm^{-1} is due to the stretching vibrations of its hydroxyl groups and a significant amount of water less strongly associated with the structure. And also in the IR spectrum of the original vermiculite, absorption bands were found at 1656 OH, 1429.72 Fe ion, 949.70 Si-O, 665.10 Me-O-Si (Fe, Al, Mg), 421.44 Si-O -Mg^{2+}, 417.59 Si-O-Ca-OH absorption bands 674 cm^{-1} and 998 cm^{-1} due to stretching vibrations of the Si-O bond. The splitting of the frequencies of the stretching and bending vibrations is associated with the OH of water due to the presence of the existence of H_2O with varying degrees of bonding. After treatment with acid, the appearance of an amorphous phase can be easily identified by the appearance of a band at 1200 cm^{-1} (Fig. 1 a, c), which refers to the Si–O stretching vibrations of silicates.

Our further study was carried out to treat wastewater from surfactants and indigo dye with a modified organosorbent. At higher concentrations, the degree of clarification increases dramatically for solutions of both dyes, by increasing their recovery. Curves illustrating these changes are shown in Fig. 2.

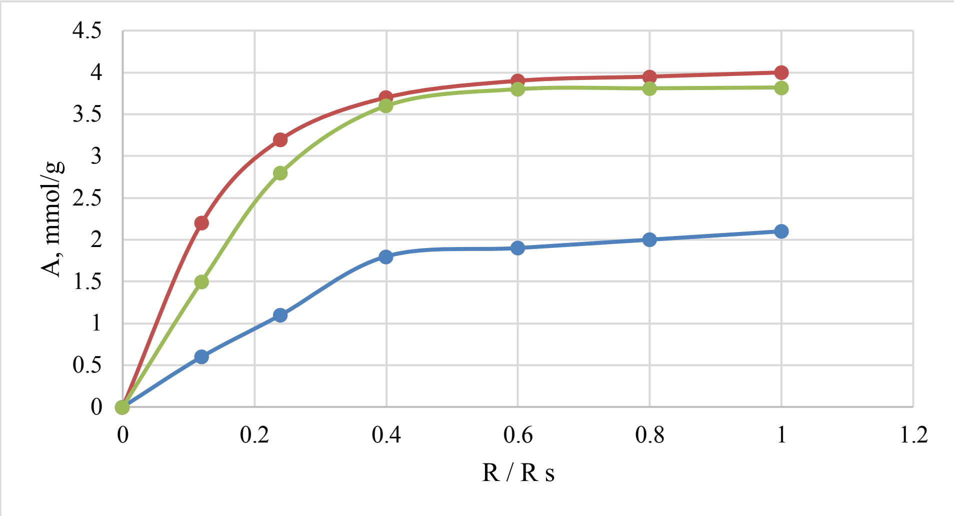
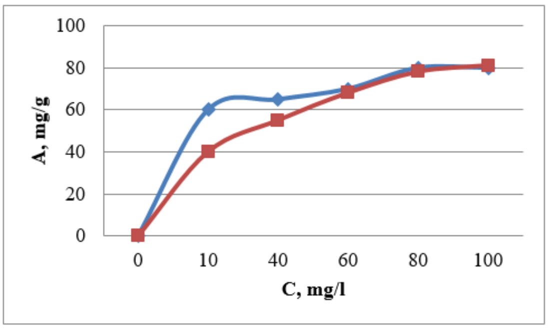


Fig. 2. Adsorption isotherms on the VVK sample - X H: 1) benzene; 2) water; 3) pyridine.

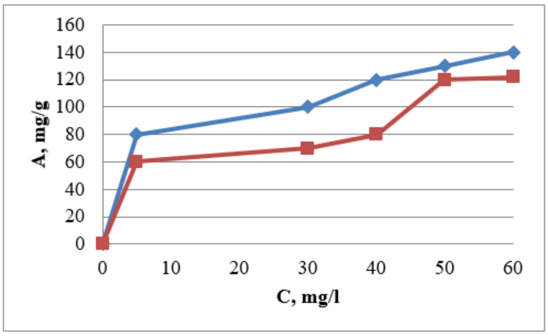
It can be seen from Fig. 2 that the sharp change is probably due to the partial solubilization of large dye molecules between the hydrophobic radicals of the surfactant and the adsorbent.

Our further study was carried out for wastewater treatment from indigo dye with modified sorbents and VVK+H Cl; and KhZ-VVK (Fig. 3). As shown in Fig. 3, a sample of VVK + HClCl has a higher adsorption capacity, which is clearly seen with an increase in the concentration of surfactant negatively at a surfactant concentration of up to 160 mg/l.

As a result of laboratory studies on the sorption of indigo dye, the technological scheme for the use of organermiculite for wastewater treatment of the textile enterprise JSC «Bukhara cotton textile» was compared.



A)



B)

Fig. 3. Adsorption isotherms of indigo dye on organosorbents: 1) VVK+H Cl ; 2) HZ-VVK from a solution with an impurity Surfactants in the amount: A) 100 mg/l; B) 160 mg/l.

The scheme (Fig. 4). includes a preparation stage, to adjust the pH, hydrochloric acid is supplied from the tank (1), then aluminum sulfate coagulant (2) is added to the reactor with a stirrer to precipitate and mixed with water (2) at a mass ratio of 1:3 and stirred for 2 hours. After 24 hours of swelling in water, the clay is broken into a suspension using a mechanical mixer, then water is added in a ratio of 1:2 and the suspension is thoroughly mixed. After sedimentation, the water was drained through the upper side siphon, the raw material from the middle part of the tank was removed into a flat tank for air drying.

Through the lower part of the sedimentation tank, coarse sand and other sedimentary substances that settled on the bottom of the tank were separated and did not participate in the further technological process. The dispersed raw material was laid out in a thin layer (7) and subjected to air drying for 24-48 hours. Then, the semi-dried raw material was preliminarily crushed using a manual grinder, which can be a disk mill. This was followed by drying in an oven at a temperature of 110°C for 4 hours to a residual moisture content of 20%. Dried samples of vermiculite were fed into a planetary mill, where certain portions of modifiers (hydrochloric acid, then chitosan) were fed using a dispenser (3) and subjected to modification and dispersed for 30 min.
As a result of extrusion molding of the sorbent, cylindrical granules with a diameter of 0,5–2 mm and a height of 1–2,5 mm were formed, which were subjected to heat treatment. Further, the obtained granules were sent to the packer.

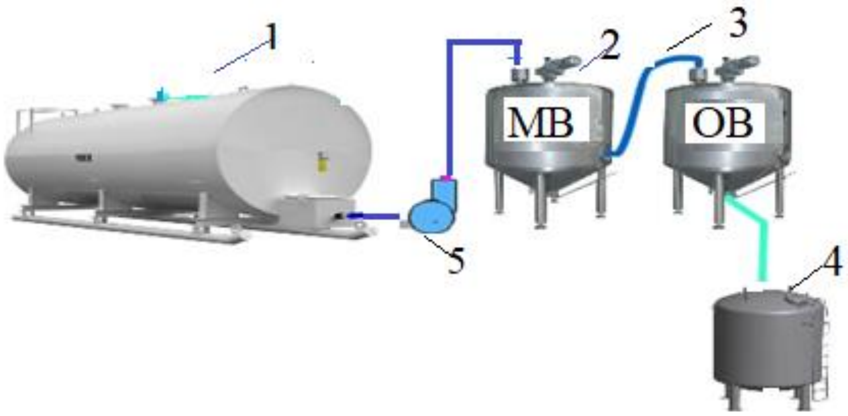


Fig. 4. Technological scheme of wastewater treatment of the textile enterprise JSC «Bukhara cotton textile» simplified developed technology: 1) tank; 2) hoppers for hydrochloric acid and vermiculite; 3) reactor with stirrer for coagulant; 4) tank for sedimentation; 5) lower siphon for draining water.

4. Conclusions

The proposed technological scheme for crafting an experimental batch of adsorbent, founded on natural vermiculite and chitosan, stands out for its simplicity, cost-effectiveness, and positive environmental impact. One noteworthy advantage is its ability to curtail the need for coagulants, contributing to resource conservation. Furthermore, the scheme prioritizes chemical safety and demonstrates a commitment to environmental responsibility.
A scaled-down version of this scheme was successfully executed within the laboratory facilities of the Department of General Chemistry at Tashkent State Technical University (TSTU). This miniaturized process provided valuable insights and served as the foundation for the subsequent transition to production conditions. This approach was seamlessly applied within the operational context of the enterprise, culminating in the creation of various adsorbents, specifically M-VVK and OV, each weighing 1 kilogram.
The culmination of this effort was the transfer of these adsorbents to "Bukhara Cotton Textile" for pilot production testing. This collaborative initiative represents a pivotal step in assessing the practical viability and effectiveness of the adsorbents in real-world operational settings.
The combination of simplicity, affordability, environmental consciousness, and successful transition from laboratory-scale experimentation to industrial production demonstrates the potential of the proposed adsorbent manufacturing scheme to effectively address the challenges associated with textile wastewater treatment.

References

1. Hu, Q., Xu, Z., Qiao, S., Haghseresht, F., Wilson, M., and Lu, GQ, A novel color removal adsorbent from hetero coagulation of cationic and anionic clays. *Journal of colloid and interface science*, 308, pp 191-199. (2007).
2. Khalchenko I. G., Shapkin N. P., Svistunova I. V., Turner E. A. , Chemical modification vermiculite And study his physical - chemical properties "*International scientific forum Butlerovskoye heritage – 2015*". http://foundation.butlerov.com/bh-2015/ (2015)
3. Marchenko L.A. Investigation of the possibility of sorption cleaning during the elimination of oil pollution / L.A. Marchenko, E.A. Belogolov, A.A. Marchenko, O.N. Bugaets, T.N. Bokovikova //*Scientific journal Cube GAU*.– –No. 84 (10).– p. 23-32. (2012).

4. Ozcan AA, Ozcan AS Characterization of natural- and organobentonite by XRD, SEM, FT-IR and thermal analysis techniques and its adsorption behavior in aqueous solutions *// Journal Clay Minerals*, V.47, pp.31-44. (2012)
5. Hazratova DA, Umarov BN, Seytnazarova OM Extraction of chitozan from died honey bee *Apis mellifera* // *International scientific and technical journal Chemical technology control and management*. Iss.2, -№3.- pp.15-20. (2020)
6. Umarov BN, Turabdjanov SM, Mengliyev AS, et all. Physicochemical properties of chitin and chitosan from died honey bees *Apis Mellifera* of Uzbekistan. // *Journal of Critical Reviews*. Vol 7., Issue 4, pp. 120-124. (2020).
7. Umarov B., Isomitdinova D., Turobdzhanov S.M. Wastewater treatment of a textile enterprise of compositions based on vermiculite and modified chitosan. *Journal Composite Materials*. -#4. pp.116-118. (2021).
8. Umarov B.N , Isomitdinova D.S. Turobdzhanov S.M. Wastewater treatment of a textile enterprise of compositions based on vermiculite and modified chitosan. *Journal Composite Materials*. -#4. -p.116-118. (2021).
9. Ikhtiyarova GA, Umarov BN, Turabdjanov SM Purification of textile wastewater with vermiculite modified with chitosan. // *International Journal of innovative research*. -V 9. Issue 9. pp. 9780-9786. (2021).
10. Ergashev Y.; Egamberdiev E.; Turabdzhanov S.; Akmalova G.; Isanova R.; Rashidov R.; Sobitov O.: Obtaining filter material from natural fiber composition and areas of its use. *E3S Web of Conferences*, 371, 01047, (2023).
11. Egamberdiev E.; Ergashev Y.; Turabdjanov S.; Abdumavlyanova M.; Makhkamov A.; Rashidov Sh.; Karimov Sh.: Effect of chitosan on the surface properties of cellulose-based paper obtained from the flax plant. *E3S Web of Conferences* 371, 01010 (2023).