

Synthesis and characterization of adsorbent biopolymer composite pellets and their potential application for VOCs removal from pharmaceutical effluents

NP Simelane¹, JKO Asante¹, PP Ndibewu², LL Sibali³

¹ Department of Physics, Faculty of Science, Tshwane University of Technology, Private Bag X680, 175 Nelson Mandela Drive, Arcadia, Pretoria 0001, South Africa.

² Department of Chemistry, Faculty of Science, Tshwane University of Technology, Private Bag X680, 175 Nelson Mandela Drive, Arcadia, Pretoria 0001, South Africa.

³ Department of Environmental Sciences, College of Agriculture and Environmental Sciences, University of South Africa, Florida Campus, South Africa.

E-mail: AsanteJKO@tut.ac.za

Abstract. This study focussed on investigating the effectiveness of using a newly prepared pelletized biopolymeric composite material for the adsorption of VOCs pharmaceutical effluents. Composite materials have received a great deal of scientific and technological attention due to the potential benefits associated with their unique properties, such as ease of preparation, high durability, good recyclability and high adsorption capability. In this study, the biosorbent was created by blending/coating a synthetic polymer (carboxen-1000) with activated *Moringa oleifera* seed husks (MOSH) under optimized conditions to create a new biopolymeric composite material. This material was then tested for its effective removal of three selected VOCs (BTE: benzene, toluene and ethylbenzene) in pharmaceutical effluents. Advanced techniques like FTIR, SEM, XRD, N₂-BET and TGA were used to characterize the material. A recovery efficiency of >98% was recorded for the BTE. The material was also still effective after being used in 3 cycles.

1. Introduction

Water pollution caused by toxic organic pollutants found in pharmaceutical effluents is currently a major threat to public health not only in South Africa, but also around the world. Volatile organic compounds (VOCs) such as benzene, toluene and ethylbenzene (BTE) are among the most toxic in this group of compounds, thus, are referred to as emerging dangerous environmental pollutants carried along by pharmaceutical effluents. Human exposure to these VOCs has been linked to the development of various diseases, including cancer (Amann et al., 2014).

To address this issue, the adsorption technique, which employs adsorbent materials such as activated carbons among others (Liew et al., 2018), has received considerable attention. However, traditional adsorbents typically have low adsorption capacity. As a result, biopolymeric composite materials, which combine the benefits of several materials, are gaining attention as potential materials for

addressing global challenges in water purification. Recently, agricultural wastes such as *Moringa oleifera* seed husks (MOSH) have been used in the preparation of these biopolymer composite materials. This is because they are inexpensive, biodegradable, and readily available, making them suitable for use even in developing countries. A study conducted by Ibrahim et al. (2022) reported that biopolymer composite materials have a high adsorption capacity of pollutants such as dyes and heavy metals during wastewater treatment.

Biopolymer composite pellets were created in this study by combining activated MOSH powder with a synthetic polymer (carboxen-1000) powder in an optimized ratio. The pellets were prepared using a Spark Plasma Sintering (SPS) instrument. The pellets were then characterized using a variety of techniques and tested for BTE removal from pharmaceutical wastewater samples.

2. Materials and methods

2.1. Materials

All chemicals and solvents used in this study were purchased from Sigma-Aldrich (Germany). The synthetic carboxen-1000 polymer was also purchased from Sigma-Aldrich (Germany). The *Moringa oleifera* seed husks (MOSH) were collected from a farm in Zvezda Game Resort, located in the North West province of South Africa.

2.2. Methods

2.2.1. Preparation of the biopolymer composite pellets

Activated *Moringa oleifera* (MO) powder was prepared according to a method reported by Bezzera et al. (2020). The activated MO powder was blended with the synthetic polymer powder in an optimized ratio using a tubular mixer. The mixtures were consolidated by Spark Plasma Sintering (HPD 25, FCT System GmbH Germany) instrument in order to produce the pellets. The powders were loaded into a graphite die, 20 mm diameter and sintered using an optimized temperature and time of 300°C and 5min., respectively. The mixed powders were uniaxial pressed at 50Mpa at a heating rate of 100°C/min.

2.2.2. Characterization of the synthesized pellets

The functional groups formed in the material were identified using FTIR. SEM, XRD and the N₂-BET method coupled with Nitrogen gas were used to investigate the microstructure of the material produced. The thermal stability of the pellets was investigated using TGA.

2.2.3. Batch adsorption studies on the prepared adsorbents

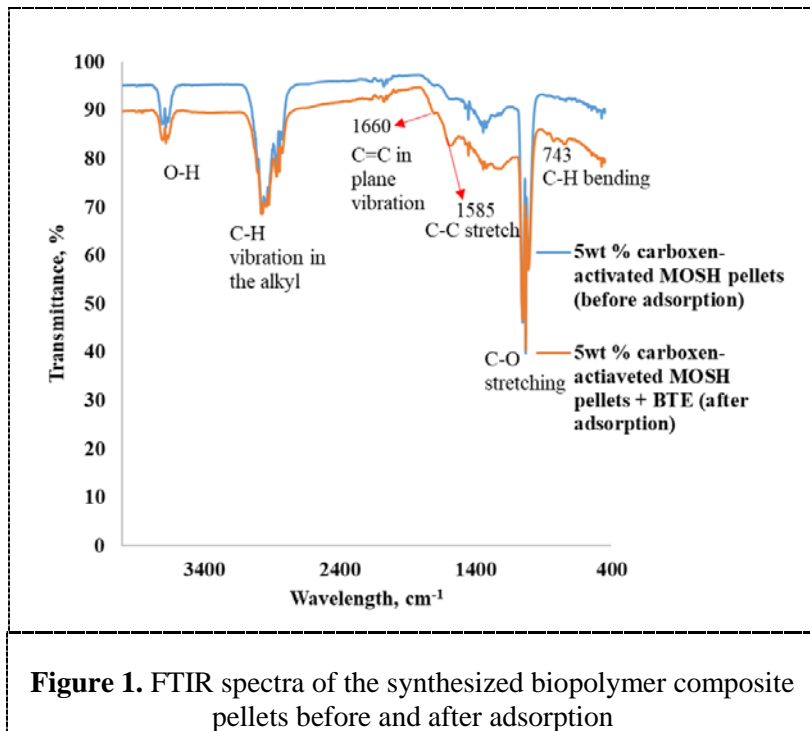
Preliminary experiments were conducted on the pellets in order to investigate the effect of contact time, initial pH, initial concentration and adsorbent dosage. The effect of adsorption temperature on the pellets was also investigated.

3. Results and discussion

3.1. Characterization results

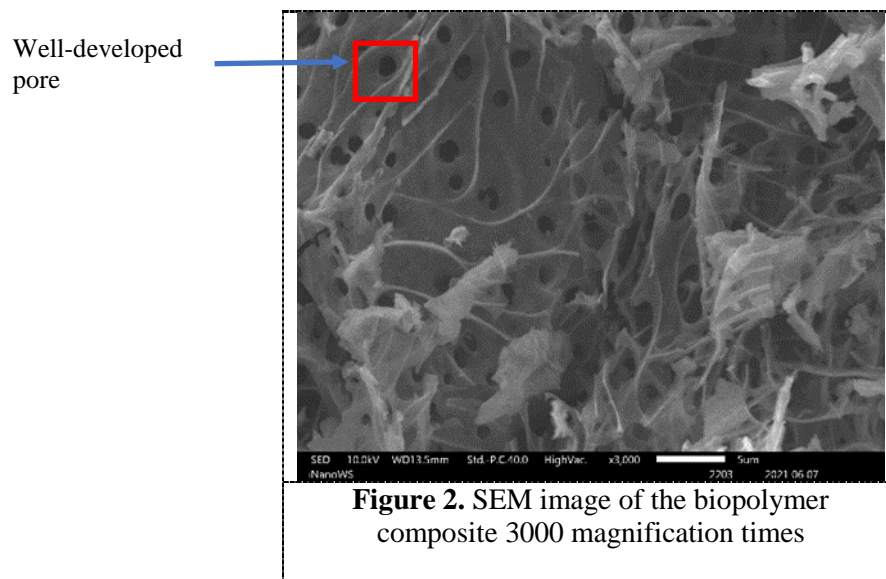
3.1.1. FTIR analysis

The FTIR spectra of the synthesized biopolymer composite pellets before and after adsorption are shown in Figure 1. The presence of functional groups such as -OH (3680 cm⁻¹), C-O stretching vibration (1033 cm⁻¹) as well as carbonyl groups can be seen in the spectra. These identified functional groups all play a role during the adsorption process in agreement with similar findings reported in the literature (Ambaye et al., 2021).



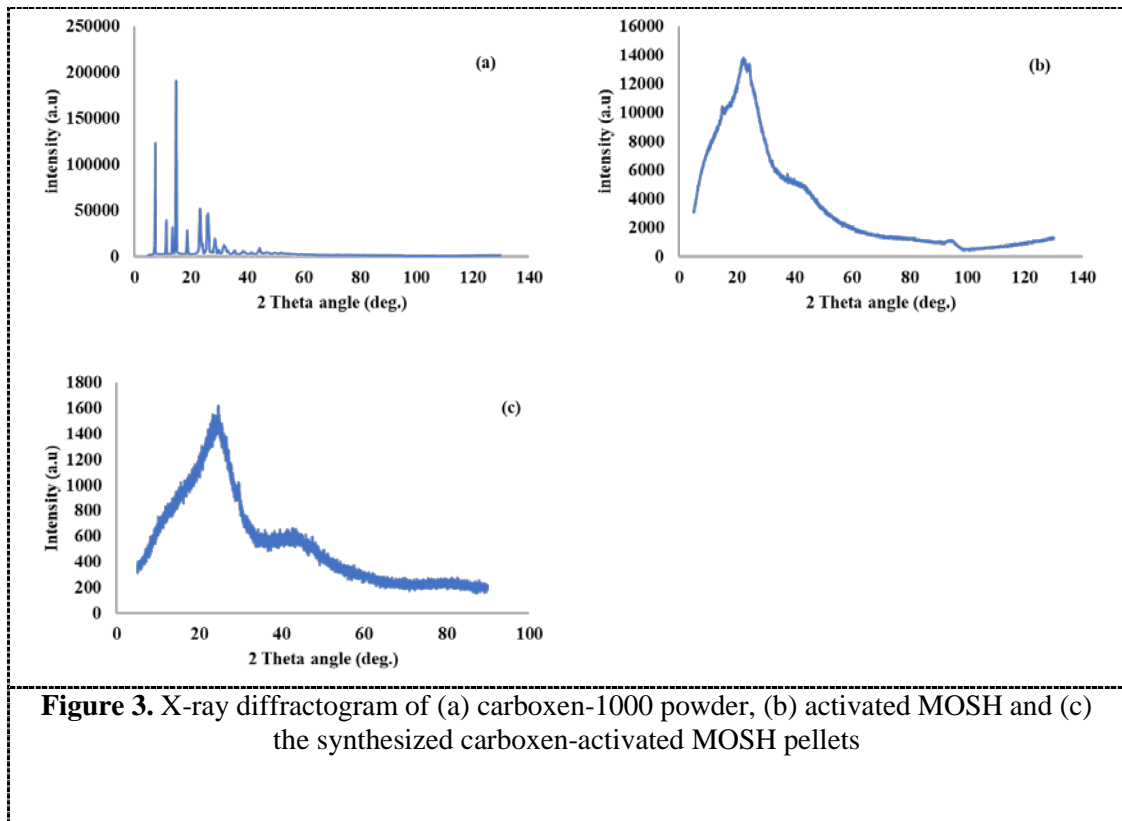
3.1.2. SEM analysis

The SEM micrograph of the synthesized biopolymer composite pellets is shown in Figure 2. The pellets, as seen in the image, had a heterogeneous morphology with some well-defined pores. Because of their high porosity, these pellets would therefore make excellent adsorbents according to Avci et al. (2018).



3.1.3. XRD analysis

The carboxen-1000 synthetic polymer structure (fig.3a) was very crystalline, as evidenced by the presence of sharp peaks, whereas the structure of activated MOSH (fig.3b) was amorphous. The biopolymer composite pellets structure had a few sharp peaks due to the presence of the very crystalline carboxen-1000 synthetic polymer, but their overall structure was amorphous, similar to that of the matrix, which was activated MOSH.



3.1.4. N₂-BET analysis

The N₂-BET method was used to study the micro and mesoporous structure of the pellets in a nitrogen environment. Table 1 compares the particulate structural properties of biopolymer composite pellets to those of neat pellets. The biopolymer composite pellets' higher specific surface area makes them suitable for the adsorption process (Ma et al., 2014).

Table 1. Results of the relative densities and micro hardness of sintered sample.

Sample	Specific surface area (m ² .g ⁻¹)	Total pore volume (cm ³ .g ⁻¹)	Average pore size (nm)
Neat activated MOSH pellets	1.403	0.027	2.259
5 wt.% carboxen-activated MOSH pellets	3.497	0.033	1.927

3.1.5. TGA analysis

TGA was used to investigate the thermal stability of the synthesized biopolymer composite pellets. Figures 4a and b show that the pellets degraded at high temperatures, indicating that they are very

thermally stable. The first (low) degradation stage occurred around 428 °C, followed by the second (large) degradation stage at 628 °C. A similar study (Moussout et al., 2016) found that the degradation of their adsorbents occurred at temperatures ranging from 500 to 600 °C, implying that these synthesized biopolymer composite pellets have greater thermal stability.

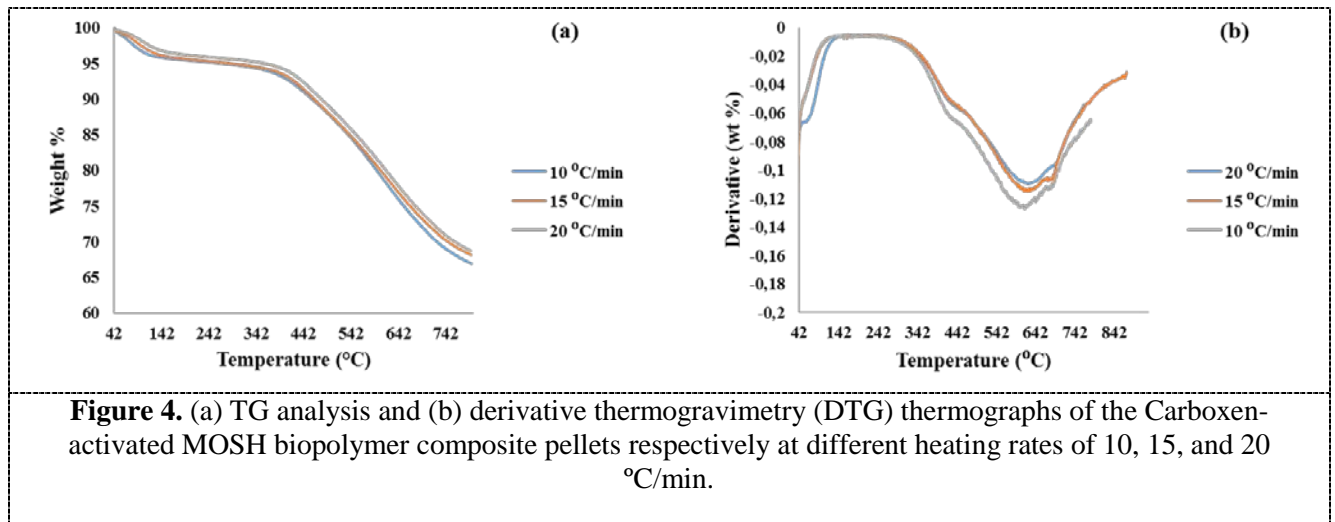


Figure 4. (a) TG analysis and (b) derivative thermogravimetry (DTG) thermographs of the Carboxen-activated MOSH biopolymer composite pellets respectively at different heating rates of 10, 15, and 20 °C/min.

3.2. Batch adsorption results

3.2.1. Effect of temperature

The effect of environmental temperature on the pellets was studied at various temperature. Figure 5 shows that the highest removal of BTE occurred at a temperature of 30 °C. Increasing the temperature from 25 to 30 °C increased the adsorption capacity from around 95 % to approximately 99 %. From 30 to 40 °C, the adsorption capacity decreased indicating that the adsorption process is exothermic (Albadarin et al., 2012).

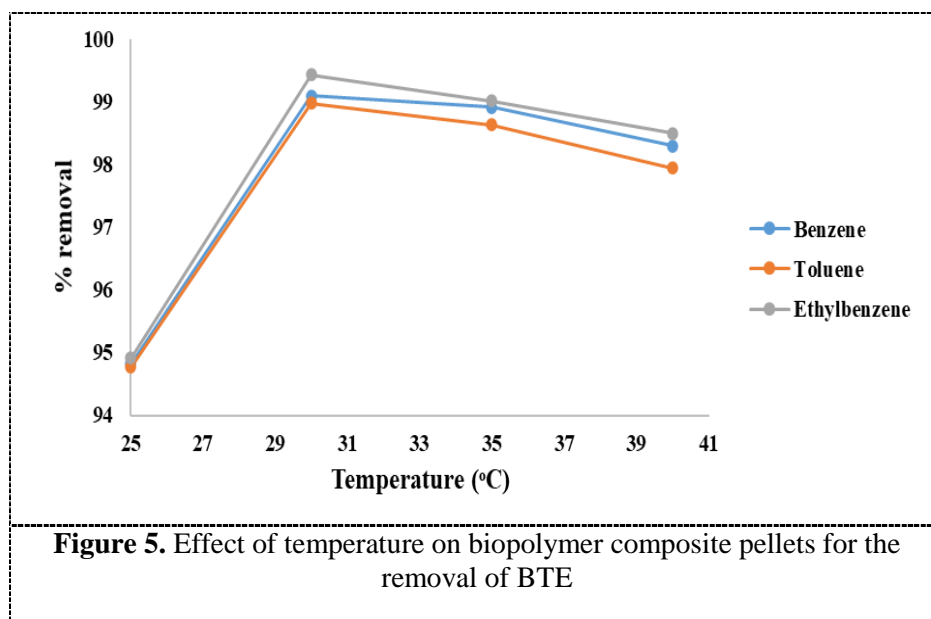


Figure 5. Effect of temperature on biopolymer composite pellets for the removal of BTE

3.2.2. Effect of time

Batch adsorption studies of BTE onto biopolymer composite pellets were carried out over a 4hr period at four different temperatures. After 3hrs, the highest removal rate was achieved.

The pellets were also regenerated and reused. It was found that they were mechanically stable and capable of removing more than 90 % BTE even after three cycles of use or three adsorption cycles.

4. Conclusion

Biopolymer composite pellets were synthesized and effectively tested for removing three selected toxic VOCs namely: benzene, toluene and ethylbenzene, from pharmaceutical effluents. Characterization results revealed that these pellets contained useful functional groups, which play an important role during the uptake of VOCs. It was also revealed that they had a high surface area and good pore distribution, which are both beneficial during adsorption process. The pellets were very efficient because after batch adsorption studies, it was shown that they were able to remove more than 98 % of BTE from the wastewater samples. In addition, these pellets are economically efficient since they can be regenerated and reused several cycles (at least 3 times) before they become exhausted.

References

- [1] Albadarin, A.B., Mangwandi, C., Ala'a, H., Walker, G.M., Allen, S.J. and Ahmad, M.N., 2012. Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. *Chemical engineering journal*, 179, pp.193-202.
- [2] Amann, A., de Lacy Costello, B., Miekisch, W., Schubert, J., Buszewski, B., Pleil, J., Ratcliffe, N. and Risby, T., 2014. The human volatilome: volatile organic compounds (VOCs) in exhaled breath, skin emanations, urine, feces and saliva. *Journal of breath research*, 8(3), p.034001.
- [3] Ambaye, T.G., Vaccari, M., van Hullebusch, E.D., Amrane, A. and Rtimi, S., 2021. Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. *International Journal of Environmental Science and Technology*, 18(10), pp.3273-3294.
- [4] Avci, G., Velioglu, S. and Keskin, S., 2018. High-throughput screening of MOF adsorbents and membranes for H₂ purification and CO₂ capture. *ACS applied materials & interfaces*, 10(39), pp.33693-33706.
- [5] Bezerra, C.D.O., Cusioli, L.F., Quesada, H.B., Nishi, L., Mantovani, D., Vieira, M.F. and Bergamasco, R., 2020. Assessment of the use of Moringa oleifera seed husks for removal of pesticide diuron from contaminated water. *Environmental technology*, 41(2), pp.191-201.
- [6] Ibrahim, N.A., Abdellatif, F.H., Hasanin, M.S. and Abdellatif, M.M., 2022. Fabrication, characterization, and potential application of modified sawdust sorbents for efficient removal of heavy metal ions and anionic dye from aqueous solutions. *Journal of Cleaner Production*, 332, p.130021.
- [7] Liew, R.K., Azwar, E., Yek, P.N.Y., Lim, X.Y., Cheng, C.K., Ng, J.H., Jusoh, A., Lam, W.H., Ibrahim, M.D., Ma, N.L. and Lam, S.S., 2018. Microwave pyrolysis with KOH/NaOH mixture activation: a new approach to produce micro-mesoporous activated carbon for textile dye adsorption. *Bioresource technology*, 266, pp.1-10.
- [8] Ma, Y., Zhou, Q., Li, A., Shuang, C., Shi, Q. and Zhang, M., 2014. Preparation of a novel magnetic microporous adsorbent and its adsorption behavior of p-nitrophenol and chlorotetracycline. *Journal of Hazardous Materials*, 266, pp.84-93.
- [9] Moussout, H., Ahlafi, H., Aazza, M. and Bourakhouadar, M., 2016. Kinetics and mechanism of the thermal degradation of biopolymers chitin and chitosan using thermogravimetric analysis. *Polymer Degradation and Stability*, 130, pp.1-9.