A Biopolymer-based Nanocomposite as a Multifunctional Sustainable Material for Water Pollutants Degradation

Anny Leudjo Taka*, Sandra Ngningone Obiang, Xavier Yangkou Mbianda, Michael Klink and Fanyana Mtunzi

***Abstract*—** Currently, the nanotechnology adsorption method is regarded as the most promising method for water decontamination. Among nanomaterials adsorbents, biopolymer-based nanocomposite materials have attracted significant research attention because they possess multifunctional properties beneficial for removing different types of pollutants from wastewater. Therefore, the main focus of this study is to synthesize and characterize a biopolymer-based nanocomposite, i.e., phosphorylated chitosan cross-linked multiwalled carbon nanotubes doped silver-titanium dioxide nanoparticles (pCh-MWCNTs@Ag-TiO_2). The biopolymer nanocomposite was synthesized using combined phosphorylation and cross-linking polymerization methods. Then, it was characterized using thermal gravimetric analysis, a range of spectroscopy, and microscopy techniques. The developed pCh-MWCNTs@Ag-TiO_2 will be used as a potential multifunctional nano-sorbents for the simultaneous removal of diverse pollutants from wastewater.

***Keywords*—** :Biopolymer, nanocomposite, nano-sorbents, phosphorylation, cross-linking polymerization**.**

I. INTRODUCTION

Water is essential in many aspects of human life such as health, food, economy and energy. However, the access to safe drinking water around the world and especially in southern Africa has been limited [1]. For instance, water scarcity due to climate change and its pollution by increase industrial activities, sewages and domestic wastes are currently the major concern. In order to resolve the issue, various water treatment techniques have been employed. Among these water treatment techniques, the nanotechnology adsorption method is currently regarded as the most promising method for water decontamination [1,2].

This nanotechnology adsorption method involves the use of nanomaterials as adsorbents. However some of these nanomaterials adsorbents are not used to their full potential, due to their specificity to certain type of pollutants and the surface area of the adsorbent material affecting the adsorption efficiency. Therefore, the challenge is to develop nanomaterial adsorbents with high adsorption efficiency and capable of removing various classes of pollutants including emerging pollutants from wastewater to accepted regulatory levels [3,4]**.**

In this perspective, biopolymer-based nanocomposite materials have attracted great research attention. They can be defined as polymer nanocomposites made of non or less toxic nanomaterials using naturally derived polymers such as chitosan (non-toxic, biodegradable, environmental green, and biocompatible) as polymer matrix [5–8]. These biopolymer-based nanocomposites are made of multi phases where one of the phases has nanoscale additives. They possess excellent multifunctional properties resulting from each component's combination. These excellent multifunctional properties are vital for their use in various applications and to remove also different types of pollutants including emerging pollutants from wastewater [9,10]**.**

Furthermore, these biopolymer-based nanocomposites can be synthesized using a variety of methods based on *ex-situ* or *in-situ* techniques. The *in-situ* technique is known as chemical methods (e.g., precipitation, reduction, impregnation, sol-gel, oxidation, cross-linking polymerization, and electrospinning method) and it refers to the direct production of the inorganic metal or metal oxide NPs in the polymer matrix solution used as a reaction medium.

On the other hand, the *ex-situ* technique is known as physical methods and requires first the preparation of the NPs, followed by their addition to the polymer matrix used as a dispersion medium. Among these two techniques, the *in-situ* technique is mostly recommended because it favors the polymer matrix (e.g., chitosan) to act both as a stabilizer or capping agent in order to prevent the agglomeration of NPs, control the size and the shape of the NPs during the preparation process [5,6,9,11]. Therefore,

Manuscript received March 15, 2022. This work was supported in part by the NRF Grants 120740.

A. Leudjo Taka was with the Institute of Chemical & Biotechnology, Vaal University of Technology, Southern Gauteng Science and Technology Park, Sebokeng Campus, 1983 and Department of Chemistry, Vaal University of Technology, Vanderbijlpark Campus South Africa.

Sandra Ngningone Obiang is with Department of Chemistry, Vaal University of Technology, Vanderbijlpark Campus South Africa.

X. Y. Mbianda is with the Department of Chemical Sciences, University of Johannesburg, Doornfontein, Johannesburg 2028 South Africa.

M. Klink is with the Department of Chemistry/Biotechnology, Vaal University of Technology, Vanderbijlpark Campus South Africa.

Fanyana Mtunzi is with the Institute of Chemical & Biotechnology, Vaal University of Technology, Southern Gauteng Science and Technology Park, Sebokeng Campus, 1983 and Department of Chemistry, Vaal University of Technology, Vanderbijlpark Campus South Africa.

the most significant contribution of this research study was to develop a simple on-pot synthesis using *in-situ* method to obtain phosphorylated chitosan cross-linked multiwalled carbon nanotubes doped silver-titanium dioxide nanoparticles (pCh-MWCNTs@Ag-TiO_2) to be used as a potential multifunctional nano-sorbents for the simultaneous removal of diverse pollutants from wastewater.

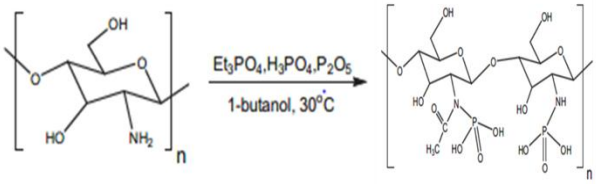
II. Experimental Methodology

A. Materials and Chemicals

MWCNTs (purity > 90%), Titanium tetraisopropoxide (TTIP), N,N Dimethylformamide (DMF, 99.9 %), Hexamethylene diisocyanate (HMDI, 98.0 %), raw chitosan, phosphoric acid (H_3PO_4, 85%), 1-butanol (99,8%), triethyl phosphate (Et_3PO_4), phosphorous pentoxide (P_2O_5), acetone were purchased from Sigma-Aldrich, South Africa. Silver nitrate (99.8 %), Sulfuric acid (H_2SO_4) 98,08% and nitric acid (HNO_3) 55% were obtained from Rochelle Chemicals, South Africa.

B. Synthesis of the biopolymer nanocomposites

Preliminary studies were first conducted such as phosphorylation of chitosan and functionalization of MWCNTs. The phosphorylation of chitosan was conducted as illustrated in scheme 1 and reported in previous literature [12]. On the other hand, the functionalization of MWCNTs to obtained oxidized MWCNTs (oxiMWCNTs) was achieved by acid treatment using a mixture of sulfuric and nitric acid (ratio = 3:1) as described in previous studies [13,14].



Scheme 1: Phosphorylation of chitosan [12].

The one-pot synthesis of the biopolymer nanocomposites by cross-linking polymerization was achieved as follow: 0.251g of phosphorylated chitosan (pCh) and 0,0140g of OxiMWCNTs (obtained in preliminary studies) were dispersed in 15 ml of DMF while stirring for 30 min under nitrogen gas and followed by the addition of the cross-linking agent HMDI (4ml) at room temperature to the reaction mixture. Then, the reaction temperature was increased to 60ºC and allowed to reflux for 24 h. After 24h, a solution mixture of TTIP (0.5 ml) and $AgNO_3$ (0.0128 g) (previously dispersed in 20 ml DMF) was added to the polymer solution (in the 3 necks round flask covered with a foil paper) while stirring under inert atmosphere. Then, the polymerization reaction was allowed to continue and reflux at 60ºC for 24h. After the 24 h, the polymerization reaction was stopped and the solution was allowed to age for 3 days; then an excess of acetone was added to the polymer solution in order to precipitate the product. To allow the complete precipitation reaction to occur, the solution was kept in the fridge for 24h. Finally, the solution was filtrated to recover the precipitate which was dried under vacuum. The product obtained was in good yield (3.87 g).

C. Characterization techniques

The developed biopolymer nanocomposite pCh-MWCNTs@Ag-TiO_2 and the intermediate product (pCh-MWCNTs) were characterized using thermal gravimetric analysis, BET method, Fourier-transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) spectroscopy.

III. Results and Discussion

The synthesized biopolymer nanocomposite pCh-MWCNTs physically appears as a light grey powder whereas pCh-MWCNTs@Ag-TiO_2 looks more as dark green crystals. FTIR analysis (Fig. 1) was conducted in order to confirm the different functional groups present on the surface of the polymers synthesized. The strong absorption band ranging from 3443 cm^{-1} to 3337 cm^{-1} can be assigned to O-H and N-H stretching vibrations. The peaks around 2933 cm^{-1} and 2860 cm^{-1} can be attributed to the asymmetric and symmetric C-H stretching in CH_2 bonded to oxygen. The peak between 2067 cm^{-1} and 2000 cm^{-1} correspond to the C-H bending vibrations in aromatic group. The C=O group of the carbamate linkage NH(CO) (which confirms the polymerization) was observed around 1685 cm^{-1} and 1530 cm^{-1}. The phosphate groups such as P=O stretch (1110 cm^{-1}) and P-O stretch (1090 cm^{-1}) were also observed. The peak observed at 1380 cm^{-1} corresponds to the Ti-O-C group in the pCh-MWCNTs@Ag-TiO_2 polymer. Furthermore, it is important to note that these electron rich functional groups are suitable for the chelation of metal cations, and removal of organic pollutants via various mechanism [2,13].

Fig. 2 illustrates the TGA curves of the developed biopolymer nanocomposites. TGA analysis was conducted to evaluate the thermal stability of the synthesized polymers. From the result obtained, three different parts of thermal decomposition can be noticed. The first thermal decomposition (from 50°C to 200°C) corresponds to the loss of moisture or water and solvents present in the biopolymer nanocomposites prepared. Then, the second part, from 250°C to below 400°C, can be assigned to the decomposition of the carbamate groups in the polymer. Finally, the third thermal decomposition (400°C to above) can be ascribed to the decomposition of the MWCNTs present in the polymers and the complete decomposition of the chitosan polymer skeleton.

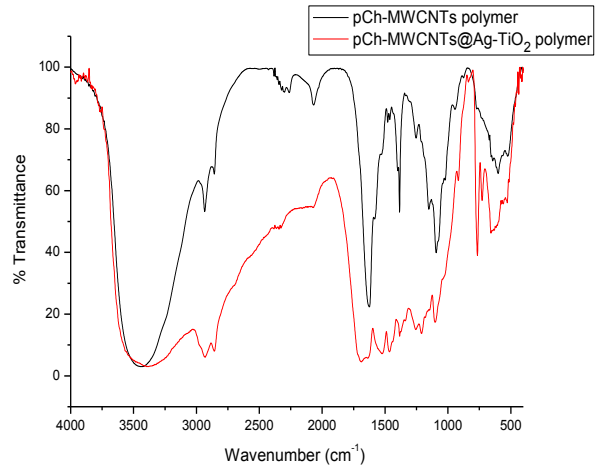


Fig.1. FTIR spectra of the synthesized biopolymer nanocomposites

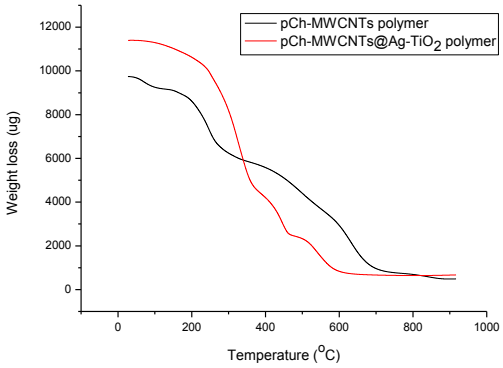


Fig. 2. TGA curves of the developed biopolymer nanocomposites.

Table 1 presents the BET results of the biopolymer nanocomposites prepared. BET analysis was done to determine the surface area and the pore size of the developed polymers. In general, from the results obtained, the surface area of the biopolymer nanocomposites synthesized were low; this could be due to the harsh degassing conditions used before BET analysis. These harsh degassing conditions could have affected the materials, hence resulting to a low surface area. However, the surface area of pCh-MWCNTs polymer was the highest.

Fig. 3. shows the XRD patterns of the biopolymer nanocomposites synthesized. XRD analysis was conducted in order to confirm the purity and the crystallinity of the polymer prepared. From the results observed, we can clearly see that the major peaks obtained are broad amorphous peaks. Only few crystalline peaks were observed on the XRD patterns of the pCh-MWCNTs polymer and phosphorylated chitosan. Therefore, one can confirm that chitosan is a semi-crystalline polymer; however, the crystallinity in the polymer chain of chitosan is destroy when chitosan is further modified (functionalized) with additional nanomaterials.

Fig. 4 and Fig. 5 present the SEM micrographs and the EDS spectra of the biopolymer nanocomposites prepared. From the pictures obtained, the surface morphologies of these biopolymer nanocomposites look like a porous and sponge material. In addition, the EDS spectra obtained confirm the elemental composition of the synthesized biopolymer nanocomposites.

TABLE I: RESULTS SUMMARY OF THE BET SURFACE AREA ANALYSIS

Nano-sorbent Polymers	Surface Area (m^2 / g)	Pore size (nm)
pCh-MWCNT@Ag-TiO_2	0.5784	1811.7
pCh-MWCNT	7.4696	15688

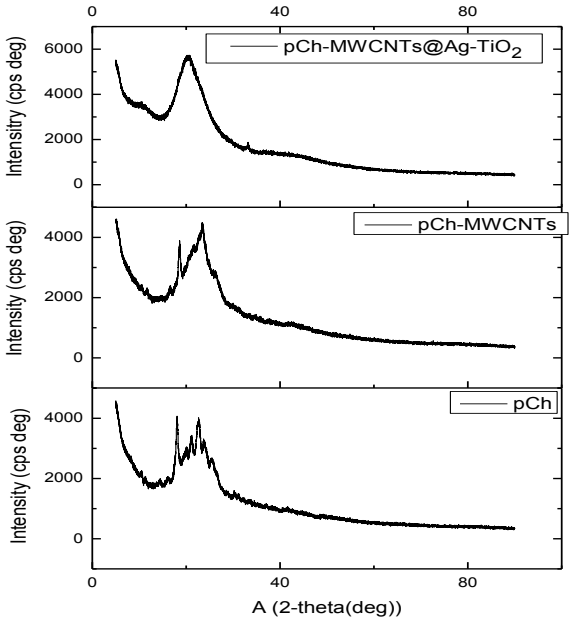


Fig. 3. XRD patterns of the polymers prepared.

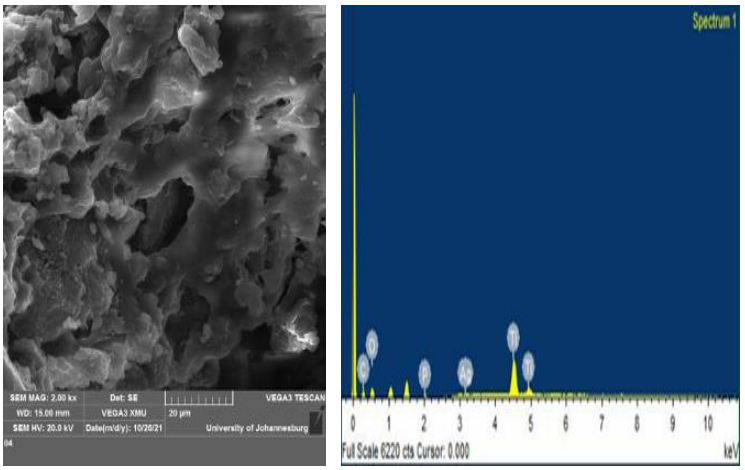


Fig. 4. SEM and EDS spectrum of pCh-MWCNTs@Ag-TiO_2 biopolymer nanocomposite.

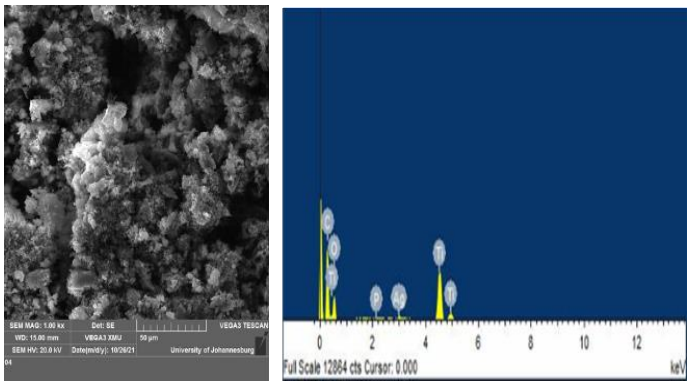


Fig. 5. SEM and EDS spectrum of pCh-MWCNTs biopolymer nanocomposite.

IV. Conclusion and Future Work

The developed pCh-MWCNT@Ag-TiO_2 biopolymer nanocomposite was successfully synthesized, characterized and has demonstrated good characteristic properties. The developed pCh-MWCNTs@Ag-TiO_2 will be used as a potential multifunctional nano-sorbents for the simultaneous removal of diverse pollutants from wastewater in our future work.

Acknowledgment

The National Research Foundation (NRF) and the Vaal University of Technology for their financial supports. The University of Johannesburg is gratefully appreciated for the analytical facilities to this work. The God Almighty for knowledge and wisdom.

References

[1] A. Leudjo Taka, K. Pillay, X. Mbianda Yangkou, Nanosponge cyclodextrin polyurethanes and their modification with nanomaterials for the removal of pollutants from waste water : A review, Carbohydr. Polym. 159 (2017) 94–107. https://doi.org/10.1016/j.carbpol.2016.12.027

[2] A. Leudjo Taka, E. Fosso-kankeu, K. Pillay, X.Y. Mbianda, Removal of cobalt and lead ions from wastewater samples using an insoluble nanosponge biopolymer composite : adsorption isotherm, kinetic, thermodynamic, and regeneration studies, Environ. Sci. Pollut. Res. 25 (2018) 21752–21767. https://doi.org/10.1007/s11356-018-2055-6

[3] E. Fosso-kankeu, H. Mittal, F. Waanders, S. Sinha, Thermodynamic properties and adsorption behaviour of hydrogel nanocomposites for cadmium removal from mine effluents, J. Ind. Eng. Chem. 48 (2017) 151–161. https://doi.org/10.1016/j.jiec.2016.12.033

[4] A. Leudjo Taka, E. Fosso-Kankeu, K. Pillay, X. Yangkou Mbianda, Metal nanoparticles decorated phosphorylated carbon nanotube/cyclodextrin nanosponge for trichloroethylene and Congo red dye adsorption from wastewater, J. Environ. Chem. Eng. 8 (2020) 1–11. https://doi.org/10.1016/j.jece.2019.103602

[5] A. Leudjo Taka, E. Fosso-Kankeu, E.B. Naidoo, X. Yangkou Mbianda, Recent development in antimicrobial activity of biopolymer-inorganic nanoparticle composites with water disinfection potential: a comprehensive review, Environ. Sci. Pollut. Res. 28 (2021) 26252–26268. https://doi.org/10.1007/s11356-021-13373-z

[6] A. Leudjo Taka, M.J. Klink, X. Yangkou Mbianda, E.B. Naidoo, Chitosan nanocomposites for water treatment by fixed-bed continuous flow column adsorption: A review, Carbohydr. Polym. 255 (2020) 117398. https://doi.org/10.1016/j.carbpol.2020.117398

[7] Z. Moridi, V. Mottaghitalab, A.K. Haghi, A Detailed review of recent progress in carbon nanotube/ chitosan nanocomposites, Cellul. Chem. Technol. 45 (2011) 549–563.

[8] F. Mohammad, H.A. Al-lohedan, H.N. Al-haque, C. Chitosan-mediated fabrication of metal nanocomposites for enhanced biomedical applications, Adv. Mater. Lett. 8 (2017) 89–100. https://doi.org/10.5185/amlett.2017.6925

[9] M. Alsuhybani, A. Alshahrani, A.S. Haidyrah, Synthesis, characterization, and evaluation of evaporated casting MWCNT/Chitosan composite membranes for water desalination, J. Chem. 2020 (2020) 1–9. https://doi.org/10.1155/2020/6661196

[10] W.S. Wan Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: A review, Carbohydr. Polym. 83 (2011) 1446–1456. https://doi.org/10.1016/j.carbpol.2010.11.004

[11] J. Yang, B. Hou, J. Wang, B. Tian, J. Bi, N. Wang, X. Li, X. Huang, Nanomaterials for the removal of heavy metals from wastewater, Nanomaterials. 9 (2019) 1–39. https://doi.org/10.3390/nano9121698

[12] K. Wang, Q. Liu, Chemical structure analyses of phosphorylated chitosan, Carbohydr. Res. 386 (2014) 48–56. https://doi.org/10.1016/j.carres.2013.12.021

[13] A. Leudjo Taka, K. Pillay, X.Y. Mbianda, Synthesis and characterization of a novel bio nanosponge filter (pMWCNT-CD/TiO2-Ag) as potential adsorbent for water purification, in: P. Ramasami, M.G. Bhowon, S.J. Laulloo, H. Li, K. Wah (Eds.), Emerg. Trends Chem. Sci., © Springer International Publishing AG, 2018: pp. 313–343. https://doi.org/10.1007/978-3-319-60408-4_18

[14] M.A.M. Motchelaho, H. Xiong, M. Moyo, L.L. Jewell, N.J. Coville, Effect of acid treatment on the surface of multiwalled carbon nanotubes prepared from Fe-Co supported on CaCO3: Correlation with Fischer-Tropsch catalyst activity, J. Mol. Catal. A Chem. 335 (2011) 189–198. https://doi.org/10.1016/j.molcata.2010.11.033

Dr. Anny Leudjo Taka was born in Douala, Cameroon. She completed and received her BSc. Degree in chemical Sciences, BSc. Degree Honours, MSc. Degree and Ph.D. in Chemistry at the University of Johannesburg. She is currently a postdoctoral researcher in the Department of Chemistry, Vaal University of Technology. Her research interests lie in the synthesis & characterization of multifunctional novel carbon-based nanobiocomposites, and nanocomposites as nanosponge filters for water purification.