Sol-gel Preparations of ZnO/SnO_2 Composite Photocatalysts Applied for the Degradation of PAH's under Visible Light

Nthambeleni Mukwevho, Elvis Fosso-Kankeu*, Frans Waanders, John Bunt, Dewald de Bruyn, Neeraj Kumar and Suprakas Sinha Ray

***Abstract*— Wastewater treatment challenges faced by conventional methods have necessitated the need for alternative/complementary methods that are environmentally benign and efficient especially toward recalcitrant organic pollutants. In this regard, ZnO/SnO_2 composite photocatalysts were synthesized using sol-gel method and employed in the photocatalytic degradation of Phenanthrene, benzo(a)pyrene and naphthalene, typical PAH's in water solution. The photocatalyst material was characterized with scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) to confirm the properties of the nanocomposite. The photocatalytic degradation activities of these nanocomposites towards phenanthrene, naphthalene and Benzo(a)pyrene were then investigated by measuring the effects irradiation time. In addition, the first-order kinetic model was used to determine the rate constant for the degradation reaction. The photocatalytic degradation data exhibited a trend fitting the pseudo first-order kinetics as defined by the Langmuir-Hinshelwood model, which allowed prediction of the faster degradation rate by the ZnO/SnO_2 nanohybrid (NH).**

***Keywords*- :** *Photocatalyst, Polycyclic aromatic hydrocarbons, composite*

I. INTRODUCTION

Prior to the widespread use of natural gas, manufactured gas plants (MGPs) supplies gaseous fuel derived from coal, coke and/or oil [1;2]. A major by-product of manufactured gas processes is coal tar, which today is often associated with subsurface contamination at former MGP sites [2]. Coal tars are denser than water nanoqueous phase liquids, primarily composed of polycyclic aromatic hydrocarbons [3]. Naphthalene is often the most abundant PAH compound in such coal tars. One of the main disease caused by PAHs viz naphthalene is hemolytic anemia in children [4, 5; 6]. Benzo[a]pyrene which has been found to be persistent organic toxin, is of environmental worry due to its known cancer-causing nature and bioaccumulation potential [7]. Pure, safe and satisfactory freshwater is essential to every single living organism and normal functioning of ecosystems and communities [8-19]. Therefore, special methods which are cost effective and environmental friendly are required to degrade these organic pollutants in water. Numerous efforts have been focused on developing visible-light photoctalysts such as oxides (Cu_2O) [20], sulfides (SnS_2, Cds) [21], nitrides (g-C_3N_4) [10], composite metal oxides ($Gd_2O_2CO_3$.ZnO. CuO) [22] and Ag-based compounds (ZnO/Ag) [23]. Among them, Semiconductor photocatalysts have drawn much consideration due to their optical properties, Cheapness, long-term steadiness and resistance to photo-corrosion. Tin oxide has gotten a lot of attention as a photo anode in view of its great energy level position, high photoactivity, chemical stability and inexpensiveness [24]. The majority of the properties are beneficial for catalysis and detecting. The principal issue is its moderately extensive bandgap, ~3.5ev, which restricts its photo response to noticeable light, the second is quick recombination of electron-hole pairs in SnO_2 and the third is the challenge related to the reuse of powder photocatalyst [25]. To beat these constraints, different strategies have been utilized, such as doping transition metal ions, including Au, Ag, Fe and Mg or doping nonmetals such as S and N [26]. These days, doping of two kinds of molecules into SnO_2 or TiO_2 has pulled in significant interest, since it could result in a higher photocatalytic activity and enhanced characteristics compared with single-element doping into semiconductor oxides [27]. Among these materials, the ZnO-SnO_2 heterostructural nanomaterials attract much interest in particular due to the low cost of SnO_2 species and the compatibility of some specific crystallographic planes of SnO_2 and ZnO nanocrystals. When the ZnO-SnO_2 heterojunction is radiated by UV light with the photon energy higher or equal to

E. Fosso-Kankeu is with the Water Pollution Monitoring and Remediation Initiatives Research Group in the School of Chemical and Minerals Engineering of the North West University, South Africa.

F. Waanders is with the Water Pollution Monitoring and Remediation Initiatives Research Group in the School of Chemical and Minerals Engineering of the North West University, South Africa.

Nthambeleni Mukwevho is with the Water Pollution Monitoring and Remediation Initiatives Research Group in the School of Chemical and Minerals Engineering of the North West University, South Africa.

John Butn if with the Coal Group in the School of Chemical and Minerals Engineering of the North-West University, South Africa.

Neeraj Kumar is with the DST-CSIR National Centre for Nanostructured Materials, Council for Scientific and Industrial Research, Pretoria 0001, South Africa.

Suprakas S. Ray is with the DST-CSIR National Centre for Nanostructured Materials, Council for Scientific and Industrial Research, Pretoria 0001, South Africa.

the band gaps of ZnO and SnO_2, the photogenerated electrons can move to the C_B of SnO_2 and the photogenerated holes to the V_B of ZnO [28]. As a result, the formation of the ZnO-SnO_2 heterojunction could hinder the charge recombination and improve the photocatalytic efficiency [29]. The present study features a facile sol–gel synthesis route for the preparation of ZnO/SnO_2 photocatalysts. In this work, we have chosen naphthalene, phenanthrene and Benzo(a)pyrene as a test probes for remedial experiment. In addition, the functional behavior of the acquired hetero-catalyst in the photocatalytic degradation of naphthalene, phenanthrene and Benzo(a)pyrene is presented in detail. We gauged the photocatalytic properties of ZnO/SnO_2 heterocatalyst and compared it with pure ZnO catalyst. We believe our work can be a premise for further investigations and applications.

II. Materials And Methods

A. Preparations of photocatalysts

Zinc acetate dihydrate (Sigma–Aldrich) and tin chloride pentahydrate (Sigma–Aldrich) were used as starting materials. Methanol (Sigma–Aldrich) and 28% ammonium hydroxide solution (Fluka) were used as solvent and additive, respectively. All the chemical products were used as received without any further purification. The synthesis of the ZnO–SnO_2 mixed photocatalysts was carried out by slowly adding 0.1 M methanol solution of $Zn(CH_3COO)2{\cdot}2H_2O$, previously prepared at 70 °C under vigorous stirring, to a 0.1 M methanol solution of $SnCl_4{\cdot}5H_2O$ prepared in the same conditions. Tipically, 8.12g of $Zn(CH_3COO)_2{\cdot}2H_2O$ were dissolved in 370 mL of methanol and the amount of $SnCl_4{\cdot}5H_2O$ solution was opportunely determined in order to obtain powders ZnO/SnO_2. The obtained solutions were continuously stirred for 2 h, keeping the temperature at 70 °C. Then, the NH_4OH solution was added dropwise until pH reached the value of 8. The solutions became gels which were dried for 20 h at 110 °C to produce xerogels. Finally, the photocatalysts were obtained by calcining the xerogels for 2 h at 500°C. The pure ZnO was synthesized in the same way by using only the corresponding precursors.

B. Characterization of the composites

Various characterisation methods were conducted to determine if successful synthesis was achieved, and to determine the purity of the catalysts. The morphology of the catalysts was investigated and evaluated by utilising Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis or FTIR Spectroscopy, was used to determine the adsorption affinity and potential of each of the photocatalysts. A Perkin-Elmer Spectrum 100 spectrometer (USA) was used for the FTIR analysis utilising the KBr pellet method in the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}

C. Photodegradation experiment

The photocatalytic degradation of PAH's was investigated in a photocatalytic chamber using the prepared photocatalysts (vz, ZnO and ZnO/SnO_2). A UV filter was utilized to cut off wavelengths <400 nm. All experiments were performed by suspending the photocatalysts into the chamber containing PAH's solution (100 ppm), and the reactions were carried out at 25 °C. After the desired time interval (30 min), the concentrations of residual phenanthrene, Naphthalene and Benzopyrene in each solution were measured by recording the absorbance intensity of the solution at a maximum absorbance wavelength of 271 nm, 288 nm and 400 nm, respectively.

III. Results and Discussion

A. Structural and morphological characterization

Following preparation of the different photocatalysts, the functional groups present in the prepared samples were then examined by FTIR and the results are presented in Fig. 1. More specifically, in the spectrum of ZnO, the peak observed at the 2163 cm^{-1} wavelength could be due to the C=C vibration, resulting in a weak bond for the ranges between 2260 cm^{-1} and 2100 cm^{-1}. Peaks in the range between 665 and 950 cm^{-1} can be allocated to the N-H wagging, described as a strong broad band between these two wavelengths, which could be the result of the addition of NH_4OH during the synthesis process. The peaks at 1407 and 1556 cm^{-1} are the results of C-C stretching (in-ring) as well as a N-O asymmetric stretch respectively.

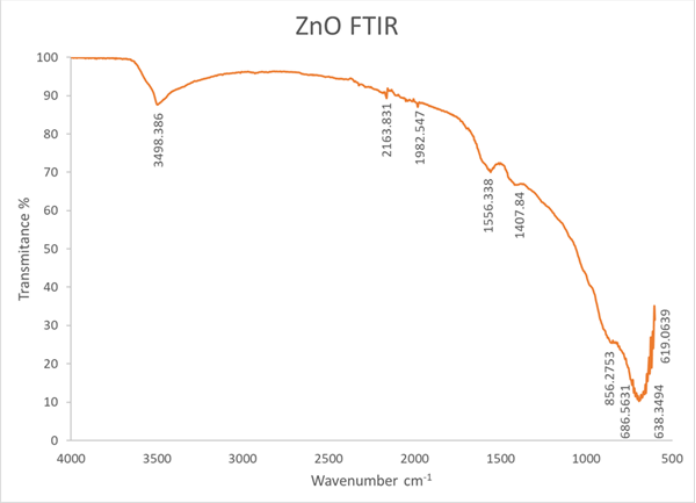


Fig 1. FTIR spectra of the ZnO photocatalyst.

In the case of the ZnO/SnO_2 heterocatalyst as shown in Fig 2, The peak seen at the 1733 cm^{-1} wavelength falls within the C=O stretching vibration, which is described as a strong bond, it can thus be said that the pure oxide has formed and in turn successful synthesis of a heterogenous catalyst was achieved. therefore, the infrared spectra indicate that the absorptions at 3469 cm^{-1} are evidently related to the presence of hydroxyl groups of water molecules on the outer surface of SnO_2 nanoparticles. In addition, the weak band at 633 cm^{-1} for ZnO-SnO_2 heterocatalyst is assigned to O–Sn–O.

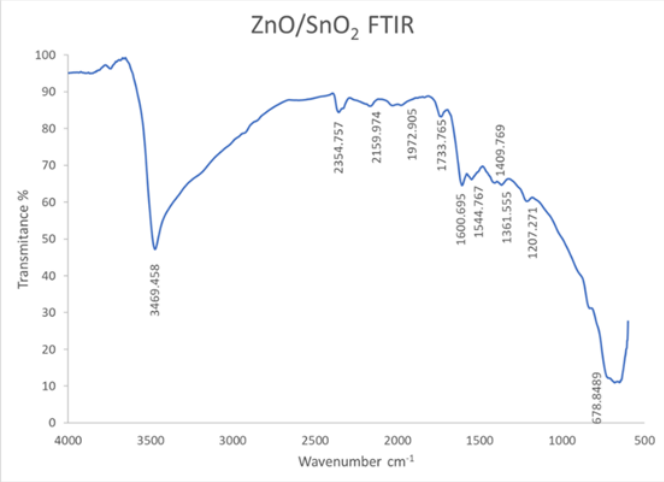
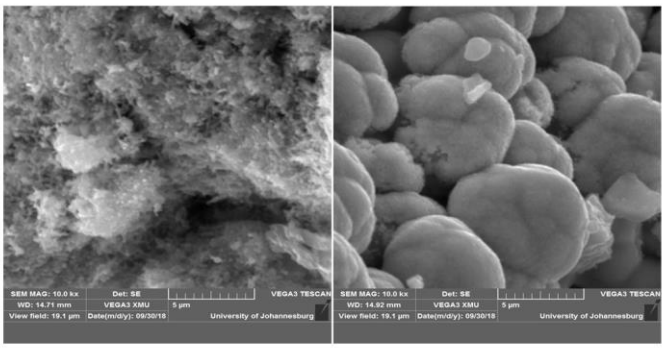


Fig 2. FTIR spectra of ZnO/SnO_2 photocatalyts.

The morphologies and sizes of ZnO NPs and ZnO/SnO_2 heterocatalyst were investigated by SEM. Typical SEM images of as-prepared ZnO NPs and ZnO/SnO_2 NH are displayed in Fig. 3. ZnO exhibited mixed morphologies of smaller nanoparticles (40-120 nm) and nanorods with ~6.5 µm length and 100-230 nm width (see Fig 3a). ZnO morphology appeared to be fibrous or crystalline due to the presence of acetate groups which are directing the growth of ZnO crystals. For ZnO/SnO_2, it can be clearly seen that the morphology is dominated by oval beads resulting from the gelation of SnO_2 NPs which entrapped ZnO crystals (see Fig 3b).



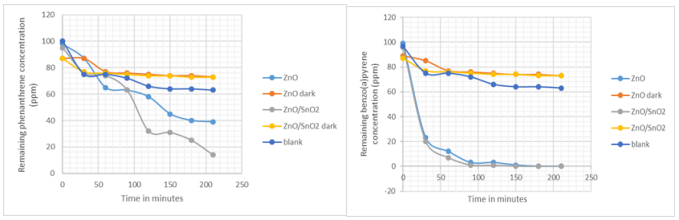
A) B)

Fig 3. SEM image of ZnO NPs(a), SEM image of ZnO/SnO_2 NH(b)

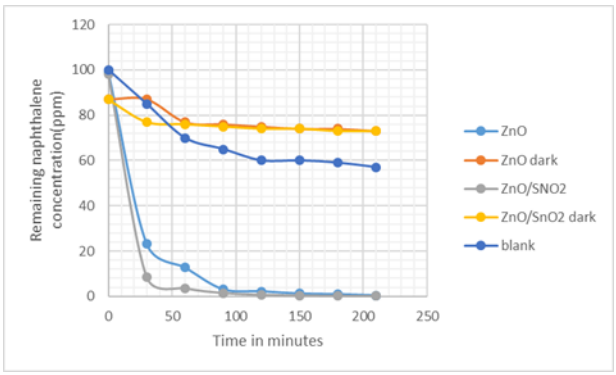
As shown in Fig. 3b, it can be concluded that the morphology of ZnO/SnO_2 particles was mainly influence by the formation of SnO_2 during the synthesis.

B. Evaluation of the photocatalytic activities of the prepared photocatalysts

The photocatalytic activity of the synthesized photocatalysts were evaluated through degradation of phenanthrene, benzo(a)pyrene and naphthalene under visible light in a chamber. It is clear from the results that pure oxide showed less degradation as compared to the heterocatalyst (see fig 4). As shown in Fig. 4(a-c), the rate of PAH's degradation increased with time due to the adsorption of PAH's molecules on the catalyst surface and their subsequent degradation. However, in the absence of visible light or a catalyst, no significant degradation of PAH's was observed, thereby indicating that phenanthrene, benzo(a)pyrene and naphthalene are relatively stable under the above mentioned conditions. These results confirm that both visible light and a photocatalyst are required for the effective degradation of above mentioned PAH's.



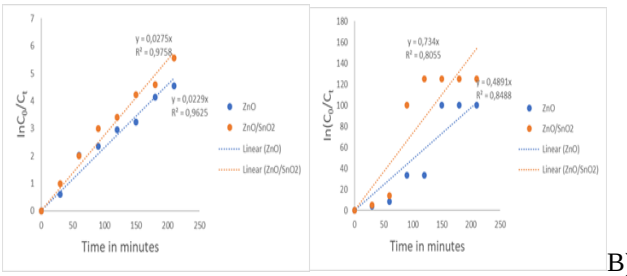
A) B)



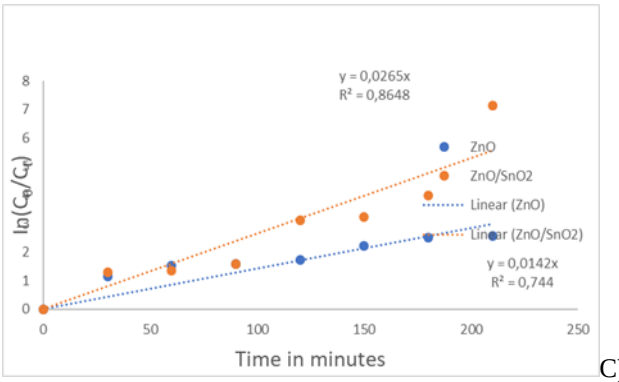
C)

Fig 4. Photocatalytic activity of (a) Phenanthrene, (b) Benzo(a)pyrene, and (c) Naphthalene,

It was additionally discovered that the underlying photodegradation rate was high because of the accessibility of various dynamic synergist sites. The exposure of phenanthrene, benzo(a)pyrene and naphthalene to ZnO resulted in the decrease of their concentrations to 39, 0 and 0.37ppm respectively, while ZnO/Sno_2 heterocatalyst degraded phenanthrene, benzo(a)pyrene and naphthalene to concentrations as low as 14, 0 and 0ppm respectively, subsequently showing that the ZnO/SnO_2 is the most effective photocatalyst for PAH's degradation in a solution under the condition utilized in this study. In fact, when the ZnO/SnO_2 NH was utilized, total naphthalene and benzo(a)pyrene removal was achieved within 120 min. Phenanthrene appeared as a recalcitrant PAH to degrade in a solution under the above conditions (see Fig 4(a).



A) B)



C)

PAH's	Photocatalysts		R^2	$Kmin^{-1}$	(ppm)
Naphthalene	ZnO		0.9625	0.0229	0.37
	ZnO/SnO_2		0.9758	0.0275	0
Benzo(a)pyrene	ZnO	0.8488	0.489	0	
	ZnO/SnO_2	0.8055	0.734	0	
Phenanthrene	ZnO	0.744	0.0142	39	
	ZnO/SnO_2	0.8648	0.0265	14	

D)

Fig 5. Degradation kinetics of (a)Naphthalene, (b) Benzo(a)pyrene (c) Phenanthrene (d) table of remaining concentration of PAHs and rate constants.

Photodegradation kinetics followed the Langmuir-Hinshelwood (L-H) model (Fig. 5) [30], The reaction rate is dependent on the concentration of the pollutant according to the equation below:

$$\frac{dc}{dt} = \frac{kK_{PAH'S}C_0}{1 + K_{PAH'S}C_0} \quad (2)$$

$$\ln(C_0/C_t) = kK_{PAH'S}t \quad (3)$$

$$\ln(C_0/C_t) = K_{app}t \quad (4)$$

where K_PAH'S represents the adsorption coefficient of PAH'S on the photocatalyst (L.mg−1), while K_app represents the calculated apparent rate constant (min−1), and t is the reaction time (min). As shown in Fig. 5, plots of ln (C0⁄Ct) vs. t gave a linear relationship, thereby indicating that the kinetics data fit well with pseudo first order kinetics. The rate constant of pure ZnO photocatalyst was lower than that of the heterocatalyst when degrading all PAH's. These results indicate that the photocatalytic degradation activity of ZnO NC was extremely low under visible light, potentially due to its high recombination rate of photogenerated charge carriers.

IV. Conclusion

In summary, we have successfully prepared the ZnO/SnO_2 composite photocatalyst via a simple, inexpensive sol-gel method. The photocatalytic experiment indicated that the composite used in this paper was effective for the degradation of PAH's employed herein. Up to 100 ppm concentration of naphthalene and benzo(a)pyrene was removed within 120 min under visible light. From the results above, Photodegradation kinetics followed the Langmuir-Hinshelwood. The composite used in this study is simple and cost effective and might have successful application for treatment of wastewaters.

Acknowledgement

The authors are grateful to the sponsor from the North-West University and the National Research Foundation (NRF) in South Africa. Any opinion, findings and conclusions or recommendations expressed in this material are those of the authors and therefore the NRF does not accept any liability in regard thereto. The contributions of Mr E. Kalenga and Ms N. Baloyi from the University of Johannesburg in South Africa are really appreciated by the authors.tao

References

[1] Brian L. M, Taryn S, Walter J. S (2007). Manufactured Gas Plants—Processes, Historical Development, and Key Issues in Insurance Coverage Disputes. Environmental Forensics, 6:161–173,

[2] Palanisami T, Mallavarapu M, Krishnamurti G.S.R, Ross M, Ravi N (2011). Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: Implications to bioremediation. Environmental international.37:184-189 https://doi.org/10.1016/j.envint.2010.08.017

[3] Khethane T.C, Fosso-Kankeu E, Waanders F, Bunt J (2017) PAHs content of tar produced from Fischer assay of medium rank C bituminous South African coal. 9th Int'l Conference on Advances in Science, Engineering, Technology & Waste Management (ASETWM-17). 27-28 November 2017, Parys, South Africa. Editors: F. Waanders, E. Fosso-Kankeu, B. Topcuoglu, M. Plaisent, Y. Thaweesak. ISBN: 978-81-934174-6-1. Pp. 161-164.

[4] Haritash A.K, Kaushik C.P (2009). Biodegradation aspects of polycyclic aromatic hydrocarbons: A review. Journal of Hazardous material. 169: 1-15 https://doi.org/10.1016/j.jhazmat.2009.03.137

[5] Kim K, Shamin A.J, Ehsanul K, Richard J.C (2013). A review of airbone polycyclic aromatic hydrocarbons and their human health effects. Environment international.60:71-80. https://doi.org/10.1016/j.envint.2013.07.019

[6] Atif K, Alessandra C, Tania M, Riffat N. M (2015). A review of PAH exposure from the combustion of biomass fuel and their less surveyed effect on the blood parameters. Environmental science and pollution research.22:4076-4098. https://doi.org/10.1007/s11356-014-3748-0

[7] Rentz J.A, Alvarez J.J.P, Schnoor J.L (2008). Benzo[a]pyrene degradation by Sphingomonas yanoikuyae JAR02. Environmental Pollution. 151: 669-677. https://doi.org/10.1016/j.envpol.2007.02.018

[8] E. Fosso-Kankeu, A. Mulaba-Bafubiandi, B.B. Mamba, T.G. Barnard, Mitigation of Ca, Fe, and Mg loads in surface waters around mining areas using indigenous microorganism strains. Journal of Physics and Chemistry of the Earth, Vol. 34, pp. 825-829, 2009. https://doi.org/10.1016/j.pce.2009.07.005

[9] E. Fosso-Kankeu, H. Du Preez, P. Jagals, The health implication of relationships between bacterial endotoxin, cyanobacteria, coliforms and water stored in domestic containers of rural

households in South Africa. Journal of Water and Health, Vol. 8, no. 4, pp. 601-610, 2010.
https://doi.org/10.2166/wh.2010.094

[10] E. Fosso-Kankeu, A. Mulaba-Bafubiandi, B.B. Mamba, L. Marjanovic, T.G. Barnard, A comprehensive study of physical and physiological parameters that affect biosorption of metal pollutants from aqueous solutions. Journal of Physics and Chemistry of the Earth, Vol. 35, pp. 672-678, 2010.
https://doi.org/10.1016/j.pce.2010.07.008

[11] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, B.B. Mamba and T.G. Barnard, Prediction of metal-adsorption behaviour in the remediation of water contamination using indigenous microorganisms. Journal of Environmental Management. Vol. 92, no. 10, pp. 2786-2793, 2011.
https://doi.org/10.1016/j.jenvman.2011.06.025

[12] H. Mittal, E. Fosso-Kankeu, Shivani B. Mishra, Ajay K. Mishra, Biosorption potential of Gum ghatti-g-poly (acrylic acid) and susceptibility to biodegradation by B. subtilis. International Journal of Biological Macromolecules. Vol. 62, pp. 370-378, 2013.
https://doi.org/10.1016/j.ijbiomac.2013.09.023

[13] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, T.G. Barnard, Establishing suitable conditions for metals recovery from metal saturated Bacillaceae bacterium using experimental design. International Biodeterioration and Biodegradation. Vol. 86, pp. 218-224, 2014.
https://doi.org/10.1016/j.ibiod.2013.09.022

[14] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi and T.G. Barnard, Clayey materials in river basin enhancing microbialogical contamination of river water. Journal of Physics and Chemistry of the Earth. Vol. 67-69, pp. 236-241, 2014.
https://doi.org/10.1016/j.pce.2013.10.001

[15] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, Implication of plants and microbial metalloproteins in the bioremediation of polluted waters. Journal of Physics and Chemistry of the Earth. Vol. 67-69, 242-252, 2014.
https://doi.org/10.1016/j.pce.2013.09.018

[16] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, Challenges in the escalation of metal-biosorbing processes for water treatment: applied and commercialized technologies. African Journal of Biotechnology. Vol. 13, no. 17, pp. 1756-1771, 2014.
https://doi.org/10.5897/AJB2013.13311

[17] E. Fosso-Kankeu, H. Mittal, S.B. Mishra, A.K. Mishra, Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes. Journal of Industrial and Engineering Chemistry. Vol. 22, pp. 171-178, 2015.
https://doi.org/10.1016/j.jiec.2014.07.007

[18] E. Fosso-Kankeu, H. Mittal, F. Waanders, S.S. Ray, Thermodynamic properties and adsorption behaviour of hydrogel nanocomposites for cadmium removal from mine effluents. Journal of Industrial and Engineering Chemistry. Vol. 48, pp. 151-161, 2017.
https://doi.org/10.1016/j.jiec.2016.12.033

[19] Santosh K, Christopher M.A. P, Mark A. I, Danielle V. J, Richard E. D, Martin C.R. C, Adam F. L (2016). Facile synthesis of hierarchical Cu2O nanocubes as visible light photocatalysts. Applied Catalysis B: Environmental. 189: 226–232
https://doi.org/10.1016/j.apcatb.2016.02.038

[20] Shaohua S, Xiaobo C, Feng R, Coleman X. K, Samuel S. M, Liejin G (2011). Solar light-driven photocatalytic hydrogen evolution over ZnIn2S4 loaded with transition-metal sulphides. Nanoscale Research Letters. 6:290
https://doi.org/10.1186/1556-276X-6-290

[21] Kumar S, Karthikeyan S, Lee F.E(2018). g-C3N4-Based Nanomaterials for Visible Light-Driven Photocatalysis. A review. Catalysts.1:1-74
https://doi.org/10.3390/catal8020074

[22] Mukwevho N, Fosso-kankeu E, Waanders F, Kumar N, Ray S.S, Mbianda X.Y(2018). Photocatalytic activity of Gd2O2CO3.ZnO.CuO nanocomposite used for the degradation of phenanthrene. SN Applied Sciences.

[23] Mukwevho N, Fosso-kankeu E, Waanders F, Kumar N, Ray S.S (2017). Synthesis and Properties of ZnO/Ag/Graphene Oxide Composites Photocatalyst. 9th Int'l Conference on Advances in Science, Engineering, Technology & Waste Management (ASETWM-17). 27-28 November 2017, Parys, South Africa. Editors: F. Waanders, E. Fosso-Kankeu, B. Topcuoglu, M. Plaisent, Y. Thaweesak. ISBN: 978-81-934174-6-1. Pp. 161-164.

[24] Fosso-Kankeu E, Waanders F, Geldenhuys M (2016). Impact of Nanoparticles Shape and Dye Property on the Photocatalytic Degradation Activity of TiO2. International Journal of Science and Research.5:528-535.

[25] Elsalamony R.A (2016). Advances in Photo-catalytic Materials for Environmental Applications. Research & Reviews: Journal of Material Sciences.4:26-50.

[26] Binas V, Venier D, Kotzias D, Kiriakidis G (2017). Modified TiO2based photocatalysts for improved air and health quality. Journal of Materiomics.3:3-16
https://doi.org/10.1016/j.jmat.2016.11.002

[27] Xu S and Wang Z.L (2011). One-Dimensional ZnO Nanostructures: Solution Growth and Functional Properties. Review article. Nano research
https://doi.org/10.1007/s12274-011-0160-7

[28] Mohamed M. R, Adel A. I, Osama I, Ibrahim I.A., Abdel-Hakim T. K (2014). Photocatalytic decomposition of dyes using ZnO doped SnO2 nanoparticles prepared by solvothermal method. Arabian Journal of Chemistry. 7: 71–77.
https://doi.org/10.1016/j.arabjc.2013.08.016

[29] Kumar N, Ray SS, Ngila JC (2017), Ionic liquid-assisted synthesis of Ag/Ag2Te nanocrystals via a hydrothermal route for enhanced photocatalytic performance, New J. Chem. 41: 14618-14626.
https://doi.org/10.1039/C7NJ03295A

Mukwevho Nthambeleni started work on the synthesis of nano-structural layered materials and their heterostructures/nanocomposites during his Masters as a chemical engineering student. These nanomaterials will be applied to find sustainable solutions for water purification. He now carries on this work as part of a PhD degree at the North West University under the tutelage of Professors Elvis Fosso-Kankeu, Frans Waanders, Neeraj Kumar and Suprakas Ray. Vhundikha.3@gmail.com