

Introduction

The fast and rapid growth of unwanted microbes distributed far and wide in the environment pose a threat to human health and other animals. These unwanted and harmful microbes grow and multiply in air, soil and water causing both environmental and health hazard. Water borne diseases alone account for millions of deaths annually worldwide [1]. Water borne transmission of parasitic protozoa has caused the eruption of almost two hundred human diseases in a span of just 7 years (2004-2010) [2]. The fast growing global population and contamination of water resources by human activities and/or industries poses a challenge in achieving clean, microbe-free water for drinking and other domestic purposes. Scientists worldwide believe that waterborne diseases are affecting both the developed and the developing nations [1-4]. Acquiring pure water free of contaminants and pathogens is a matter of concern which calls for new, effective and low cost water disinfection techniques.

Conventional disinfection mainly involves chlorination or ozonization. Another cheap alternative for disinfection is using direct sunlight (SODIS) (solar disinfection) [4]. But these methods face limitations like production of harmful by products, involving high cost, limited water volume and time consuming. In order to overcome these inadequacies, remarkable efforts have been carried out to develop more effective water disinfection methods than the conventional systems that will be environment friendly, cost effective and highly efficient [1-6]. Photocatalytic disinfection of water is gaining much interest as it involves three components that are individually harmless to the biological environment namely the photosensitizer, light and molecular oxygen [7].

Some organic and inorganic catalyst on light irradiation in presence of oxygen produce reactive oxygen species (ROS) like singlet oxygen, hydroxyl radical (superoxide anion) that are cytotoxic species and are capable of killing bacteria, fungi and viruses [1, 5, 6, 8, 9]. Not only disinfection, but these ROS can also cause the oxidation of unwanted contaminants present in water, thereby carrying out dual function of disinfection and decontamination [1, 10, 11, 12]. Organic dyes like methylene blue, rose bengal, porphyrins and phthalocyanines are used as photosensitizers [5, 8, 12] for water disinfection while common

inorganic catalysts are TiO₂, ZnO, ZnS, CdS, Fe₂O₃ and WO₃ [1, 8, 13, 14]. Among the inorganic semiconductors, TiO₂ is the most widely used in photocatalysis.

In consideration with the above theoretical evaluation, the PhD project is aimed at developing new organic materials that upon light irradiation are able to produce reactive oxygen species (ROS) especially singlet oxygen, which is responsible for destroying pathogens in contaminated water. The project is mainly carried out in the following steps:

- Immobilization of TPP (5-*p*-carboxyphenyl-10,15,20-triphenyl porphyrin) on solid supports :
 - Magnetic porphyrin nanoconjugate (SPION-TPP)
 - Polymeric porphyrin composite (PVC-TPP)
- Phototreatment of contaminated water using immobilized and free photosensitizers.
- Synthesis of expanded porphyrins and their characterization.

Photodynamic therapy undoubtedly is a potential technique for destruction of unwanted microbes. But analysing recovery and reusability of photosensitizers can be an important breakthrough in the field of photodisinfection.

Magnetic nanoparticles are not gaining the required attention in water photodisinfection although they are used to a greater extent for biomedical applications. Magnetic nanoparticles can prove to be potential carriers for photosensitizers as they allow to be recovered at the end of treatment and thereby reuse the photosensitizer. Here we report a successful immobilization of TPP on SPION and the evaluation of photodisinfection efficiency of the nanoconjugate.

Another support studied was a common polymer polyvinyl chloride (PVC). To our knowledge, PVC has not been used in the past as a support for photosensitizer. The study has proved that PVC can be a promising support for photosensitizers with high yield of singlet oxygen/ROS generation and significant toxicity against *S. aureus* in presence of light

Trial syntheses of new photosensitizers were performed to study the behaviour of expanded porphyrins. The desired characteristics can be tailored by choosing the right precursors with different functional groups in expanded porphyrins . The study performed has given an insight for future modelling of novel photosensitizers.

References

- [1] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco and W. Gernjak, "Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends," *Catalysis Today*, vol. 147, pp. 1-59, 2009.
- [2] S. Baldursson and P. Karanis, "Waterborne transmission of protozoan parasites: Review of worldwide outbreaks: An update 2004-2010," *Water research*, vol. 45, pp. 6603 -6614, 2011.
- [3] D. Schoenen, "Role of disinfection in suppressing the spread of pathogens with drinking water: possibilities and limitations," *Water Research*, vol. 36, pp. 3874-3888, 2002.
- [4] M. Muruganandham, R. P. S. Suri, Sh. Jafari, M. Sillanpää, G. J. Lee, J. J. Wu, and M. Swaminathan, "Recent developments in homogenous advanced oxidation processes for water and wastewater treatment," *International Journal of Photoenergy*, vol. 2014, article no. 821674, 21 pages, 2014.
- [5] G. Jori, M. Magaraggia, C. Fabris, M. Soncin, M. Camerin, L. Tallandini, O. Coppellotti and L. Guidolin, "Photodynamic inactivation of microbial pathogens: disinfection of water and prevention of water-borne diseases," *Journal of Environmental Pathology, Toxicology and Oncology*, vol. 30, no. 3, pp. 261-271, 2011.
- [6] M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, "Recent developments in photocatalytic water treatment technology: A review," *Water Research*, vol. 44, pp. 2997-3027, 2010.
- [7] T. Zhang, X. Wang, and X. Zhang, "Recent Progress in TiO₂-Mediated Solar Photocatalysis for industrial wastewater treatment," *International Journal Of Photoenergy*, Vol. 2014, Article ID 607954, 12 pages, 2014.
- [8] M. C. DeRosa and R. J. Crutchley, "Photosensitized singlet oxygen and its applications", *Coordination Chemistry Reviews*, vol. 233-234, pp. 351-371, 2002.
- [9] Ž. Lukšienė, "New Approach to Inactivation of Harmful and Pathogenic Microorganisms by Photosensitization," *Photosensitization:*

- An Overview, *Food Technology and Biotechnology* Vol. 43, no. 4, pp 411-418, 2005.
- [10] B. D. McGinnis, V. D. Adams, and E. J. Middlebrooks, "Evaluation Of Methylene Blue And Riboflavin For The Photosensitized Degradation Of Ethylene Glycol," *Environment International*, Vol. 25, No. 8, pp. 953-959, 1999.
- [11] P. Kluson, M. Drobek, S. Krejcikova, J. Krysa, A. Kalaji, T. Cajtham and J. Rakusan, "Molecular structure effects in photodegradation of phenol and its chlorinated derivatives with phthalocyanines," *Applied Catalysis B: Environmental* Vol. 80, pp. 321-326, 2008.
- [12] E. Alves, M. A.F. Faustino, M. G.P.M.S. Neves, Â. Cunha, H. Nadais, and A. Almeida, "Potential applications of porphyrins in photodynamic inactivation beyond the medical scope," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 22, pp. 34-57, 2015.
- [13] A. Mills and S. L. Hunte, "An overview of semiconductor photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 108, pp. 1-35, 1997.
- [14] O. Seven, B. Dindar, S. Aydemir, D. Metin, M. A. Ozinel, S. Icli, "Solar photocatalytic disinfection of a group of bacteria and fungi aqueous suspensions with TiO₂, ZnO and Sahara desert dust," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 165, pp. 103-107, 2004.
- [15] A. K. Benabbou, C. Guillard, S. Pigeot-Rémy, C. Cantau, T. Pigot, P. Lejeune, Z. Derriche and S. Lacombe, "Water disinfection using photosensitizers supported on silica," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 219 pp. 101-108, 2011.
- [16] A. K. Haylett, F. I. McNair, D. McGarvey, N. J. F. Dodd, E. Forbes, T. G. Truscott, J. V. Moore, "Singlet oxygen and superoxide characteristics of a series of novel asymmetric photosensitizers," *Cancer Letters* vol. 112, pp. 233-238, 1997.
- [17] I. J. Macdonald and T. J. Dougherty, "Basic principles of photodynamic therapy," *Journal of Porphyrins and Phthalocyanines*, vol. 5, pp. 105-129, 2001.
- [18] M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H.