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**A NOVEL APPROACH TO THE CONTROL OF *Aedes Aegypti*, A
VECTOR OF DENGUE FEVER AND POLLUTION ABATEMENT BY
THE USE OF PORPHYRIN DERIVATIVES**

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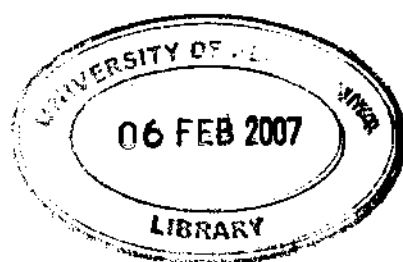
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A NOVEL APPROACH TO THE CONTROL OF *Aedes Aegypti*, A VECTOR OF DENGUE FEVER AND POLLUTION ABATEMENT BY THE USE OF PORPHYRIN DERIVATIVES

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The discharge of hazardous chemicals by the activities of mankind has been a serious threat to the environment. Among the pollutants, pesticides, coloured dyes and heavy metals are significant in terms of their detrimental consequences to living organisms. Therefore, the development of efficient and reliable techniques for the removal of these pollutants from the environment is essential. In the pollution abatement studies, it was demonstrated that porphyrin derivatives such as haematoporphyrin dihydrochloride (HPDHC) and protoporphyrin dimethylester (PPDME), in the presence of visible light and oxygen, could be utilized for the destruction of coloured organic dyes in aqueous media.

The visible light irradiation of oxygenated aqueous solutions of coloured dyes magenta (MaG), crystal violet (CrV) and hematoxylin in the presence of HPDHC or PPDME showed complete colour bleaching after 12 hours. The rate of photobleaching was found to be sensitive to the medium pH. At low pH (pH = 3.2), a higher oxidative degradation rate for MaG was observed in comparison to the low rate at pH 6.0. Analysis of photoproducts of MaG and CrV in acidic as well as basic media showed the formation of micromolar levels of NO_3^- ions resulting from the destruction of amine moieties of the dyes.

Photobleaching experiments were carried out in the presence of different quenchers such as 1,4-diazabicyclo[2.2.2]octane (DABCO) for singlet oxygen and 1,4-benzoquinone (BQ) for the superoxide anion ($\text{O}_2^{\cdot-}$). Only BQ was able to stop photobleaching suggesting that the photooxidation of these dyes are mainly caused by $\text{O}_2^{\cdot-}$, which is generated by an electron transfer from the excited sensitizer to ground state oxygen in the photosensitization process. The participation of singlet oxygen in dye destruction process is comparatively low.

Solubility of porphyrins in water is an essential requirement when they are used in aqueous medium. Water soluble cationic porphyrin derivatives 5,10,15,20-tetrakis(4-*N*-pentyl-pyridyl) porphyrin, $[(\text{TPePyP})\text{H}_2]^{4+}$, and its zinc analogue $[(\text{TPePyP})\text{Zn}^{II}]^{4+}$ were synthesized by introducing cationic pyridyl groups into the *meso* positions of the porphyrin core. Photobleaching studies carried out in aqueous solutions of varying pH show that, in the presence of oxygen, $[(\text{TPePyP})\text{H}_2]^{4+}$ undergoes fast photodegradation when the solution is irradiated with 560 nm light. The steady-state singlet oxygen quantum yields (Φ_Δ) measured in DMF for $[(\text{TPePyP})\text{H}_2]^{4+}$ and its Zn analogue were 0.80 and 0.85,



respectively. These values are in the same order of magnitude as those of well-known porphyrins such as HPDHC and PPDME.

The aggressive and destructive nature of $O_2^{\cdot-}$ towards most of the organic materials is an important advantage in pollution abatement. A method generally employed to indirectly test for $O_2^{\cdot-}$ is the study of a $O_2^{\cdot-}$ driven reaction in the presence of a scavenger like superoxide dismutase or benzoquinone. It was found that $O_2^{\cdot-}$ was effectively quenched when 1,2,3-triketohydrindene hydrate (NHy) was added to an oxygen-saturated solution, where $O_2^{\cdot-}$ is electrochemically generated at a glassy carbon electrode by applying a potential of -0.75 V vs Ag/AgCl wire. The suppression of the oxidation peak of $O_2^{\cdot-}$ with the addition of NHy in cyclic voltammetry was in close agreement with the results obtained in rotating ring disk voltammetric experiments. It was revealed that the decolouration of MaG by the $O_2^{\cdot-}$ produced by HPDHC in the presence of light in DMF was retarded in the presence of NHy.

The syntheses of porphyrin dyads in the combination of free-base and Zn porphyrin units with different redox potentials was attempted. In this respect, several porphyrin derivatives, *meso*-5-(4-hydroxyphenyl)-10,15,20-trisphenyl porphyrin (HPT_rPP), *meso*-5-(4-hydroxyphenyl)-10,15,20-tris(4-methoxy phenyl)porphyrin (HPT_rMPP), *meso*-5-(4-hydroxyphenyl)-10,15,20-tris(4-sulfonatophenyl)ammonium porphyrin [NH₄]₄[HPT_rSPP] and their Zn derivatives were synthesized and characterized by UV-Visible, ¹H NMR spectroscopy and cyclic voltammetry.

The porphyrin-sensitized photoinactivation of the 2nd and late 3rd instar larvae of the urban dengue mosquito *Ae. aegypti* was investigated as a novel approach in controlling the mosquitoes. In this study it was revealed that haematoporphyrin dimethylester (HPDME), HPDHC, PPDME and haematoporphyrin (HP) caused a high level of phototoxicity to the 2nd and late 3rd instar larvae of *Ae. aegypti* in Pyrex and clear plastic containers. In contrast, the mortality under natural conditions was less in coconut shells, tin caps and PVC gutters. Least larvicidal activity was observed in tires. These results suggest that the efficacy of mortality depends on the amount of light reaching the photosensitizer (this is maximum only in case of Pyrex glass and clear plastic containers), the nature of the surface of the container, the concentration of the sensitizer and unit volume per larvae.

Out of four sensitizers tested, a high level of larvicidal activity was observed with aqueous solutions of HP which showed the highest phototoxic effect at 2.5 ppm in laboratory experiments. Field experiments set up inside and outside houses also showed that a high larvicidal activity with HP (100% mortality in four days) in the presence of light (outside). Conversely, the mortality was less inside the houses (36.79 %).

The Phototoxic studies extended using HP and HPDHC towards other fresh water fauna, mayfly larvae, *Poecilia reticulata* (guppy) and *Bufo melanostictus* (tadpole) did not show any apparent toxic effect even after seven days at 100 ppm. This concentration is 40 times higher than that used in bringing about the effective killing of *Ae. aegypti* larvae. Based on field experiments as well as toxicity studies, both HP and HPDHC could be used effectively and safely to hasten the larval killing process, thus controlling the adult mosquito population.