



Research Article

Photodegradation of ibuprofen using 5-10-15-20-tetrakis(4-bromophenyl) porphyrin conjugated to graphene quantum dots

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ABSTRACT

Ibuprofen (IBU) is a common anti-inflammatory drug that is consumed by many individuals in the world. As such, analytical studies have detected high concentrations of the drug in many waterbodies, which poses a risk of harmful effects on the environment and public health. The hydroxyl radical technologies, a collective of techniques also known as advanced oxidation processes (AOPs), can be utilized to degrade this emerging pollutant. In this study, the photodegradation of ibuprofen using 5,10,15,20-tetrakis(4-bromophenyl) porphyrin conjugated to graphene quantum dots was investigated using a custom-built photoreactor. Three different concentrations of IBU (200, 300 and 500 μM) were utilized as initial concentrations. The pH of the IBU was varied between acidic (pH 3.0), natural (pH 5.0) and alkaline (pH 9.0) to note the effect on IBU degradation as a function of time. The Highest Φ_{Δ} was obtained for InTBrP-GDQs ($\Phi_{\Delta} = 0.80$), followed by InTBrP ($\Phi_{\Delta} = 0.74$). The photodegradation efficiency of the TBrP-GDQs and InTBrP-GDQs were determined to be 43.2 and 76.1% respectively.

1. Introduction

Over the last few years there has been a growing concern of emerging contaminants (ECs) being detected in surface, groundwater, wastewater effluents globally [1–3]. This is due to the inability of conventional wastewater treatment plants to effectively remove these ECs. Currently, to remove ECs from various water matrices techniques such as membrane technology, activated carbon adsorption, biological processes as well as advanced oxidation processes (AOPs) have been employed [4]. Of these techniques, AOPs is the most promising and is based on the *in-situ* generation of radicals such as hydroxyl ($\cdot\text{OH}$) and sulphate ($\text{SO}_4^{\cdot-}$) and typically utilizes light irradiation. In most AOPs applications semiconducting materials such as TiO_2 and ZnO have been extensively used, and recently the use of graphene quantum dots (GQDs) in AOPs applications has gained a lot of traction [5].

In this study, the use of metalloporphyrins (MPs) as photocatalysts in the degradation of ECs is investigated. Metalloporphyrins are biomimetic photocatalysts that possess large π -electron systems which results in high absorption in the visible light region and have been investigated in oxidation reactions [6–9]. The drawbacks of using

metalloporphyrins as homogeneous photocatalysts include difficulty in recovery and reuse, intermolecular self-oxidation, dimerization, or decomposition during the reaction and are easily deactivated [10–12]. To mitigate some of these limitations, metalloporphyrins can be immobilized on a solid surface; in the current study, we propose the use of graphene quantum dots (GQDs) as solid support to enhance both the photophysical and photocatalytic performance of the metalloporphyrins.

The 5,10,15, 20-tetrakis(4-bromophenyl) metalloporphyrins employed in this work is conjugated to the GQDs *via* non-covalent π - π interactions. The non-covalent interactions between GQDs and porphyrins undergoes rapid electron transfer. An indium-metalated derivative of the porphyrin was deployed because the presence of the heavy indium metal promotes intersystem crossing to the triplet state where singlet oxygen is generated [13]. Previously, Managa et al. [14] used a similar approach to immobilize pyrene-derivatized porphyrins on GQDs. While Lu et al. [12] functionalized GQDs with a zinc porphyrin (GQDs/ZnP) and used it as a photocatalyst for the degradation of methylene blue. In this work, the target pollutant is ibuprofen (IBU); which is an analgesic, anti-inflammatory and antipyretic drug that has

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