ABSTRACT

Pharmaceuticals are one of the persistent emerging contaminants which are ubiquitous in the aquatic environment due to their extensive applications as human and veterinary medicines. The ecotoxicity and microbial resistance are considered to be the major adverse environmental and health impact of pharmaceuticals even when present in trace amounts. The recalcitrant nature of these pollutants restrict the application of the conventional treatment system for their remediation, and this triggers extensive research on the various advanced oxidation processes (AOPs) as a promising treatment system. Among them, visible light assisted semiconductor driven photocatalysis has significant potential as an efficient, low-cost, and green technology, which can use even solar energy as a clean and sustainable light source.

A novel perovskite Bi_4NbO_8Cl (BNOC) nanosheet was synthesized by molten salt flux method and was employed in the photocatalytic degradation of tetracycline hydrochloride (TCH) and oxytetracycline (OTC), under visible Light Emitting Diode (LED) irradiation. A multivariate approach using response surface methodology (RSM) coupled with face-centered central composite design was performed to model and optimize the synthesis process parameters targeting the enhancement of degradation efficiency. The characterization of BNOC prepared at various synthesis conditions illustrated the interactive effect of the influencing parameters on their physicochemical properties. Bi_4NbO_8Cl nanosheet photocatalyst displayed 2.2 times higher degradation efficiency as compared to bulk Bi_4NbO_8Cl. The enhanced efficiency could be attributed to the increased surface area and reduced charge recombination rate. The effects of coexisting inorganic salts and real wastewater sources were also studied. A detailed study showed that a complex between Bi_4NbO_8Cl nanosheets and TCH led to TCH degradation by inducing strong visible-light absorption. The radical trapping experiments showed that $^{\bullet}O_2^-$ was primarily responsible for the degradation of TCH. Based on these findings, the photocatalytic mechanism was proposed. The inorganic ions like CO_3^{2-}, Cl^- and SO_4^{2-} were found to hinder the degradation efficiency of Bi_4NbO_8Cl nanosheets slightly. Efficiency of 95.9 % was achieved towards degradation of TCH present in a real wastewater sample. The photocatalyst had high mineralization efficiency and was found to be quite stable. This study proved that Bi_4NbO_8Cl

nanosheets possessed tremendous potential as a visible-light-reactive photocatalyst in prospective wastewater treatment applications.

A novel visible-light-responsive nano-composite photocatalyst of graphitic carbon nitride (g-C_3N_4) and Bi_4NbO_8Cl was synthesized hydrothermally and was termed as 2D/2D g-C_3N_4/Bi_4NbO_8Cl. The proportion of g-C_3N_4 added to Bi_4NbO_8Cl, was varied to achieve maximum photocatalytic efficiency towards OTC. It was observed that the photocatalytic efficiency of 20g-C_3N_4/Bi_4NbO_8Cl was maximum and about 1.2 and 1.8 times higher as compared to that of pure Bi_4NbO_8Cl and g-C_3N_4, respectively. This improved performance was attributed to the formation of type-II heterojunction, which resulted in better visible-light absorption and reduced recombination of photogenerated electron-hole pairs. Moreover, it was observed that after four cycles of degradation experiments, the nano-composite was stable. The results of this work not only demonstrate the construction of 2D/2D g-C_3N_4/Bi_4NbO_8Cl nano-composite for successful low-cost and energy-efficient photocatalytic degradation of recalcitrant pollutant but also motivate the production of similar photocatalysts targeting environmental remediation.

Keywords: Pharmaceutical pollutants, Tetracycline, Bi_4NbO_8Cl, g-C_3N_4/Bi_4NbO_8Cl, Type-II heterojunction, 2D/2D nano-composite, Phtotocatalysis, Visible-light photocatalyst, Advanced oxidation process (AOP), Multivariate optimization, Response surface methodology (RSM).