ABSTRACT

The occurrence of pharmaceuticals in the aqueous environment and their associated ecotoxicological effects raises global concern, which in turn promotes extensive research on pharmaceutical removal from wastewater. The present research stems from the necessity of the development of heterojunction photocatalysts and their subsequent application for photocatalytic degradation of pharmaceuticals from wastewater. An atomically thin sulfur-doped g-C_3N_4/ZnO (or SCZ) nanosheet was prepared using a facile synthesis method, and the major synthesis process parameters, viz. the S-C_3N_4 fraction for the zinc precursor and calcination temperature, were optimized targeting the ciprofloxacin removal. The multivariate optimization was performed through response surface methodology coupled with a face-centered central composite design. The characterization of the photocatalysts displayed that the variation of the process parameters has a significant impact on elemental composition, crystallinity, surface morphology, oxygen vacancies, and other physicochemical properties of the photocatalyst. The SCZ catalyst has been successful in ciprofloxacin removal and showed good energy efficiency, COD removal efficiency, and reusability. The presence of different ions and organics in water matrices and experimental conditions have significantly affected the ciprofloxacin removal. Superoxide radical was identified as the driving radical and was predominantly involved in ciprofloxacin degradation. The spent photocatalyst has also shown similar physicochemical properties as the pristine SCZ catalyst. Further, the powdered SCZ catalyst was immobilized on chitosan hydrogels (named SCZ-CH hydrogels), which facilitated their separation from the aqueous solution. SCZ-CH hydrogels also successfully degraded the ciprofloxacin from the wastewater. Pristine and used SCZ-CH hydrogels showed multifaceted physicochemical properties supporting their reactions with the ciprofloxacin molecules. SCZ-CH hydrogels also showed better energy efficiency, COD removal efficiency, and reusability.

Considering the enhanced performance of the SCZ catalyst and SCZ-CH hydrogels, both catalysts were used to degrade diclofenac and tetracycline and achieved a high degree of removal. Both catalysts showed better energy efficiency, COD removal efficiency, and reusability. The degradation pathways of diclofenac and tetracycline using both catalysts were delineated, which showed their reaction mechanisms and transformed product formation. The removal of co-existing pharmaceuticals was also successfully assessed. Further, the continuous photocatalytic reactor was developed to treat the synthetic and real wastewater in continuous mode, which was further modified using a biological reactor to deal with the highly polluted real wastewater originating from pharmaceutical industries and households. The watering of the plants using treated wastewater and inductively coupled plasma-mass spectroscopy (ICP-MS) were also carried out to assess the toxicity of the treated effluent and stability of the catalyst, respectively, which showed no effects on the plants and the presence of acceptable amounts of trace metals, respectively. Hence, the proposed catalysts and the photocatalytic systems could be potential sustainable measures for the treatment of micropollutants and other pharmaceuticals from wastewater at the field scale.

KEYWORDS: Advanced oxidation processes, Artificial neural network, Continuous and integrated photocatalytic systems, Degradation efficiency, Ecotoxicological effects, Heterojunction catalyst, Hydrogels, Immobilization, Industrial wastewater, Microscopy, Multivariate optimization, Pharmaceuticals, Photocatalysis, Sources and pathways, Spectroscopy, Sustainability, Toxicity analysis, Transformed products, Water matrices, Wastewater treatment