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Diclofenac degradation using mont-La (6%)-$Cu_{0.6}Cd_{0.4}S$ as photocatalyst under NUV–Vis irradiation. Operational parameters, kinetics and mechanism

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ABSTRACT

We report the aqueous photodegradation -under NUV–Vis radiation- of diclofenac, a common non-steroidal anti-inflammatory drug found to be persistent in the environment, using mont-La(6%)-$Cu_{0.6}Cd_{0.4}S$, a nanocomposite prepared by simple cation exchange and impregnation method. Operational parameters relevant for the process have optimized: amount of catalyst, dissolved oxygen concentration, initial diclofenac concentration and pH. Heterogeneous suspensions of 1 g L^{-1} of mont-La(6%)-$Cu_{0.6}Cd_{0.4}S$ nanocomposite allowed removal of *ca.* 92% of 10 mg L^{-1} solution of diclofenac at pH = 5.9 with natural dissolved oxygen from air within 240 min, meanwhile TOC removal was 67%. The photocatalytic process is adequately described by the Langmuir-Hinshelwood kinetic model, following apparent pseudo-first order kinetics. A suitable reaction mechanism has been proposed, based on the available kinetic evidences and the reaction products observed by HPLC–MS analysis.

1. Introduction

Pollution of the aquatic environment with microcontaminants can be attributed to different sources, such as emissions from production sites, direct disposal in households, excretion, and human and animal medical care products [1]. The use of pharmaceuticals and personal care products (PPCPs) is increasing steadily because of the increasing World population and fast urbanization.

PPCPs have been frequently detected in water ways as micro-pollutants (ranging from ng L^{-1} to μg L^{-1}) that can have potentially harmful environmental effects, even at concentrations as low as ppt, [2] and their bioaccumulation in the aquatic life will become a threat to the environment [3,4].

Pharmaceuticals are a class of emerging environmental contaminants that are extensively and increasingly being used in human and veterinary medicine [5]. Pharmaceuticals are often classified according to therapeutic purpose (*i.e.*, antibiotic, analgesic, anti-depressant, *etc.*), and their worldwide consumption is substantial. Their active ingredients comprise a variety of synthetic chemicals produced by pharmaceutical companies in both the industrialized and the developing world [6].

Non-steroidal anti-inflammatory drugs (NSAIDs) are of the greatest environmental interest due to their widespread availability [7]. Diclofenac (2-(2,6-dichlorophenylamino) phenylacetic acid (DIC), $C_{14}H_{11}NO_2Cl_2$ (Scheme 1), is one of the most consumed and commonly used NSAIDs, mainly for symptomatic treatment of low back pain, post-surgery pain, musculoskeletal injuries and chronic pain associated with cancer [7,8], but also for the treatment of hyperthermia, rheumatoid arthritis, osteoarthritis, and ankylosing spondylitis, soft tissue disorders, renal colic, acute gout, dysmenorrhea and migraine [9]. It is sold in different presentations depending on the intake mode: tablets, capsules, suppositories, and intravenous solutions, and in ointments and gels for dermal application [10,11]. Accumulation of DIC in the food chain and its toxicity to liver, kidney, gill cells, as well as renal lesions even at low concentrations may cause a major ecological damage to different species, such as vultures [12]; therefore, it is urgent and necessary to remove this compound from wastewater.

Recently, attention has been paid to different methods for DIC

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