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Research paper

Degradation of aqueous ketoprofen by heterogeneous photocatalysis using Bi_2S_3/TiO_2–Montmorillonite nanocomposites under simulated solar irradiation

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ABSTRACT

The photocatalytic degradation of Ketoprofen (KP), 2-(3-benzoylphenyl)-propionic acid was studied under near UV–Vis irradiation (NUV-Vis) using supported photocatalysts. Bi_2S_3/TiO_2-montmorillonite (Bi_2S_3/TiO_2-Mt) photocatalysts were synthesized using a two- step ion exchange and impregnation method, and characterized using different techniques: Fourier transform infrared spectra (FTIR), X-ray fluorescence (XRF), X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS) and photo-electrochemistry. Successful intercalation of TiO_2 and Bi_2S_3 in the montmorillonite (Mt) was carried out, and the corresponding energy diagram for the Bi_2S_3/TiO_2 heterojunction has been proposed. The resulting Bi_2S_3/TiO_2-Mt nanocomposites were able to degrade KP under NUV–Vis irradiation. KP photodegradation was monitored by HPLC. The kinetics of photocatalytic transformation followed the Langmuir-Hinshelwood kinetic model. Pseudo-first-order kinetics adequately fitted the experimental data ($t_{½}$*ca.* 17 min at pH 11, $t_{½}$*ca.* 44 min at pH 3. 0.5 $g{\cdot}L^{-1}$ Bi_2S_3/TiO_2 (25/75)-Mt nanocomposite). Factors affecting the kinetics of the process, such as the different Bi_2S_3/TiO_2 ratio and initial pH solution have been discussed. KP photoproducts were identified using HPLC-MS, and the corresponding reaction mechanism has been proposed. Photodegradation of KP over Bi_2S_3/TiO_2-Mt nanocomposites under NUV-Vis irradiation starts with the decarboxylation of KP and subsequent hydroxylation by $HO^{\bullet}$ and oxidation by $HO^{\bullet}$ and other reactive oxygen species (ROS) leads to the formation of photoproducts. TiO_2 and Bi_2S_3 intercalated in the montmorillonite are cheap and efficient nanocomposites for the abatement of persistent organic pollutants (POP), such as KP, using NUV-Vis light.

1. Introduction

In the past decade, there has been a growing interest in the occurrence of pharmaceuticals and personal care products (PPCPs) in aquatic environments. Common wastewater treatment processes are not efficient enough for the elimination of a variety of PPCP because of their low biodegradability (Halling-Sørensen et al., 1998; Huber et al., 2003; Petrović et al., 2005). Consequently, these compounds occur in sewage treatment plant (STP) effluents, and are discharged into surface waters (Halling-Sørensen et al., 1998; Huber et al., 2003; Petrović et al., 2003 and Petrović et al., 2005). Besides classical biological treatments, photochemical processes and advanced oxidation processes (AOP) may be a solution for the elimination and degradation of PPCP (Burrows et al., 2002; Ternes et al., 2002).

Ketoprofen (2-(3-benzoylphenyl) propionic acid, KP -Scheme 1-, is one of the worldwide most-used non-steroidal anti-inflammatory drugs (NSAID), also used as analgesic and antipyretic. Anti-inflammatory and analgesic effects are due to inhibition of prostaglandin synthesis, while its antipyretic effect is attributed to a resetting of the hypothalamic temperature-regulating center. These drugs are widely used as non-prescription drugs (Abdel-Hamid et al., 2001; Dvorak et al., 2004; Marco-Urrea et al., 2010).

Heterogeneous photocatalysis is an alternative remediation technology and has attracted attention of many research groups around the

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