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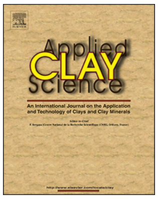

Research paper

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 $HO^•$ and oxidation by $HO^•$ 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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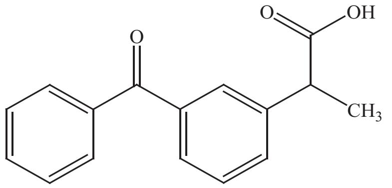

Scheme 1. Chemical structure of ketoprofen (KP).

World (Canle et al., 2017). This technique has often been reported to offer a number of key advantages, including the potential use of sunlight irradiation, operation at ambient conditions, and potential reuse of the catalyst. Hetereogeneous photocatalysis of KP with TiO_2 has been thoroughly investigated previously by some of us (Martínez et al., 2013). A number of studies are available summarizing the fundamentals of heterogeneous photocatalytic degradation processes, (Konstantinou and Albanis, 2004; Canle et al., 2017) and it is widely accepted that the primary step is the adsorption of the substrate on the support (Konstantinou and Albanis, 2004; Canle et al., 2017). The second step concerns the photo-redox reactions between the adsorbed substrate and TiO_2. The photocatalytic process is initiated when a photon with energy ($h\nu$) equal to or higher than the band gap energy (E_g) reaches the photocatalyst, with transfer of electrons (e^-) to the conduction band (CB) and subsequent formation of positive holes (h^+) in the valence band (VB). The so-formed e^-/h^+ pairs can recombine and dissipate energy as heat, get trapped in metastable surface states or migrate to the surface to react with electron donors and acceptors adsorbed on the semiconductor surface or within the immediate surrounding electrical double layer of the charged particles. Free hydroxyl radicals ($HO^\bullet$) are directly produced by reaction of h^+ with H_2O or OH^- at the surface of the catalyst. $HO^\bullet$ radicals are extraordinarily reactive, highly unselective species, exhibiting second order rate constants *ca.* 10^6–$10^9\,M^{-1}\cdot s^{-1}$, and very high electrophilicity (Ling et al., 2015; Valdés et al., 2015).

The use of TiO_2 as photocatalyst for water treatment is well documented (Hermann, 1999; Konstantinou and Albanis, 2004). Nevertheless, the practical recovery of the powder when used as an aqueous dispersion still remains difficult. TiO_2 supported on different minerals or TiO_2 thin films therefore appeared to be a promising way to enlarge application fields, and to overcome TiO_2 recovery problems (Zhiyong et al., 2008). TiO_2, intercalated in the interlayer spaces of montmorillonite (Mt), could have high photocatalytic activity because of its dispersion. The adsorption capacity of clays, related to their high surface area, could facilitate the retention of pollutants and their intermediate products of photocatalytic degradation. Finally, clays easily flocculate (Khalaf et al., 1997). On the other hand, organophilic clays can also be used for adsorbing poorly soluble pollutants, and the contaminated clay can be treated subsequently by photocatalysis over TiO_2 (Ilisz et al., 2002).

Since TiO_2 can be activated by UV light of $\lambda < 365$ nm, it can make use of only about 4% of sunlight at ground level. Different strategies have been adopted to improve its photocatalytic efficiency, such as ion doping (Reddy et al., 2006), dye- sensitization (Kaur and Singh, 2007), polymer-sensitization (Khalfaoui-Boutoumi et al., 2013) and doping with junction semiconductors (Bessekhouad et al., 2005 and Bessekhouad et al., 2006; Brahimi et al., 2007; Brahimi et al., 2008; Bessekhouad et al., 2012; Brahimia et al., 2012; Khalfaoui-Boutoumi et al., 2013). However, these doping processes modify other physical properties such as the lifetime of e^-–h^+ pairs, adsorption characteristics and photoelectrochemical stability (Table 1).

Bi_2S_3 is an important III–VI semiconductor that has been the subject of intensive research over the last decades owing to its small band gap E_g*ca.* 1.3 eV (Huaqiang et al., 2006; Zhou et al., 2008; Yang et al., 2011;), optoelectronic properties and low cost (Bessekhouad et al., 2004a, 2004b).

Table 1
Bi_2S_3/TiO_2 content in the nanocomposites.

Nanocomposite	Bi_2S_3 (%)	TiO_2 (%)
Bi_2S_3/TiO_2 (25/75)-Mt	25	75
Bi_2S_3/TiO_2 (50/50)-Mt	50	50
Bi_2S_3/TiO_2 (75/25)-Mt	75	25

The aim of this work is to extend the absorption spectra of TiO_2 to the visible region by using the expected advantages of the TiO_2/Bi_2S_3 junction to increase sunlight absorption efficiency. The obtained nanocomposites were characterized by Fourier transform infrared (FTIR), X-ray fluorescence (XRF), X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (UV– Vis DRS) and photo-electrochemistry. The photocatalytic activity of these nanocomposites was tested by the photocatalytic degradation of KP under near UV–Vis irradiation. The supported photocatalysts, Bi_2S_3/TiO_2-Mt nanocomposites, were synthesized using a two-step ion exchange and impregnation method. The effect of various operating parameters such as the load of nanocomposite and initial pH of the dispersion was studied. Reaction intermediates produced during the photodegradation process were detected, and a suitable mechanism is proposed for the degradation of KP based on HPLC/MS analysis.

2. Experimental

2.1. Materials

A bentonite clay sample from the Roussel deposit of Maghnia (Algeria) was used. It was purified using a sedimentation process to obtain purified bentonite with high montmorillonite (Mt) content. Some samples of pure bentonite were modified through cation exchange with 1 M sodium chloride solution to obtain Na—Mt (Khalaf et al., 1997). Hydrochloric acid (HCl) was purchased from Chiminova. Titanium (IV) isopropoxide (($Ti(OC_3H_4)_4$) (100%) and thiourea ($SC(NH_2)_2$) were acquired from Fluka. $Bi(NO_3)_3{\cdot}5H_2O$ was obtained from Panreac Quimica S.A. Experimental KP VETRANAL®, analytical standard, was purchased from Sigma–Aldrich. All reagents were used without further purification. Milli-Q water was obtained from a Millipore apparatus with a resistivity of 18.2 MΩ·cm at 298.0 K, and a measured total organic carbon (TOC) ≤ 5 $\mu g{\cdot}L^{-1}$ (ppb). Triply distilled water was also used for washing purposes.

2.2. Synthesis of nanocomposites

2.2.1. Preparation of TiO_2 pillaring solution

A “sol-gel method” was used, where a colloidal solution was prepared by the addition of (Ti $(OC_3H_4)_4$ and 1 N HCl, with a molar ratio [HCl]:[Ti] = 4 (Damardji et al., 2009a; Damardji et al., 2009b). The mixture was stirred for 3 h at room temperature (*ca.* 293 K).

2.2.2. Preparation of Bi_2S_3 pillaring solution

$SC(NH_2)_2$ was dissolved in water, and then $Bi(NO_3)_3{\cdot}5\ H_2O$ was added to this solution and stirred for 30 min at room temperature (*ca.* 298 K).

2.2.3. Synthesis of Bi_2S_3/TiO_2-Mt nanocomposites

1 g of Mt. was dispersed into 100 mL of water with vigorous stirring for 18 h to obtain 1.0% (mass) Mt. dispersion. The Bi_2S_3 pillaring solution was added dropwise to this dispersion, with vigorous stirring, for 24 h, to have 25% Bi_2S_3. The mixture was autoclaved at 120 °C for 30 min. After cooling to room temperature, the obtained solution was centrifuged and washed several times with water to remove impurities. A TiO_2 solution was added dropwise to the Mt-Bi_2S_3 solution, with strong stirring for 24 h, to 75% TiO_2. The resulting mixture was