



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Influence of operational parameters on photocatalytic amitrole degradation using nickel organic xerogel under UV irradiation

Miguel A. Álvarez^a, Francisco Orellana-García^a, M. Victoria López-Ramón^{a,*}, José Rivera-Utrilla^b, Manuel Sánchez-Polo^b

^a Department of Inorganic and Organic Chemistry, Faculty of Experimental Science, University of Jaen, 23071 Jaen, Spain

^b Department of Inorganic Chemistry, Faculty of Science, University of Granada, 18071 Granada, Spain

Received 16 June 2016; accepted 11 October 2016

KEYWORDS

Ni xerogel;
Amitrole;
Photodegradation;
Catalysis

Abstract The objectives of this study were to analyze the influence of different operational variables and to determine the time course of total organic carbon (TOC) and medium toxicity during amitrole (AMT) photodegradation in the presence of Ni xerogel (X-Ni) as photocatalyst. A further study objective was to analyze the influence of the type of water on the photodegradation process. Results show that the degradation rate is directly proportional to the initial X-Ni concentration up to a maximum of 250 mg/L with a slight decrease thereafter, indicating progressive photon absorption saturation of the catalyst for a given incident radiation flow. At concentrations close to 250 mg/L X-Ni, the AMT photodegradation rate is not affected by further increases in X-Ni concentration. In addition, AMT photolysis is highly pH-dependent and is generally favored at pH values at which AMT is in its ionic form. The increase observed in AMT degradation rate under alkaline conditions can be attributed to the higher generation of HO[•] radicals. The presence of chloride reduces the AMT degradation rate, because Cl⁻ anions behave as h⁺ and HO[•] radical scavengers. The degradation rate is also decreased by addition to the medium of organic matter, which acts as a filter. The behavior of TOC removal kinetics during AMT degradation in the presence of X-Ni is similar to that observed for AMT degradation kinetics. Finally, we highlight that photocatalysis is more effective in ultrapure water than in wastewater or tap water. In all systems, the optimal catalyst concen-

Abbreviations: AMT, amitrole; AOPs, Advanced Oxidation Processes; BET, Brunauer-Emmett-Teller; DR, Dubinin-Radushkevich; HPLC, high performance liquid chromatography; LP, low-pressure; MP, medium-pressure; NOM, natural organic matter; pH_{PZC}, pH of the point zero charge; TNM, tetranitromethane; TOC, total organic carbon; UV, ultraviolet; X-Ni, nickel xerogel.

* Corresponding author. Fax: +34 953211876.

E-mail address: mvlro@ujaen.es (M.V. López-Ramón).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

<http://dx.doi.org/10.1016/j.arabjc.2016.10.005>

1878-5352 © 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Please cite this article in press as: Álvarez, M.A. et al., Influence of operational parameters on photocatalytic amitrole degradation using nickel organic xerogel under UV irradiation. Arabian Journal of Chemistry (2016), <http://dx.doi.org/10.1016/j.arabjc.2016.10.005>

tration is 250 mg/L. The medium toxicity increases with longer treatment time, indicating the formation of by-products that are smaller than AMT and can more readily penetrate the cell.

© 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Amitrole (AMT) is a non-selective herbicide with a very wide spectrum of activity against annual and perennial broad leaf and grass type weeds. It is sometimes used instead of prohibited herbicides and is extensively employed for weed control in agriculture and along roadsides and railways (Catastini et al., 2004; Da Pozzo et al., 2005; Oesterreich et al., 1999). Due to its high solubility, relatively high AMT levels can be found in surface water and contribute to ground-water contamination *via* leaching. AMT has been reported to be an endocrine disruptor and possible carcinogen (Andersen et al., 2013; Da Pozzo et al., 2005; Mugadza and Nyokong, 2010; Watanabe et al., 2005). Increasingly strict environmental restrictions in the presence of these compounds in effluents and natural systems require treatment technologies that minimize environmental risks at a reasonable cost.

Advanced Oxidation Processes (AOPs) are promising technologies for the removal of organic compounds resistant to biological treatments. They include photocatalytic processes that involve the use of luminous radiation capable of electronically activating the catalyst; the energy content of this radiation must be in the visible or ultraviolet (UV) region. Moreover, the photocatalyst should be made of a semiconductor material with an electron structure capable of generating electron/hole pairs after irradiation at a given wavelength. The electron/hole pairs promote the formation of highly reactive radical species that participate in the pollutant degradation. These radicals result from reduction and oxidation reactions when promoted by the electron and by the positive hole generated, respectively (Ahmed et al., 2011; Rivera-Utrilla et al., 2012; Velo-Gala et al., 2013).

TiO₂ is one of the most widely used photocatalysts in water treatments, either alone or in combination with others that act as dopers and/or material supports (Ahmed et al., 2011; Leon and Radovic, 1994; Shan et al., 2010; Teh and Mohamed, 2011). However, there are drawbacks to the use of these materials, including the following: (i) their difficult removal from the treated effluent, (ii) the need for their recovery and reutilization, (iii) their reduced percentage solar spectrum radiation absorption, and (iv) their high electron/hole recombination level. Recent studies have centered on photocatalysis processes that reduce these shortcomings, including the preparation of semiconductors that have a large surface area or are placed on porous carbon materials (Baek et al., 2013; Cordero et al., 2007; Leary and Westwood, 2011; Li Puma et al., 2008; Lim et al., 2011; Rivera-Utrilla et al., 2012; Tryba et al., 2003). The textural and chemical properties of activated carbons improve the performance of photocatalytic processes when used as photocatalyst supports, largely attributable to the increased contact surface between photocatalyst and pollutant (Figueiredo and Pereira, 2010; Matos et al., 2009; Rodriguez-

Reinoso, 1998; Wang et al., 2007). In these cases, carbon plays a mere support function, although it was recently demonstrated (Haro et al., 2012; Velasco et al., 2012; Velasco et al., 2013) that activated carbons may act as photocatalysts under the action of UV light, which constitutes a new and promising approach to pollutant treatment. Garcia-Cruz et al. (2014) studied the immobilization of nickel (Ni) on various carbon supports and its application as electrocatalyst to oxidize propargyl alcohol in alkaline medium. The results revealed the importance of the phase of the metal within the carbon structure, with nanoparticles Ni yielding the highest performances. The combined effect of UV radiation and carbon has been widely studied by Velo-Gala et al. (2013), who analyzed the effectiveness of four commercial carbons to remove sodium diatrizoate in the presence of UV radiation. The results demonstrated that the catalytic contribution exceeds 53% after 1 min of treatment. This catalytic activity is increased in samples with higher percentage surface oxygen, mainly when this is formed by ester/anhydride groups and carbon atoms with sp² hybridization.

There have been few studies on herbicide removal from water by photocatalysis (Andersen et al., 2013; Catastini et al., 2004; Mugadza and Nyokong, 2010; Watanabe et al., 2005). Orellana et al. (2016) analyzed AMT photocatalytic degradation in aqueous solution in the presence of organic aerogels and xerogels doped with different transition metals. The results suggest that the positive holes generated in the valence band and the electrons that promote the conduction band play an essential role in the mechanism by which xerogels promote AMT photodegradation. Band-gap energy values are closely related to the presence of —C=O—OH groups in the structure of the gels. Thus, Ni xerogel (X-Ni) has the highest —C=O—OH group content and photocatalytic activity.

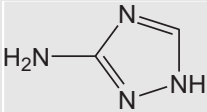
With this background, the objectives of the present study were as follows: to determine the influence of different operational variables on the photodegradation process, including the initial herbicide and catalyst concentrations, medium pH, ionic strength, natural organic matter (NOM), light intensity, and the presence of TiO₂; to analyze the time course of total organic carbon (TOC) and medium toxicity during AMT photodegradation with Ni xerogel; and to establish the influence of the type of water (ultrapure, tap, and wastewater). Determination of these parameters is essential for the correct design of technological applications of this photocatalytic process.

2. Materials and methods

2.1. Reagents

All chemical reagents used in this study (amitrole, hydrochloric acid, monobasic sodium phosphate, dibasic sodium phos-

Table 1 Chemical properties of amitrole.

Structure	Molecular formula	Molecular weight g/mol	Solubility in water mg/L	pK ₁	pK ₂
	C ₂ H ₄ N ₄	84.1	28 × 10 ⁴	4.3	10.4

Download English Version:

<https://daneshyari.com/en/article/7691544>

Download Persian Version:

<https://daneshyari.com/article/7691544>

[Daneshyari.com](https://daneshyari.com)