

Performance of the polymeric g-C₃N₄ photocatalyst through the degradation of pharmaceutical pollutants under UV–vis irradiation



D.B. Hernández-Uresti^{a,*}, A. Vázquez^b, D. Sanchez-Martinez^c, S. Obregón^{a,*}

^a Universidad Autónoma de Nuevo León, Centro de Investigación en Ciencias Físico Matemáticas, Facultad de Ciencias Físico Matemáticas, Av. Universidad S/N, San Nicolás de los Garza, 66455 Nuevo León, Mexico

^b Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Av. Universidad S/N, San Nicolás de los Garza, 66455 Nuevo León, Mexico

^c Universidad Autónoma de Nuevo León, Departamento de Ecomateriales y Energía, Facultad de Ingeniería Civil, Av. Universidad S/N, San Nicolás de los Garza, 66455 Nuevo León, Mexico

ARTICLE INFO

Article history:

Received 1 December 2015

Received in revised form 18 January 2016

Accepted 24 January 2016

Available online 18 March 2016

Keywords:

g-C₃N₄

Photocatalysis

Tetracycline

Ciprofloxacin

Ibuprofen

ABSTRACT

The graphite-like C₃N₄ was prepared by means the polycondensation of melamine at 500 °C for 4 h. The polymeric photocatalyst was characterized by several techniques such as X-ray powder diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS) and scanning electron microscopy (SEM). Also, nitrogen adsorption-desorption measurements were performed in order to estimate the surface area (BET) and pore size distribution (BJH) of the photocatalyst. The g-C₃N₄ material was used in the degradation of four different pharmaceutical compounds in aqueous solution under UV–vis irradiation. In this way, the photocatalyst showed the capacity to degrade the pharmaceutical compounds in the following sequence: tetracycline > ciprofloxacin > salicylic acid > ibuprofen. However, the degree of mineralization was different with the sequence: tetracycline > salicylic acid > ciprofloxacin > ibuprofen. Also, several scavengers agents were used in order to elucidate the importance of the different reactive oxidizing species during the photocatalytic process.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, anthropogenic pollution creates major environmental problems worldwide and the consequences will increase if the proper precautions are not taken [1,2]. In this sense, one of the most important issues is the presence of pharmaceutical compounds in natural water systems and groundwater [3,4]. These contaminants are usually present in concentrations of part per million (ppm) or even part per billion (ppb), reaching the water effluents due to the release of industrial wastewater and to the secretion of non-metabolized drugs by human or animal urine and feces. Within these pharmaceutical contaminants, the most common chemicals are the antibiotics and nonsteroidal anti-inflammatory drugs (NSAIDs).

During the past 20 years, the heterogeneous photocatalysis has been positioned as a promissory technology to solve a wide variety of environmental and energetic problems [5]. Although the anatase TiO₂ remains as the most widely used photocatalyst, new visible-light-driven photocatalysts have received a significant interest due to

its possible application in a broader range of the solar spectrum [6,7]. In this sense, during the last years the graphite-like carbon nitride (g-C₃N₄) has received a wide attention due to its considerable photoactivity under visible-light irradiation, metal-free composition, high chemical stability as well as an easy preparation through the polycondensation of nitrogen-rich organic compounds such as melamine, cyanamide and urea [8–10]. Among the most reported applications of this polymeric photocatalyst we can find the hydrogen production via water splitting process [11], the selective oxidation of alcohols and saturated hydrocarbons [12,13], the degradation of dyes [14] and the formation of heterojunction systems with other semiconductors acting as a sink of the photo-generated charge carriers in order to increase the photoactivity of the coupled photocatalytic systems [15–17]. In the present work, the performance of the polymeric photocatalyst g-C₃N₄ is reported by first time on the photodegradation of several pharmaceutical compounds in aqueous solution under UV–vis irradiation.

2. Experimental

2.1. Preparation of g-C₃N₄ powder

The preparation of the g-C₃N₄ powder was performed by means the polycondensation of melamine (Aldrich, 99%) at 500 °C for 4 h

* Corresponding authors.

E-mail addresses: ing.dianahdz@gmail.com (D.B. Hernández-Uresti), sergio.obregon@uanl.edu.mx (S. Obregón).

in a covered crucible in order to prevent the sublimation of the precursor [15].

2.2. Materials characterization

Structural characterization was carried out by X-ray powder diffraction using a Siemens D-501 diffractometer with Ni filter and graphite monochromator. The CuK α radiation with wavelength of 0.15406 nm was used as X-ray source and the diffraction data were registered between 10° and 70° (2 θ) with a scanning rate of 0.05° s⁻¹. Diffuse reflectance spectroscopy (DRS) was performed using an Agilent Technologies UV-vis-NIR spectrophotometer model Cary 5000 series equipped with an integrating sphere. The energy band gap was calculated using the equation $\alpha(h\nu) = A(h\nu - E_g)^2$, where α is the absorption coefficient, $h\nu$ is the photon energy and A is a constant [18]. For the estimation of the band gap value from the UV-vis spectrum, a straight line was extrapolated from the absorption curve to the abscissa axis. When α has a value of zero, then $E_g = h\nu$. The surface area (BET) and the mean pore size diameter (BJH) were determined by nitrogen adsorption-desorption measurements using a Surface Area & Pore Size analyzer Micromeritics ASAP-2000. The sample was evaluated at -196°C after a pretreatment at 150°C for 12 h. The morphology of g-C₃N₄ was observed by field emission scanning electron microscopy using a JEOL JSM 6701F microscope. The powder was ultrasonically dispersed in absolute ethanol and dropped on a holey carbon coated copper grid. The point of zero charge (pH_{PZC}) was measured through a modified batch equilibrium method [19]. Several samples were prepared by dispersing 20 mg of the photocatalyst in 100 mL of an aqueous solution of KCl 10⁻² mol/L at different pH values. The samples were leaving in equilibrium overnight and the change in the pH value was estimated from the difference between the final and initial pH values of each sample using a HI98103Checker pH Tester (Hanna Instruments).

2.3. Photodegradation of pharmaceutical pollutants

The photochemical reactor employed consisted in a borosilicate glass beaker surrounded with a cold water jacket to maintain the reaction temperature at 25 ± 1 °C. A Xenon lamp of 35 W was used as UV-vis irradiation source [20]. The photocatalytic behavior of g-C₃N₄ was evaluated in the degradation of four different pharmaceutical compounds in aqueous solution. According to the molar extinction coefficients, the initial concentration was established in 20 mg/L for tetracycline (≥98.0%, Sigma), ibuprofen

(≥98%, Sigma) and salicylic acid (ACS reagent ≥99.0%, Sigma-Aldrich) while the concentration of ciprofloxacin (≥98.0%, Fluka) was set in 10 mg/L. The molecular structures of the pharmaceutical compounds are depicted in Fig. 1. In order to develop the photocatalytic test, 200 mL of the aqueous solution containing the pollutant was mixed with 200 mg of the g-C₃N₄ powder and the mixture was placed in an ultrasonic bath for 15 min to remove aggregates. Then, it was left under dark conditions for 60 min to achieve the adsorption-desorption equilibrium of the contaminant on the photocatalyst surface. After this period of time, the Xe lamp was turned on. During the reaction, samples of 3 mL were taken at given time intervals and then separated through centrifugation (4000 rpm, 20 min). The concentration of each pollutant was followed through the evolution of its characteristic absorption band at 357, 222, 296 and 270 nm for tetracycline, ibuprofen, salicylic acid and ciprofloxacin, respectively.

The photon efficiency for the decomposition of the pharmaceutical compounds was estimated from the reaction rate and the flux of incoming photons for an irradiation wavelength of 400 nm:

$$\zeta = \frac{V \times \Delta c}{J \times A \times \Delta t} \quad (1)$$

where V is volume (L); Δc the change in concentration (mol/L); J the flux of photons (mol s/m²); A the illuminated area (m²), and Δt is the change in time (s) [21,22]. Also, the flux of photons was calculated by means of the following equation:

$$J = \frac{I \times \lambda}{N_A \times h \times c} \quad (2)$$

where I is the light intensity (W/m²); $\lambda = 400$ nm; N_A the Avogadro constant; h the Planck's constant and c is the speed of light.

The mineralization degree was estimated by analyzing the total organic carbon content (TOC) after 48 h of irradiation. In this case, the initial concentration of the pharmaceutical compound was established in 50 mg/L. The aliquots were analyzed in a Shimadzu VSCN8 Total Organic Content analyzer.

3. Results and discussion

3.1. Samples characterization

Structural characterization of g-C₃N₄ photocatalyst was carried out by X-ray powder diffraction. Fig. 2 shows the pattern obtained

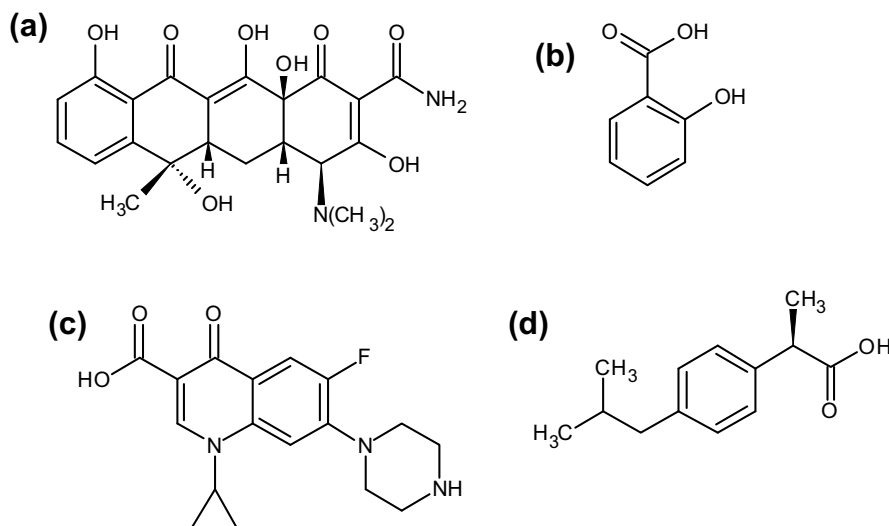


Fig. 1. Molecular structure of (a) tetracycline, (b) salicylic acid, (c) ciprofloxacin, and (d) ibuprofen.

دانلود مقاله



<http://daneshyari.com/article/26054>



- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات