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The effect of C-doping on the properties and photocatalytic activity of ZrO_2 prepared via sol-gel route

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ABSTRACT

This work explored the synthesis and characterization of zirconium oxide/carbon xerogel composite, using the material as a photocatalyst in the photodegradation of methylene blue. The band gap energy of the samples was determined using diffuse reflectance spectroscopy. The crystallographic phase, morphology, elemental analysis, analysis of metal content and porosity of the samples was examined by X-ray diffraction, scanning electron microscopy, energy dispersive spectrometry and infrared spectrometry, respectively. The methylene blue concentration was determined using a UV–vis spectrophotometer. The analysis results confirm the formation of zirconium oxide in its monoclinic crystal structure in the pure oxide. The composite presented amorphous structure. The zirconium oxide/carbon xerogel composite presented a higher radiation absorption, in all wavelengths tested. The results regarding the degradation of methylene blue confirm the existence of photocatalytic activity of the materials when submitted to the UVC wavelength. The XZrC composite presented considerably superior photocatalytic efficiency, when compared to the pure semiconductor, as the degradation obtained with the composite was 67% higher than the one obtained with the ZrO_2.

1. Introduction

We can point out that, nowadays, environmental pollution by industrial effluents is a significant problem due to the potential damage it may involve. Based on this fact, global awareness has been raised to the development and study of new effluent treatment processes. Among these, advanced oxidation processes, or AOP's, are a promising alternative, due to their versatility. As an AOP, heterogeneous photocatalysis has been extensively studied, mainly in the last decades [1].

The decontamination of wastewaters containing organic compounds by heterogeneous photocatalysis is a very interesting approach to the effluent treatment issue, as it allows the decomposition of these compounds into non-toxic molecules, such as carbon dioxide and water [2–4]. A wide array of semiconductors can be applied as photocatalysts, such as: TiO_2, ZnO, CdS, WO_3, Nb_2O_5, CeO_2 and ZnS. Among those, TiO_2 is the most commonly used, due to its stability and effectiveness in photocatalytic processes [5].

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In this context, zirconium oxide (ZrO_2) is a semiconductor of high importance, presenting a wide variety of applications. Due to its extraordinary thermal properties, such as high melting point and low expansion coefficient, it is one of the main components used in the production of refractory equipment. It is also the only oxide from a transition metal that has acidic and basic sites in its surface and, therefore, can be oxidized or reduced, encouraging the use of this material as a photocatalyst [6]. However, due to its high band gap (5.3 eV), this oxide presents low efficiency in photocatalytic processes, when compared to TiO_2 (3.3 eV) [7]. Therefore, to enhance its photocatalytic properties, modifications in the material can be developed. These modifications are aimed at promoting a higher charge separation and an increased wavelength response range [8].

To that intention, the use of carbon xerogel as a support for photocatalysts is a promising alternative to increase the efficiency of the photocatalytic process, as the material presents high surface area and high electrical conductivity [9]. However, the resorcinol molecule, commonly used in the synthesis of these materials, it's a high priced reactant, constituting 80% of the xerogel production cost [10]. One way of avoiding the high production costs of the carbon xerogel is the use of cheaper precursor materials. Natural condensed tannins may be a suitable alternative for the resorcinol molecule, generally used in the synthesis of carbon xerogels [11,12]. The commercial tannin used in this work was supplied by TANAC S.A. and sold under the trade name PHENOTAN AP for less than 1 US$ kg^{-1}. This material is obtained through the processing of the black wattle bark. The black wattle tannin is a macromolecule that has a polyhydroxyphenolic structure, so its reactivity with formaldehyde is very similar to that of resorcinol [13,14].

Therefore, we can define as the main point of this project the synthesis and characterization of the zirconium oxide/carbon xerogel composite, applied in the photocatalytic decomposition of the organic dye known as methylene blue (MB).

2. Methodology

2.1. Preparation of anhydrous zirconium oxide

Zirconium oxide was prepared using the sol-gel method. 10 g of zirconium oxychloride ($ZrOCl_2.8H_2O$) was dissolved in 0.5 mol L^{-1} hydrochloric acid solution. After complete dissolution, a solution of ammonium hydroxide (NH_4OH) of composition 3 H_2O: 1 NH_4OH (v/v) was added until precipitation of the hydrated oxide. The oxide formed was then filtered, washed with deionized water to pH ~7 and oven dried at 100 °C until constant mass was achieved. Finally, the resulting material was calcined at 650 °C for 5 h [15]. The material obtained will be referred as ZrO_2.

2.2. Preparation of zirconium oxide/carbon xerogel composite

First, 10 g of zirconium oxychloride ($ZrOCl_2.8H_2O$) was dissolved in 0.5 mol L^{-1} hydrochloric acid solution. After complete dissolution, 2 g of tannin and 2.2 ml of formaldehyde solution (37% v/v) were added. Finally, a solution of ammonium hydroxide (NH_4OH) of composition 3 H_2O: 1 NH_4OH (v/v) was added until precipitation of the hydrated oxide. The composite formed was then filtered, washed with deionized water to pH ~7 and oven dried at 100 °C until constant mass was achieved. This material will be called XZr. The XZr was then calcined at 300 °C for 30 min. The material obtained will be referred as XZrC.

2.3. Characterization

The X-ray diffractograms were obtained in a PANalytical Empyrean X-ray diffractometer, using MoKα radiation, operating in 40 kV and 30 mA, with step of 0,026° and acquisition time of 29.07 s/step. The range used comprehended the interval between 10 and 70°.

The SEM images were obtained in the HITACHI TM-3000 SEM, using secundary electrons and 15 kV operation voltage. The element mappings of the samples were obtained using a Swift ED3000 dispersive energy spectrometer.

The diffuse reflectance spectroscopy was performed in a Shimadzu UV-2600 spectrophotometer, equipped with an integrating sphere. The acquisition interval was 220–800 nm.

The infrared spectra were acquired by Fourier transform infrared spectroscopy using a universal attenuated total reflectance sensor (FTIR-UATR) (Perkin Elmer Spectrum, model Frontier). The FTIR spectrum was an average of 16 scans at a speed of 2 s per scan at range of 450–4000 cm^{-1}. The resolution of the spectrometer was set to 4 cm^{-1}.

2.4. Evaluation of the catalytic activity in the photodegradation of methylene blue

The tests for the determination of the photocatalytic activity were performed in a jacketed reactor with dimension of 30 cm in height and 10 cm in internal diameter. A PL-L lamp (UVC radiation) was placed inside a quartz tube (4 cm in diameter and 40 cm in length, with a closed end), which was immersed in the reactor.

The reactor was filled with 500 mL of methylene blue solution and known amount of photocatalyst (0.2 g/L). The temperature of the photocatalytic process was maintained at 25 °C, controlled by the passage of water through the reactor jacket. A uniform suspension of the photocatalyst in the solution was obtained by magnetic stirring. Aliquots of 2 mL were collected at regular intervals and filtered through 0.22 μm disposable filters. The concentration of dye in the filtrate was determined