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Invited feature article

Mixed α-Fe_2O_3/Bi_2WO_6 oxides for photoassisted hetero-Fenton degradation of Methyl Orange and Phenol

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ABSTRACT

Mixed oxides, α-Fe_2O_3/Bi_2WO_6, were prepared using a mechanical mixing procedure by adding to the Bi_2WO_6 previously obtained by hydrothermal method the corresponding amount of a prepared α-Fe_2O_3, the latter obtained by thermal decomposition of $Fe(NO_3)\cdot 9H_2O$. The physicochemical surface, structural, morphological characteristics and optical properties of the samples, single and mixed, were determined by BET, XRD, FE-SEM, XPS and UV–vis diffuse reflectance spectroscopy. UV–vis diffuse reflectance spectra showed that incorporating a 5%wt. of α-Fe_2O_3 to the corresponding amount of Bi_2WO_6 sample broadened the visible light absorption of Bi_2WO_6 as expected. The photocatalytic activity, of single and mixed catalysts, to degrade a selected dye such as Methyl Orange (MO) as well as the transparent substrate Phenol (Ph) was studied, in aqueous medium ($pH \approx 5.5$) under UV and sun-like illumination conditions in the absence and presence of H_2O_2. In the present study the use of a α-Fe_2O_3-Bi_2WO_6/H_2O_2 system demonstrate much higher photocatalytic efficiency to degrade both MO and Ph than pristine Bi_2WO_6or α-Fe_2O_3, single or mixed. Using the system α-Fe_2O_3-Bi_2WO_6/H_2O_2, around 85% of MO was degraded in 60 min under sun-like illumination whereas 100% was degraded in 60 min under UV-illumination. However, just around 30% of Ph was degraded in 120 min in the α-Fe_2O_3-Bi_2WO_6/H_2O_2 system under sun-like illumination whereas around a 95% was degraded in 90 min under UV-illumination. Under UV-illumination, the generation of hydroxyl radicals is favorable; whereas under sun-like illumination, only the small fraction of the UV can produces the $^{\bullet}OH$. Under illumination, the H_2O_2 could react with photoinduced electrons from the photocatalysts leading to the production of hydroxyl radicals ($^{\bullet}OH$).

1. Introduction

The increase of industrial activities has become a serious problem that leads to the augmentation of pollution in air, water and soil. To face this problem, the scientific community works to find new methods to undo the contamination. During the past few decades, a variety of practical strategies have been implemented to develop viable wastewater treatment technologies [1–6].

Those technologies are very appealing alternatives for the degradation of organic pollutants because they permit a partial or complete mineralization of pollutants. It is based on the production of the very reactive and nonselective entities (particularly the hydroxyl radicals $^{\bullet}OH$) having a higher oxidizing capacity than traditional oxidants (O_2, Cl_2, ClO_2, H_2O_2, O_3 . . .) [7–9].

Photocatalytic degradation of organic pollutants to purity wastewater from industries and household has received extensive attention in recent years. In particular, heterogeneous photocatalysis shows promising potential in depth-oxidation of pollutants to non-toxic inorganic molecules at ambient temperature [10].

Dyes are molecules commonly found in real effluents from textile and other industrial wastewaters [11,12]. Dyes are major organic pollutants, which can cause severe environmental disruption and health damages [13]. Similarly, phenol is one of the most abundant pollutants in industrial wastewaters and its toxicity, carcinogenicity and persistence, makes this compound dangerous for life at rather low concentrations. In this sense, heterogeneous photocatalysis, among a group of available technologies known as advanced oxidation processes (AOPs), is an important alternative to remove a wide range of organic compounds, including phenols and dyes, in polluted streams. Other technologies as Fenton and Photo-Fenton have been successfully used in depollution of water [14–18].

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To meet the requirement of future environmental applications, in the field of AOPs, it is still essential to not only further improve the photocatalytic activity by synthesizing new photocatalysts but also to explore new combined processes.

The development of new photocatalysts is attracting vast interest. Among them the Bismuth tungstate (Bi_2WO_6) is a typical n-type direct band gap semiconductor with a band gap of 2.8 eV and has prospective applications for the degradation of organic pollutants under visible light illumination due to their low valence band and high chemical stability [19]. In the same context, iron oxide (α-Fe_2O_3, hematite) with a narrow band gap at 2.2 eV, absorbing the light up to 600 nm and collecting about 40% of the solar spectrum energy, is also another of the promising materials for photocatalytic applications [20].

H_2O_2 is a distinctive oxidative agent and has been frequently used in practical water treatment, because it's a very common source of very active hydroxyl radicals ($^{\bullet}OH$) by its decomposition after being illuminated with ultraviolet (UV) light. The use of H_2O_2 in photochemical processes (UV/H_2O_2) and UV (H_2O_2/Fe^{3+} (Photo-Fenton)) has been investigated [1,21–24], however, long periods of UV-illumination are required, thus poor degree of mineralization is obtained, making all these processes not perspectives as potential methods for wastewater purification.

From another perspective, as an electron capture agent, H_2O_2 can also react with photogenerated electrons, from a photocatalytic process, to produce hydroxyl radicals ($^{\bullet}OH$) as established in Eqs. (1) and (2) in which (SC) is a general semiconductor photocatalyst [25].

$$(SC) + h\nu \rightarrow (SC)(e^-_{CB} + h^+_{VB}) \text{ (light absorption)} \quad (1)$$

$$(H_2O_2) + e^-_{CB} \rightarrow {}^{\bullet}OH + OH^- \quad (2)$$

$$(H_2O) + h^+_{VB} \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

The formation, the adsorption and the degradation of H_2O_2 on different samples (TiO_2 and ZnO) have been investigated to better understand its participation in the photocatalytic reactions [26]. In a typical UV/H_2O_2/TiO_2 system, the active radical formation can arises not only from the direct UV-photolysis which takes place through a homolytic process ($H_2O_2 + hv \rightarrow 2\ {}^{\bullet}OH$) but also from the photocatalytic ones (Eqs. (1)–(3)).

Thus, if the photocatalyst only absorbs in the UV region, then the hydroxyl radicals photogeneration, during the combined photochemical process UV/(SC)/H_2O_2, can take place not only by the homogeneous photolytic decomposition of H_2O_2, but also according to the processes indicated in Eqs. (1) and (2). But if the photocatalyst absorbs in the visible region, the generation of hydroxyl radicals ($OH^{\bullet}$) would be expected to occur, under visible illumination, by the photogenerated electron capture of H_2O_2, since the photolytic decomposition of H_2O_2 requires shorter wavelengths [1].

The generation of H_2O_2 and hydroxyl radicals on Bi_2WO_6 for phenol degradation under visible light has been reported [27]. From this work, Authors concluded that the observed organic degradation over the irradiated Bi_2WO_6 in aerated aqueous solution is due to the production of $^{\bullet}OH$ and H_2O_2.

Both photocatalysts, Bi_2WO_6 and α-Fe_2O_3, display potential catalytic activity to many chemicals organic degradation under conditions of sun-like illumination. However, due to the high recombination rate of photogenerated charge carriers, the ability is thereof limited. Various strategies, such as heterostructured constructing are being developed [28–30].

The aim of this work is not focused on developing a α-Fe_2O_3/Bi_2WO_6 heterostructure, but to use a physical mixture of both materials and explore their photochemical activity in the presence or absence of H_2O_2 in the degradation of two selected substrates.

Therefore, when H_2O_2 is co-present with single or physically mixed Bi_2WO_6 and α-Fe_2O_3, different activities could be displayed because, parallel to the mechanism of homogeneous degradation by hydroxyl radicals photogenerated by H_2O_2, the effect generated by the intrinsic photocatalytic activity of single or mixed systems is also expected to occur.

Methyl Orange (MO) and Phenol (Ph) are used to imitate non biodegradable, toxic organic compounds. The photocatalytic activity, under UV or sun-like Illumination, of α-Fe_2O_3, Bi_2WO_6 and mixed α-Fe_2O_3/Bi_2WO_6 samples, to Methyl Orange and Phenol degradation, in the absence and presence of H_2O_2 is reported.

2. Experimental details

2.1. Preparation of α-Fe_2O_3, Bi_2WO_6 and mixed α-Fe_2O_3/Bi_2WO_6 samples

All the reagents used in this procedure were analytical grade without further purification. The detailed synthesis procedure for single α-Fe_2O_3, Bi_2WO_6 and mixedα-Fe_2O_3/Bi_2WO_6 sample was as follow: The iron oxide was prepared by drying iron(III) nitrate nonahydrate $Fe(NO_3)\cdot 9H_2O$ at 120 °C for 2 h then submitting the samples to a further calcinations treatment at 300 °C for 2 h.

The Bi_2WO_6 was prepared according to the method previously described [31] by dissolving 4.85 g of Bi $(NO_3)_3\cdot 5H_2O$ in 10 mL of glacial acetic acid, and 1.7 g of $Na_2WO_4\cdot 2H_2O$ in 90 mL of distilled water, then those two solutions were mixed forming a white suspension (pH ≈ 2), which was kept under stirring for 1 h. The white suspension was transferred into a Teflon recipient inside a stainless steel autoclave. The hydrothermal treatment was done at 140 °C for 20 h, and then the precipitate was filtered, washed and dried overnight at 120 °C. Finally the sample was submitted to a calcination treatment at 300 °C for 4 h.

The α-Fe_2O_3/Bi_2WO_6 mixed samples were obtained with a mechanical mixing in agate mortar, by adding the prepared α-Fe_2O_3 to the corresponding amount of Bi_2WO_6 for a 5 wt.% of iron oxide in the mixture. This sample will hereafter be named as BW-Fe(5)-2 indicating a 5% of iron oxide and that Bi_2WO_6 was prepared at pH = 2.

2.2. Characterization of the photocatalysts

BET surface areas (S_{BET}) of all samples were evaluated by N_2 adsorption measurement with a Micromeritics ASAP 2010 instrument. Degasification of the samples was performed at 150 °C for 30 min in He flow.

Crystalline phase composition of the samples was estimated by X-ray diffraction (XRD). XRD patterns were obtained on a Siemens D-501 diffractometer with Ni filter and graphite monochromator using Cu Kα radiation.

The morphology for all the samples was analyzed by field Scanning electron microscopy (FE-SEM) using a Hitachi S 4800 microscope.

Light absorption properties of the samples were studied by UV–vis spectroscopy. The Diffuse Reflectance UV–vis Spectra (UV–vis DRS) were recorded on a Varian spectrometer model Cary 100 equipped with an integrating sphere and using $BaSO_4$ as reference. Band-gaps values were calculated from the corresponding Kubelka–Munk functions, $F(R\infty)$, which are proportional to the absorption of radiation, by plotting $(F(R\infty) \times h\nu)^{1/2}$ against $h\nu$.

X-ray photoelectron spectroscopy (XPS) studies were carried out on a Leybold-Heraeus LHS-10 spectrometer, working with