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Catalytic activity of the barium hexaferrite with H_2O_2/visible light irradiation for degradation of Methylene Blue

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ABSTRACT

Barium hexaferrite ($BaFe_{12}O_{19}$) is a novel and effective catalyst in the photo-Fenton like system for the rapid degradation of Methylene Blue (MB). The $BaFe_{12}O_{19}$ catalyst was synthesized by the chemical co-precipitation method and characterized by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), Brunauer–Emmet–Teller (S_{BET}) surface area and optical adsorption analysis. The $BaFe_{12}O_{19}$ catalyst generated a good catalytic activity for MB degradation for a photo-Fenton like system under visible light irradiation, this is possible due to the catalyst can be activated using photons of visible light region as a consequence of its narrow band gap estimated of ~1.77 eV, corresponding to absorption edge in the visible region from a wavelength of ~700 nm. In such conditions the $BaFe_{12}O_{19}$ was able to decolorize and to mineralize up to 70.8% and 63.7% of the dye, respectively, after 360 min using a 3 W Light Emitting Diode (LED) lamp ($\lambda = 420–700$ nm). In addition, the energy consumption of the Vis/$BaFe_{12}O_{19}$/H_2O_2 system was estimated at 11.1 W h/L/order.

1. Introduction

Wastewaters containing non-biodegradable dyes and organic materials are very toxic and usually resistant to the conventional wastewater treatments [1], such as, flocculation, precipitation, adsorption on activated carbon, air drag or inverse osmosis [2]. To overcome the drawbacks of conventional treatments, the application of different catalytic technologies [1,3] as the so-called Advanced Oxidation Procedures (AOP's) seems to be a promising field of study, as they are effective techniques for degradation of soluble organic pollutants in water [3], providing an almost complete degradation, under reasonably mild conditions of temperature and pressure [3,4].

The Fenton technology is one of the most powerful and widely used AOP's for the treatment of industrial wastewater containing non-biodegradable organic pollutants [5,6]. Furthermore, the rate of degradation of organic waste with Fenton reagent is strongly accelerated by irradiation with UV–vis light [7]. Hence this method is an efficient and inexpensive method for wastewater treatment [8].

The heterogeneous photo-assisted Fenton-like system employs the use of a visible light activated heterogeneous catalysts, which are semiconductor materials [9] with magnetic properties and the advantage of providing a wide working range of pH [5].

Moreover, photo-Fenton-like treatment of wastewater without pre-adjusting the pH could also become feasible because industrial wastewater often have a pH around 7, in such conditions the use of reactors made of materials with high corrosion resistance is unnecessary [3] which can help to reduce the operation cost. This type of treatment is accompanied by the generation of highly reactive hydroxyl radicals ($HO^\bullet$) [1,4,7] due to the catalytic decomposition of hydrogen peroxide (H_2O_2) by the iron ions [4].

The hydroxyl radical is an extremely reactive specie that attacks the majority of organic molecules with little or no selectivity [3,4,10], therefore, it is considered as the responsible of the destruction of non-biodegradable organic pollutants [3,10]. The presence of $HO^\bullet$ especially favors the decomposition of unsaturated compounds in aqueous solution [2] and due to its high oxidation potential (2.80 V) [1,9], it is capable to oxide and mineralize almost any organic molecule producing water, carbon dioxide, and other inorganic substances [1–3].

In consequence, numerous studies have focused on heterogeneous photo-Fenton-like process using iron-containing materials due to their magnetic properties and since they have interesting properties to be potentially used as heterogeneous catalysts [1,10], such as meso-$CuFe_2O_4$, meso-$CoFe_2O_4$ [5], GO-$NiFe_2O_4$ [9], $BiFeO_3$ [4], $ZnFe_2O_4$ sulfured [1], Fe_3O_4 and $MnFe_2O_4$ with activated carbon [11], $BaFe_2O_4$ [12], $BaFeO_{3-x}$ [13], $ZnFe_2O_4$ nanorods

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[14], $ZnFe_2O_4$–graphene [15], mesoporous-$ZnFe_2O_4$ [16], MFe_2O_4 (M = Fe, Co, Cu, Mn) [17], $CoFe_2O_4$–graphene [18], $SrFe_{12}O_{19}$ [19], MFe_2O_4 (M = Cu, Zn, Ni and Co) [20] which are capable of being activated by visible light due to their narrow band gap making them a technology of relatively low application cost. In all this cases the visible light photon absorption is attributed to the presence of iron ions [20,21].

On the other hand, the most important characteristic of a green catalyst designed for industrial application is the ability to be efficiently recovered after the reaction [20]. The photo-assisted magnetic catalysts have high diffusion efficiency and can be easily separated from the reaction mixture by applying a magnetic field and subsequently be reused. This particular feature makes them eco-friendly catalysts [5,10]. In consequence, the sustainability of magnetic catalysts satisfies the green chemistry principles [20].

For these reasons, we have selected $BaFe_{12}O_{19}$ to study its catalytic properties because of their excellent magnetic properties, low cost production, and good corrosion resistance [22–24]. Therefore, the goal of this work was to determine the catalytic activity of barium hexaferrite under visible light irradiation with and without the presence of H_2O_2 using MB as a model molecule and to evaluate the energy consumption of the system.

2. Experimental procedure

2.1. $BaFe_{12}O_{19}$ preparation

All the chemical reagents used for the synthesis were analytic grade and used as received. The $BaFe_{12}O_{19}$ synthesis was carried out by the chemical co-precipitation method. So that, 2.4 g of $Fe(NO_3)_3{\cdot}9H_2O$ and 0.24 g of $Ba(NO_3)_2$ were diluted in 0.1 L of deionized water and next precipitated with a 1 M tetramethylammonium hydroxide (TMAH) solution until they reach pH = 12.7 at room temperature. The obtained precursors were washed several times with deionized water and dried at 373 K. The resulting powders were taken to hand milling for 1 h and then they were sintered at 1173 K during 4 h. And finally brought again to milling for 1 h.

2.2. Characterization

The $BaFe_{12}O_{19}$ was characterized by X-ray diffraction (DRX) using an X-ray diffractometer Bruker-AXS D8 Advanced with Cu*K* radiation ($\lambda = 1.5406$ Å) in the range of 2θ from 20 to 70. The step size was 0.04° with a time measurement of 4 s/step to determine the purity and crystal structure of the sample. The size and shape of the particles were determined from the electron transmission microscopy (TEM) images obtained by using a JEOL team JEM-1230 100 kV. In addition, a dynamic light scattering (DLS) analysis was performed using a Malvern Zetasizer Nano ZS model to determine size and Zeta potential of the particles. The gas absorption method using mini Bel sorp mini II/Bel Japan INC was carried out to analyze the surface area of the synthetized particles, S_{BET} which was determined by a surface analysis using N_2 gas adsorption isotherm obtained at 77 K. The sample was outgassed under vacuum at 423 K prior to analysis. Besides, an Ocean Optics 4000-UV–vis spectrometer was used to estimate the band gap energy from the Kubelka–Munk method, applying the technique of diffuse reflectance spectroscopy, and also to measure the Methylene Blue degradation as a function of the percentage of decrease of the absorbance of the MB molecule.

In addition, residual analyses were carried out. Selected samples of degraded Methylene Blue solutions were analyzed by total organic carbons (TOC) and Fourier Transform Infrared spectroscopy (FTIR) using a Shimadzu TOC-V CPN analyzer, and a Shimadzu IRAffinity-1 spectrophotometer, respectively.

2.3. Catalytic measurements

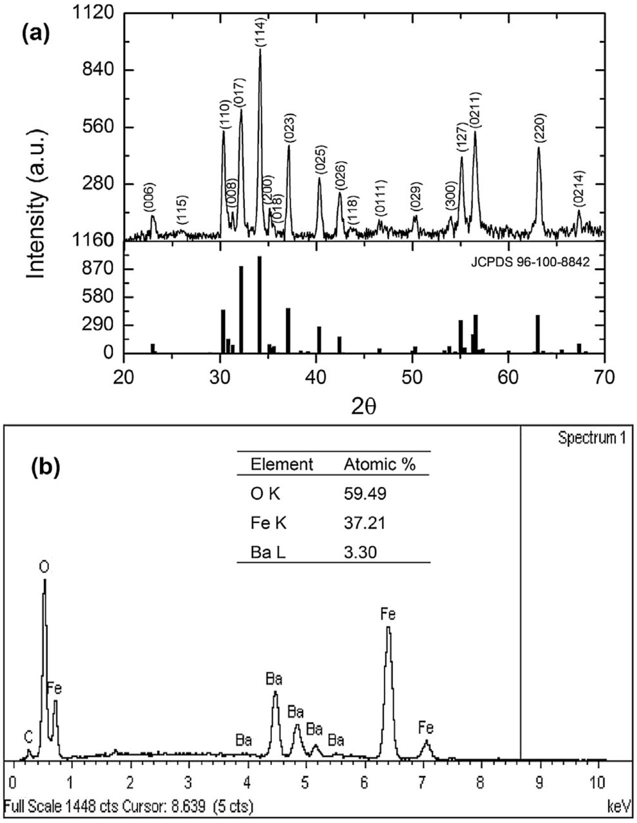
The catalytic performance of the barium hexaferrite was evaluated by the degradation of Methylene Blue solutions under irradiation of visible light and in darkness. All experiments were carried out under environment conditions. For the degradation reaction a total volume of 0.05 L and a total concentration of 10.0 ppm of MB were used. In a typical reaction, the catalyst load was from 0.25 to 1.00 g/L of barium hexaferrite. First, the catalyst suspension was magnetically stirred in dark for 60 min and then was irradiated under warm white light of a 3 W Light Emitting Diode (LED) lamp ($\lambda = 420$–700 nm) horizontally located 0.125 m from the sample. Degradation of Methylene Blue was also improved by the addition of hydrogen peroxide (3.00–15.0 mM H_2O_2) generating heterogeneous photo-Fenton type system.

The degradation of Methylene Blue in the reaction was periodically monitored. First the catalyst was magnetically separated from the solution and then the supernatant was immediately used to analyze the UV–vis absorption spectra of each sample.

3. Results and discussions

3.1. $BaFe_{12}O_{19}$ characterization

The synthesized $BaFe_{12}O_{19}$ was analyzed and characterized regarding to their crystalline structure, pure phase and crystallite size using XRD. Fig. 1(a) shows the diffraction pattern of the formed $BaFe_{12}O_{19}$ crystal phase, where all diffraction peaks corresponding to the planes (*h k l*) can be easily indexed to the formation of a hexagonal structure phase according to the JCPDS card number 96-100-8842. Crystallite size was 66.8 nm and the network parameters



Element	Atomic %
O K	59.49
Fe K	37.21
Ba L	3.30

Fig. 1. Characterization and analysis of $BaFe_{12}O_{19}$: (a) X-ray diffraction pattern (XRD), (b) energy-dispersive X-ray spectroscopy (EDS) analysis.