Increasing the efficiency of magnetic heterogeneous Fenton catalysts with a simple halogen visible lamp

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ARTICLE INFO

ABSTRACT

The effect of a simple visible halogen lamp was studied in the Fenton-type oxidation of three model aqueous pollutants differing in their structure and electrostatic charge, methylorange (MO), methylene blue (MB) and paranitrophenol (PNP), using maghemite nanoparticles (γ-Fe_2O_3 NP), or maghemite/silica nanocomposite microspheres (γ-Fe_2O_3/SiO_2 MS) as heterogeneous catalysts. These materials, which were fully characterized, differ in size, morphology, porosity and microstructure, although their catalytic activity is related to the same γ-Fe_2O_3 nanoparticles. Both have a strong magnetic susceptibility, but only the MS catalyst can be easily recovered by magnetic settlement. Whatever the catalyst, the pollutant tested, or the experimental conditions used, much better decolorization rates and mineralization efficiencies were recorded under illumination by visible light in comparison to the same tests in the dark. The large range of experimental conditions tested enabled us to propose a mechanism for photocatalytic activity. Experiments of long-term stability showed that the MS catalyst, although generally less active than the NP catalyst, retained almost all of its activity after five repeated experiments under visible light. The good stability of this catalyst was also confirmed by the low level of iron leaching, making it suitable candidate for an application as photo-Fenton catalyst in industrial wastewater treatment.

1. Introduction

Nowadays, advanced oxidation processes (AOPs) are becoming increasingly important for wastewater treatment technologies, especially for poorly biodegradable contaminants [1–5]. The common feature of these processes is the production of extremely reactive and unselective radical oxygen species, especially the highly oxidizing hydroxyl radicals (HO•), which are able to degrade even the most recalcitrant molecules into biodegradable compounds, or mineralize them into CO_2, H_2O and inorganic ions [3]. AOPs can be divided into different groups based on how the radicals are produced. One may mention the sonochemical processes, the radiolysis, the electrochemical methods, and the purely chemical processes which include the Fenton-type reactions (H_2O_2/Fe catalyst). Nevertheless, one of the most important classes of AOPs is constituted by the photochemical processes, such as water,

H_2O_2 and/or O_3 photolysis ($h\nu$/H_2O, $h\nu$/H_2O_2, $h\nu$/O_3, $h\nu$/H_2O_2/O_3), heterogeneous photocatalysis ($h\nu$/TiO_2 catalyst), and the photo-Fenton process ($h\nu$/H_2O_2/Fe catalyst) [5,6]. Their generally high efficiency is due to the assistance of UV or visible light irradiation, which is directly or indirectly responsible for the production of the radicals. UV light is usually used in the photochemical processes, because of its large energy which is able to induce the direct photolysis of an oxidant (H_2O_2, O_3, O_2, H_2O, . . .), or to activate a semiconducting catalyst such as TiO_2, leading to the generation of large amount of oxygen radicals. However, the photodegradation under UV irradiation is limited for industrial utilization, since natural UV occupies only 3–5% of the solar light energy that reaches earth, while artificial UV light generators consume large quantities of electrical power and can be expensive and unstable. Recently, much effort has been done to expand the response of the photodegradation processes to visible light irradiation, in replacement or addition to UV-light. Nevertheless, water-treatment by direct visible-light photolysis of an oxidant is unfavorable, since the rate of photolytic decomposition of the oxidants to oxygen radicals is very slow. To overcome this drawback, it is thus necessary to add a photocatalyst

[7]. In recent years, there has been an extensive interest in the use of semiconductors in photochemical degradation. Among them, TiO_2 has been widely used as an effective photocatalyst for environment purification since it can decompose a large number of pollutants [6–10], but its wide bandgap ($\sim$3.2 eV) limits its application to UV light irradiation. To the contrary, iron oxide particles (Fe_3O_4, Fe_2O_3, FeOOH, …) are suitable candidates to be used as visible-light photocatalysts for water treatment. Indeed iron oxides have a relatively small bandgap ($\sim$2.1 eV for Fe_2O_3) which is appropriate for receiving visible light, and the electron–hole pair may generates radical oxygen species in the same way as TiO_2 [11–13]. In addition, compared with TiO_2, iron oxide presents the advantages to be non-toxic and inexpensive [14,15]. However, it has been reported that iron oxides are relatively inefficient visible-light photocatalysts in the absence of additional oxidant [11–13], while they are much more active as heterogeneous photo-Fenton catalysts, i.e., when H_2O_2 is added as additional oxidant to generate the oxygen reactive species [13,16]. To explain this result, it has been proposed that large amounts of $HO^\bullet$, are generated from H_2O_2 at the surface of the iron oxide in the presence of light [17–19].

Although the photo-Fenton process is also efficient in homogeneous phase at pH 3 (i.e., with dissolved Fe^{2+} or Fe^{3+} as catalyst), the use of iron oxides as heterogeneous catalyst provides the possibility to recover and reuse the catalyst and to operate in a broader pH range [20]. In spite of these advantages, there are a relatively small number of studies on the use of iron oxides as photo-Fenton catalysts under visible light [13,17–29]. These studies have clearly shown that the efficiency of the iron oxide/H_2O_2 system in the degradation of various model pollutants is considerably increased through visible light irradiation, which might be slightly more efficient than UV light irradiation [27]. However, the impact of the experimental conditions on the efficiency of visible light irradiation is still poorly understood. This article aims to highlight the parameters affecting the efficiency of visible light irradiation in a heterogeneous photo-Fenton process, using maghemite (γ-Fe_2O_3) nanoparticles (NP) as photocatalyst. The effect of the visible light irradiation on the activity of this catalyst is studied for a large range of conditions obtained by varying several parameters such as the presence of a silica support, the nature of the model pollutant, the pH, the H_2O_2 concentration, and the amount of catalyst. The choice of γ-Fe_2O_3 nanoparticles has been dictated by several considerations. First, γ-Fe_2O_3 is characterized by a high magnetic susceptibility, which offers an additional advantage in terms of recovery and reusability of the catalyst. Indeed magnetic iron oxides can be easily separated and removed from solution by simply applying an external magnetic field with a magnet or an electromagnet [30–33]. Magnetic settlement by an appropriate magnetic field provides a convenient and low cost method for the separation of solid particles in a suspension, as it is well illustrated in sewage or drinking water plants with the Sirofloc$^\circledR$ process [34]. Second, it has been shown that γ-Fe_2O_3 and Fe_3O_4 are the most active and stable iron oxide phases in photo-Fenton processes [16]. Compared with Fe_3O_4, γ-Fe_2O_3 nanoparticles are not submitted to oxidation, and are therefore more stable in water and air. Third, the γ-Fe_2O_3 nanoparticles used in this work have been thoroughly characterized and tested as Fenton catalyst in a previous publication [35].

Among the parameters which are studied here, the presence of silica (SiO_2) microspheres (MS) as a porous support for the γ-Fe_2O_3 nanoparticles is of primary importance. It has been demonstrated that the dispersion of the catalyst on a support may considerably improve its activity, due to an increase of the adsorption of the pollutant and/or to a decrease of the recombination of the created electron–hole pairs [28]. Moreover, catalyst leaching problem can be avoided by hosting the heterogeneous catalyst onto a support [36]. In the case of a magnetic catalyst, we have shown in addition that the presence of a support can favor the recovery of the catalyst by magnetic settlement [35]. To study how the efficiency of light irradiation is affected by the nature of the pollutant, we chose to compare the degradation of three aqueous model pollutants, methylene blue (MB), methyl orange (MO) and paranitrophenol (PNP), which can be distinguished in terms of their charge, their light absorption properties, and their chemical structure. Finally, a simple halogen lamp has been taken as source of visible light. We show that this simple and cheap lamp is able to considerably increase both the decolorization and mineralization rate of the pollutant solutions without detrimental impact on the stability of the heterogeneous catalyst.

2. Experimental

2.1. Catalysts synthesis

The synthesis of the catalysts has been already described in our previous paper [35]. Briefly, magnetite (Fe_3O_4) NP were first prepared by the Massart's method, adding ammonia to an aqueous mixture of $FeCl_3$ and $FeCl_2$ [37]. Then, the Fe_3O_4 NP were oxidized to γ-Fe_2O_3 by successively adding HNO_3 and $Fe(NO_3)_3$ [38,39]. The γ-Fe_2O_3 NP were finally obtained as an aqueous acidic dispersion with a high colloidal stability, also called ferrofluid. The γ-Fe_2O_3 NP were supported on the surface of porous silica microspheres via a protocol inspired from the method originally described by Andersson et al. [35,40]. Briefly, a magnetic sol containing the γ-Fe_2O_3 NP and a silica precursor (tetraethoxysilane, TEOS) in acidic medium was added dropwise to an organic phase composed of a vegetable oil (usually commercial rapeseed oil) and a commercial emulsifier (Arlacel P135 from Uniquema), under stirring. The water-in-oil emulsion thus formed was transferred into a Büchner flask, and the ethanol formed by the hydrolysis of TEOS was evaporated from the dispersed phase under reduced pressure, which led to a rapid condensation of TEOS in silica in each water droplet. The emulsion was then broken by addition of a large amount of acetone. The silica MS containing the γ-Fe_2O_3 NP were washed several times with acetone and water, and dried at 70 °C. Finally, the beads were calcined in an oven under air at 400 °C for 18 h to remove any organic traces. In the following sections, the unsupported γ-Fe_2O_3 nanoparticles will be referred as the γ-Fe_2O_3 NP catalyst, while the γ-Fe_2O_3 nanoparticles supported on the surface of the silica microspheres will be referred as the γ-Fe_2O_3/SiO_2 MS catalyst.

2.2. Characterization of the catalysts

Transmission electron microscopy (TEM) micrographs of the γ-Fe_2O_3 NP and γ-Fe_2O_3/SiO_2 MS catalysts were taken using a JEM JEOL 100 CX microscope operating at 100 kV. In this aim, the MS were embedded in a resin (AGAR 100), which was then polymerized at 60 °C during 2 days, and cut in 70 nm thin sections using a LEICA ULTRACUT UCT microtome apparatus. The MS catalysts were also observed by scanning electron microscopy (SEM) on a SEM-FEG Hitachi SU-70 apparatus. The images were taken in secondary electron mode with an accelerating voltage of 10 kV. Prior to analysis, the beads were coated with a thin shell of gold by sputter deposition. The size distribution of the particles was determined from TEM or SEM pictures analyzed using the Image J software. The amount of γ-Fe_2O_3 NP in the MS was determined by spectrophotometry. In this aim, a given weight of material was first introduced in an HCl aqueous solution (4 mol L^{-1}). After 48 h of stirring, the γ-Fe_2O_3 NP were totally dissolved, and the iron concentration in the supernatant was analyzed by atomic absorption spectrophotometry (Perkin Elmer AA100 apparatus) and the weight fraction of γ-Fe_2O_3 in the beads, $w_{Fe_2O_3}$ was determined. A