Evaluation of the photocatalytic activity of iron oxide nanoparticles functionalized with titanium dioxide

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Abstract. Photocatalytic activity of iron oxide (IO) nanoparticles functionalized with TiO₂ was evaluated through photodegradation of phenol under UV irradiation. For this, magnetic nanoparticles were synthesized by co-precipitation method obtaining aggregates with a size of 46nm. The IO nanoparticles were encapsulated in a polysiloxane matrix and then functionalized with TiO₂ at 25°C (sample A: 0.1g TiO₂ and B: 0.3g TiO₂). Photodegradation experiments were carried out for six hours at pH 3.0 using concentrations of IO-TiO₂ nanoparticles of 0.2, 0.5, and 1.0g/L. A maximum amount of 89% of phenol photodegradation was achieved by using 0.2g/L of the IO-TiO₂-B sample. In addition, it was evaluated the possibility to re-using the nanomaterial after magnetic separation. For this, 0.2g/L of B sample were submitted for five cycles of photodegradation. A stable photocatalytic activity was observed as well as the nanoparticles were regenerated by calcination among cycles, which suggests the versatility of these nanoparticles for the photodegradation of organic pollutants.

1. Introduction
Elimination of phenolic compounds in wastewaters has been widely studied by different processes such as biological treatments, photocatalysis, adsorption, electrochemical oxidation, and Photo-Fenton oxidation [1-4]. Despite their effectiveness, many of them present disadvantages like transfer of pollutants, long degradation times and loss of valuable materials (catalysts) [1,2]. Development of new technologies to achieve the degradation of phenol in a suitable way becomes then necessary.

Titanium dioxide nanoparticles represent a promising alternative regarding contaminated wastewater treatment, thanks to their excellent photocatalytic activity and large surface area [3-5]. However, the separation of the nanoparticles from the aqueous solution once the process has finished represents a major drawback for their application. Supported titanium dioxide can face this inconvenient by allowing an easy separation of the catalysts from the reagents and products, as well as a lesser product contamination and high adaptability to continuous processes [1,2,6].

This study focuses on the evaluation of the photocatalytic activity of iron oxide (IO) nanoparticles modified with TiO₂. In order to achieve this objective, the photodegradation of phenol was studied in an aqueous solution (50ppm of initial concentration of phenol and a pH of 3.0) under constant UV irradiation. In addition, it was studied the possibility of reusing the nanomaterial by magnetic separation and calcination. From these experiments, a stable photocatalytic behaviour was observed after five photodegradation cycles.
2. Methodology

2.1. Synthesis of iron oxide nanoparticles and functionalization with titanium dioxide (IO-TiO$_2$)
Iron oxide (IO) nanoparticles were synthesized from an aqueous solution of ferric chloride (0.36M) and ferrous chloride (0.18M) [7]. This mixture was heated up to 70°C and then 10mL of NH$_4$OH were added. The synthesis was carried out at 80°C and a pH of 8.0. Afterwards, nanoparticles were washed with distilled water and dried at 80°C. On the other hand, TiO$_2$ was synthesized by reduction of titanium isopropoxide (5mM) with 15 mL of an aqueous lemongrass leaves extract. This process was carried out at 25°C at 175rpm for 24 hours. Then, nanoparticles were centrifuged at 5000rpm for 15min, washed with distilled water/ethanol, and calcinated at 550°C for 3 hours.

For the production of the IO-TiO$_2$ nanocomposite, 0.7g of IO nanoparticles were suspended in 20mL of dimethyl sulfoxide (DMSO) using an ultrasound at 8000rpm. Then, it was added 3mL of tetraethyl orthosilicate (TEOS). Reaction was carried out at 100rpm for 48 hours [2]. IO nanoparticles encapsulated in the TEOS silica matrix were later separated by centrifugation and suspended again in DMSO (1%w/v). In order to obtain multifunctional nanomaterials, TiO$_2$ nanoparticles were added to the suspension of IO nanoparticles in DMSO. For this purpose, it was added 0.1g of TiO$_2$ (sample IO-TiO$_2$-A) and 0.3g of TiO$_2$ (sample IO-TiO$_2$-B). The functionalization was carried out with mechanical agitation during 12 hours. Afterwards, the multifunctional material was separated by centrifugation at 5000rpm during 15 minutes, washed with ethanol and dried at room temperature.

2.2. Evaluation of the photodegradation of phenol using the iron oxide-TiO$_2$ nanomaterials
Photocatalytic activity was evaluated as a function of nanocomposite concentration by adding 0.2, 0.5 and 1.0g/L of the IO-TiO$_2$ nanomaterials to a synthetic phenol solution, prepared at 50ppm and a pH of 3.0. The photodegradation of phenol was performed in a UV irradiation chamber for 6 hours at 100rpm [1]. Phenol absorbance was read in an UV spectrophotometer at a wavelength of 271nm [1]. Additionally, it was tested the performance of IO-TiO$_2$ nanomaterials for continuous photodegradation applications. Thus, after finish a photodegradation cycle, IO-TiO$_2$ nanomaterials were decanted using a magnet, washed three times with distilled water/ethanol (2:1), and calcinated again at 550°C.

2.3. Characterization
Nanoparticles were characterized by dynamic light scattering (DLS) using a ZetaSizer NanoSeries/Nano-Zs90 equipment. Crystalline structure was determined through X-ray diffraction using an XPerf PRO equipped with a PW3050/60 goniometer. A JEOL JSM-6490LV scanning electron microscope coupled to an EDS was used to take images of these nanomaterials. The photocatalytic activity of phenol was determined using a Labomed Inc. UV 2650 spectrophotometer.

3. Results and discussion

3.1. Determination of size and composition
Figure 1 shows the hydrodynamic size obtained for IO nanoparticles suspended in DMSO, from which it was estimated a size of 46±2.0nm (Figure 1(a)). In the case of TiO$_2$ nanoparticles, DLS measurement was not performed because it was not possible obtain a stable colloidal suspension of this nanomaterial in DMSO media. X-ray diffraction was used to determine the crystal structure of the synthesized nanoparticles (Figure 1(b)). From this measurement it was observed the characteristic diffraction patterns of the cubic inverse spinel structure of IO nanoparticles (maghemite/magnetite) and the presence of the anatase crystal phase in the TiO$_2$ nanoparticles, both results are in accordance with the information reported in literature [8,9]. Scherrer’s equation [2] was used to estimate an average crystal size of 30±20nm for IO nanoparticles and 19±4nm for TiO$_2$ nanoparticles. These results are in agreement with the crystal size reported by Alvarez and co-workers (2010), whose calculated a crystal size of 25.8nm for IO nanoparticles and 14.5nm for TiO$_2$ nanoparticles [2].
Figure 1. (a) Hydrodynamic size measurements of the IO nanoparticles suspended in DMSO. (b) X-ray diffraction patterns of IO and TiO$_2$ nanoparticles.

Figure 2 shows images of the nanoparticles using a SEM. There, it can be observed that the IO and TiO$_2$ nanoparticles have an amorphous shape with a wide size distribution. Once the modification was performed, the elemental composition of iron, oxygen, silica and titanium atoms in the samples was analysed by EDS. Table 1 presents a summary of these results, from it was estimated a molar ratio Fe:Ti equal to 10 for sample IO-TiO$_2$-A and a molar ratio Fe:Ti equal to 55 for sample IO-TiO$_2$-B.

Table 1. Elemental composition of the synthesized nanoparticles.

| Element | IO-TiO$_2$-A, weight % | IO-TiO$_2$-B, weight % |
|---------|------------------------|------------------------|
| O       | 40.54                  | 46.88                  |
| Si      | 6.21                   | 6.61                   |
| Ti      | 4.84                   | 0.83                   |
| Fe      | 48.41                  | 45.69                  |

3.2. Evaluation of the photocatalytic activity of the IO-TiO$_2$ nanomaterials

Figure 3 shows the results obtained after the photodegradation of phenol by using the IO-TiO$_2$ nanocomposites. From this, it was observed a maximum photodegradation of 89% by using 0.2g/L of the IO-TiO$_2$-B sample. This, can be attributed to the elemental composition of this nanomaterial, which displayed a Fe:Ti ratio of ~55. Despite the protective layer of siloxanes surrounding the magnetic nanoparticles, it is possible that Fe (III) ions can be released to the solution [9]. These ions can increase the photocatalytic activity of titanium dioxide at pH of 3.0 by acting as electron acceptors and preventing the occurrence of an electron-hole recombination process [2]. The other reason can be the probable occurrence of a Fenton-like process, which could lead to the free hydroxyl radicals formation [4,9]. These additional oxidant species can increase the photodegradation rate of the phenol.

3.3. Magnetic removal and photodegradation cycles

The lifespan of IO-TiO$_2$ nanomaterial, along with its photocatalytic sensittiveness, was evaluated as a function of the operating time. For achieving this, phenol photodegradation was studied by submitting sample IO-TiO$_2$-B (0.2g/L) to five continuous cycles of UV irradiation at a pH of 3.0 for 6 hours. The
reuse of the IO-TiO₂ material was performed applying magnetic decantation and redispersion in a fresh phenol solution at 50ppm. Table 2 presents the obtained results. A ~20% decrease in the photocatalytic activity of the nanomaterial was observed. This can be attributed to the deactivation by catalyst poisoning, which causes a decrease in the active sites that are available for photodegradation. This is why the calcination of the material at 550°C was considered and evaluated after each photodegradation cycle, with the purpose of removing all of the impurities that could deactivate the catalyst. Table 2 shows these results, from which a stable photocatalytic activity was observed for the regenerated nanomaterial, suggesting its possible reutilization.

**Table 2.** Photocatalytic sensitiveness of the IO-TiO₂-B sample.

| Cycle | Photodegradation | Photodegradation/calcination |
|-------|------------------|-----------------------------|
| 1     | 89.1             | 89.7                        |
| 2     | 86.6             | 86.4                        |
| 3     | 85.0             | 86.8                        |
| 4     | 79.5             | 84.6                        |
| 5     | 72.6             | 83.5                        |

**Figure 3.** Phenol (50ppm) photodegradation using the IO-TiO₂ nanomaterials under ultraviolet irradiation by 6h.

4. Conclusions
The synthesis of iron oxide nanoparticles and their modification with titanium dioxide was presented by executing a simple and easily implemented method. The synthesized nanomaterial (IO-TiO₂-B) achieved a high photodegradation percentage of phenol by using a low concentration (0.2g/L), which contributes to the cost effectiveness of the photodegradation process. It was necessary to implement an additional regeneration process which was found to be necessary for maintaining a stable photocatalytic behaviour. All of the above characteristics show how attractive the use of this nanomaterial can be when it is intended for wastewater treatments, due to their magnetic/photocatalytic duality.

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References
[1] Laoufi N, Tassalit D and Bentahar F 2008 Global NEST Journal III 10-3 404
[2] Alvarez P, Jaramillo J, Lópe F and Plucinski K 2010 Applied catalysis B Environmental 100 338
[3] Akpan U and Hameed B 2009 Journal of Hazardous Materials 170-2-3 520
[4] Asiri A, Al-Amoudi M, Al-Talhi T and Al-Talhi A 2011 Journal of Saudi Chemical Society 15-2 121
[5] Pazokifar S, Farrokpay S, Mirabedini M and Esfandec M 2015 Progress in Organic Coatings 87 36
[6] Sood S, Ahmad U, Surinder K and Sushil K 2015 Journal of Colloid and Interface Science 450 213
[7] Wei Y, Han B, Hu X, Lin Y, Wang X and Deng X 2012 Procedia Engineering 27 632
[8] Wei Sh, Hu X, Liu H, Wang Q He Ch 2015 Journal of Hazardous Materials 294 168
[9] Zhana J, Zhangb H, Zhu G 2014 Ceramics International 40 8547