

Photocatalytic Removal of Phenol by Ferromagnetic N-TiO₂/SiO₂/Fe₃O₄ Nanoparticles in presence of Visible Light Irradiation

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Heterogeneous photocatalysis with TiO₂ has shown high efficiency in the removal of a wide range of organic contaminants. Recently, significant efforts have been made to activate TiO₂ under visible light wavelengths, and promising results were obtained by doping it with nitrogen. The main drawback of the use of nanoparticles for the purification of wastewater is their separation after the depollution treatment and this is an issue that has to be addressed for a proficient application of N-doped TiO₂ nanoparticles. The use of magnetic core Fe₃O₄ and N-doped TiO₂ shell nanoparticles could be a solution to this problem. With the aid of an external magnetic field, the removal and recycling of the photocatalyst nanoparticles become possible. For this reason, the aim of this work was to obtain nanocomposites consisting of visible active N-doped TiO₂ supported on SiO₂/Fe₃O₄ ferromagnetic nanoparticles. The nanocomposites were then evaluated in the photocatalytic removal of phenol. The photocatalytic tests were carried out in a recirculating batch cylindrical photoreactor irradiated by a strip of white LEDs surrounding the external surface of the reactor and emitting in the visible region.

The experimental results showed that N-doped TiO₂/SiO₂/Fe₃O₄ nanoparticles are effective in the removal of phenol, reaching degradation and TOC removal of about 64 and 55%, respectively, after an irradiation time of 270 min. The catalyst was collected at the photoreactor bottom after each test cycle by applying a magnet on the external surface of the photoreactor, so easily separating the treated solution from the photocatalyst. After washing with distilled water and drying at 50 °C, the photocatalyst was reused without further treatment. Photocatalytic tests on the recycled catalyst showed that N-doped TiO₂/SiO₂/Fe₃O₄ remains stable, evidencing phenol degradation in the range 59-65% after four operation/regeneration cycles.

1. Introduction

Phenolic compounds represent a threat to the environmental point of view because of their toxicity, bioaccumulation, and persistency in the environment. The representative of this class of compounds is phenol, widely used as a raw material in the petrochemical industries and oil refineries (Tao et al., 2013). Phenol and its derivatives are found in the effluents of various industries such as petrochemical, coal, pharmaceutical, wood, paint, pulp and paper industries (Ahmaruzzaman, 2008). Therefore, the increasing presence of phenol represented significant hazardous environmental toxicity (Tao et al., 2013). However, traditional techniques such as active carbon adsorption, chemical oxidation, and biological digestion have low efficiency in the removal of phenol. Advanced oxidation process (AOPs) to degrade organic pollutants in wastewater is an interesting alternative to the traditional technologies. Among AOPs, heterogeneous photocatalysis with TiO₂ have shown high efficiency in the removal of a wide range of organic contaminants, also present in low amount in wastewater. However, TiO₂ has a large band-gap (3.2 eV), meaning that it can be only active under the UV light irradiation. Recently, significant efforts have been made to activate TiO₂ under visible light wavelengths, and successful results were obtained by doping it with nitrogen through sol-gel method (Sacco

et al., 2012). The developed N-doped TiO₂ (N-TiO₂) was very active in the removal of organic dyes (Vaiano et al., 2014), atrazine (Sacco et al., 2015) and spiramycin (Vaiano et al., 2015).

However, one of the most important drawbacks of photocatalytic process is that photocatalysts are often used in slurry reactors. The limitation of the slurry process is that the N-TiO₂ nanoparticles must be separated from the system after the treatment. The cost of this separation step may even invalidate economically the technique (Pozzo et al., 1997). Among several reported methods for separating and recycling the photocatalyst particle from the treated water, magnetic separation provides a convenient approach by the means of applying an external magnetic field. Magnetic photocatalyst obtained by coating TiO₂ particles onto Fe₃O₄ has been studied in the photocatalytic removal of 2-chlorophenol (Rashid et al., 2015), organic dyes (Wang et al., 2012) and in the photocatalytic degradation of organic compounds of olive mill wastewater (Ruzmanova et al., 2013), showing in all cases good stability after several cycles of repetitive use under UV irradiation. However, very scarce is the literature reporting the use of a visible-active magnetic photocatalyst in the removal of organic compounds from wastewater. For this reason, the aim of this work was to obtain nanocomposites consisting of visible active N-doped TiO₂ supported on SiO₂/Fe₃O₄ ferromagnetic nanoparticles (N-TiO₂/FM) and to evaluate the performances and recyclability of N-TiO₂/FM in the photocatalytic removal of phenol.

2. Experimental

2.1 Synthesis of N-doped TiO₂ photocatalyst

The N-TiO₂ photocatalyst was prepared by hydrolysis and condensation reactions at 0°C between a TiO₂ precursor (titanium tetraisopropoxide, >97 wt%, Sigma Aldrich) and ammonia aqueous solution (30 wt%, Carlo Erba). The obtained gel was then centrifuged and washed with distilled water. Finally, the sample was calcined at 450° C for 30 min. The molar ratio N/Ti is 18.6, the same as in the optimized catalyst formulation found in our previous work (Sacco et al., 2012).

2.2 Synthesis of SiO₂/Fe₃O₄ core-shell nanoparticles

The core-shell SiO₂/Fe₃O₄ nanoparticles (FM) were prepared by two steps. Firstly, Fe₃O₄ magnetic nanoparticles were synthesized using a spinning disk reactor (De Caprariis et al., 2012). Then, FM nanoparticles were prepared by dispersing Fe₃O₄ particles in distilled water, followed by the addition of C₂H₅OH (Sigma Aldrich). Tetraethyl ortosilicate (TEOS), preliminarily diluted in C₂H₅OH, was added drop-wise to the Fe₃O₄ particle suspension. Then an aqueous solution of NH₃ (30 wt %) was added and the TEOS hydrolysis and condensation was allowed under overnight gentle stirring. The obtained FM particles were washed in a centrifuge using firstly water/ethanol mixtures then distilled water. Finally, they were dried and calcinated at 450 °C for 30 min.

2.3 Synthesis of N-doped TiO₂ supported on SiO₂/Fe₃O₄ nanoparticles

The FM nanoparticles were used as support for N-TiO₂ catalyst: 0.5g of FM particles were dispersed in 100 mL of HNO₃ (0.1 mol L⁻¹) aqueous solution and maintained under mechanical stirring several minutes until to obtain an uniform dispersion. Then, 4 mL of TEOS and 0.3 g of N-TiO₂ were added to the FM aqueous suspension. The mixture was kept under stirring for 48 h at 25 °C and then centrifuged. Finally, the recovered sample was calcined at 450° C for 30 min to obtain the final N-TiO₂/FM catalyst. The nominal loading of N-TiO₂ on the FM support was 37.5 wt %.

2.4 Samples characterization

Physico-chemical characterisation of samples has been performed with different techniques. Laser Raman spectra were obtained at room temperature with a Dispersive MicroRaman (Invia, Renishaw), equipped with 514 nm laser, in the range 100-2500 cm⁻¹ Raman shift. UV-Vis reflectance spectra were recorded with a Perkin Elmer spectrometer Lambda 35. X-ray diffraction (XRD) was carried out using an X-ray microdiffractometer Rigaku D-max-RAPID, using Cu-K α radiation and a cylindrical imaging plate detector. Diffraction data from 0 to 204 degree horizontally and from -45 to 45 degree vertically were collected. The incident beam collimators enable different spot sizes to be projected onto the sample. Specific surface area (SSA) of catalysts was obtained by N₂ adsorption measurement at -196 °C with a Costech Sorptometer 1040 after pretreatment at 60 °C for 120 min in He flow (99.9990 %).

The average size of the Fe₃O₄ nanoparticles was measured by dynamic light scattering instrument (Brookhaven Plus 91).

2.5 Photocatalytic tests

The photocatalytic experiments were carried out with initial concentration of phenol equal to 75 mg L⁻¹, at ambient temperature and pressure. The catalyst dosage was 3 g L⁻¹. The total volume of phenol aqueous solution was 75mL. The experiments were realized using a pyrex cylindrical photoreactor (ID=2.5 cm;

height=25 cm) equipped with an air distributor device ($Q_{\text{air}}=150 \text{ cm}^3 \text{ min}^{-1}$ (STP)). Continuous mixing of the aqueous solution was realized by external recirculation of the same solution through the use of a peristaltic pump. The photoreactor was irradiated with a strip composed of 25 white light LEDs (5W nominal power; provided by New Oralign), with wavelength emission in the range 400–800 nm with main emission peak at 475 nm. The LEDs strip was positioned around and in contact with the external surface of the photoreactor (incident light intensity 32 mW cm^{-2}). The system was left in the dark for 120 min to reach phenol adsorption equilibrium, and then photocatalytic reaction was initiated under visible light for 270 min.

The residual concentration of phenol in aqueous samples was monitored by observing the change in the absorbance at the maximum absorption wavelength of 500 nm using a UV–vis spectrophotometer (Lambda 35, Perkin Elmer), and then the concentration was calculated from a calibration curve. Total organic carbon (TOC) of aqueous samples was calculated from CO_2 obtained by catalytic combustion at $T=680^\circ\text{C}$.

3. Results and discussion

3.1 Samples characterization

The characteristics of the prepared samples are listed Table 1.

Table 1: Samples and their characteristics

Sample	SSA $\text{m}^2 \text{g}^{-1}$	Anatase average crystallite size nm	Fe_3O_4 average crystallite size nm
N-TiO ₂	30	17	-
FM	88	-	20
N-TiO ₂ /FM	46	15	20

The specific surface area (SSA) of pure N-TiO₂ (Table 1) was $30 \text{ m}^2 \text{g}^{-1}$, while a higher value ($88 \text{ m}^2 \text{g}^{-1}$) was found for FM sample. The deposition of N-TiO₂ particles on FM surface determined a decrease of the SSA value up to $46 \text{ m}^2 \text{g}^{-1}$. This last result is due to the coupling of two materials: one (N-TiO₂) with a lower SSA ($30 \text{ m}^2 \text{g}^{-1}$) and the other one (FM) with a higher SSA ($88 \text{ m}^2 \text{g}^{-1}$).

Dynamic light scattering results evidenced that Fe_3O_4 size distribution (not shown) was quite narrow with an average size of about 20 nm. Crystal phase composition of N-TiO₂, FM and N-TiO₂/FM was determined by XRD measurements (Figure 1).

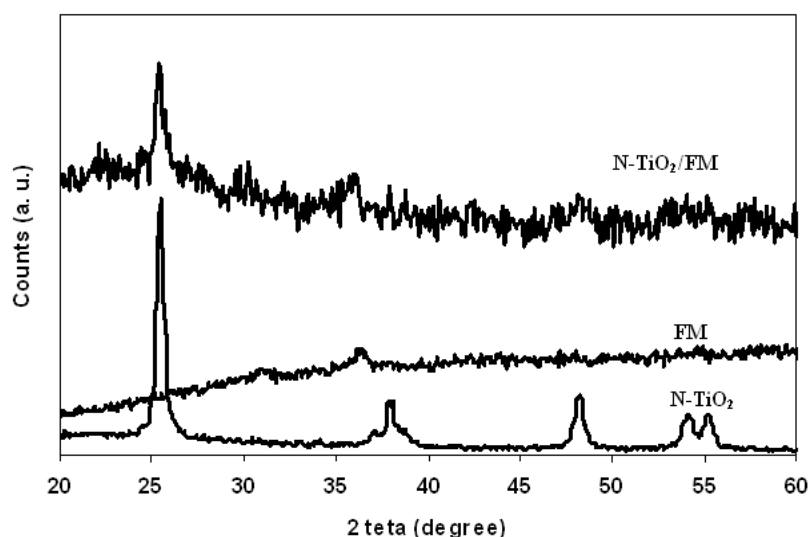


Figure 1: XRD spectra for N-TiO₂, FM and N-TiO₂/FM

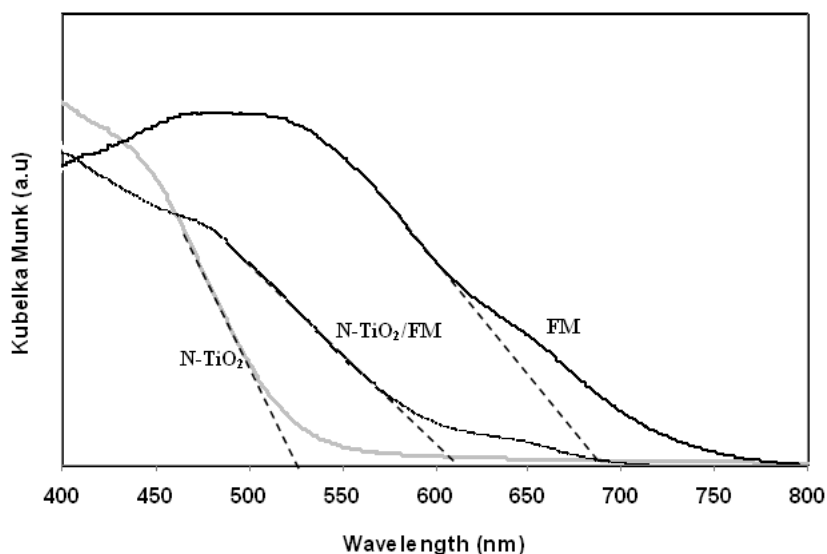


Figure 2: UV–VIS DRS spectra for N-TiO₂, FM and N-TiO₂/FM

XRD result of FM sample exhibited the presence of the crystalline form the orthorhombic phase of Fe₃O₄ (Wang et al., 2012). From the analysis of XRD spectra of N-TiO₂/FM compared with those of FM and unsupported N-TiO₂ powder, it was found the presence of the anatase-TiO₂ peaks with together the signals of FM. No diffraction peaks corresponding to SiO₂ were observed for FM and N-TiO₂/FM probably because silica has amorphous structure. The same results were obtained from Raman analysis (not shown). Anatase and Fe₃O₄ crystallite size of the samples were evaluated from XRD analysis, using the Scherrer equation (Table 1). For N-TiO₂, the anatase crystallite size was about 17 nm and slightly decreased after the deposition of N-TiO₂ on FM. Fe₃O₄ crystallite size was found to be about 19 nm which corresponds to the determined average particle size by dynamic light scattering measurement.

Figure 2 reports the UV–vis reflectance spectra in terms of Kubelka-Munk function for N-TiO₂, N-TiO₂/FM and FM. N-TiO₂ and N-TiO₂/FM samples exhibited remarkable red shift of absorption edge to the visible light region which is the typical absorption property of TiO₂ doped with nitrogen (Lindgren et al., 2003). The shifting of the absorption onset from about 530 nm (for N-TiO₂) to about 610 nm (for N-TiO₂/FM) is due to the absorption properties of FM indicating an additive effect of the specific band edges of N-TiO₂ and FM on the N-TiO₂/FM catalyst.

3.2 Photocatalytic results

Preliminary experiments were carried out in order to verify that phenol was removed by the heterogeneous photocatalytic process under visible light. It was found that in the absence of photocatalyst, no decrease in phenol concentration was observed, Therefore, photolysis phenomena didn't occur.

Figure 3 reports the photocatalytic activity of N-TiO₂, FM and N-TiO₂/FM. After 270 min of visible light irradiation, no photocatalytic activity was observed for FM sample. On the contrary, both N-TiO₂ and N-TiO₂/FM catalysts were effective in the degradation of phenol in aqueous solutions. In particular the degradation efficiency of N-TiO₂ and N-TiO₂/FM were 77 and 64%, respectively. These values are higher than those reported in the literature concerning the photocatalytic degradation of phenol under visible light irradiation (Hamzezadeh-Nakhjavani et al., 2015). In addition TOC removal of about 65 and 55 % was achieved after 270 min of irradiation for N-TiO₂ and N-TiO₂/FM, respectively. This last result evidenced that the photocatalysts were also effective in the mineralization of phenol to CO₂ and H₂O.

The lower photocatalytic activity of N-TiO₂/FM compared to N-TiO₂ particles could be attributed to the strong brown colour of N-TiO₂/FM particles, which reduces the light penetration into the aqueous medium.

However, as the separability of photocatalysts from treated wastewater in practical wastewater treatment systems is very important, magnetic N-TiO₂/FM sample was chosen for investigating the stability and efficiency after four reuse cycles (Figure 4).

N-TiO₂/FM catalyst was collected at the photoreactor bottom after each test cycle by applying a magnet on the external surface of the photoreactor, so easily separating the treated solution from the photocatalyst. After washing with distilled water and drying at 50 °C, the photocatalyst was reused without further treatment. Photocatalytic tests on the recycled catalyst showed that, after four reuse cycles, N-TiO₂/FM catalyst remained stable, evidencing phenol degradation and TOC removal in the range 59-65 and 45-56%, respectively.

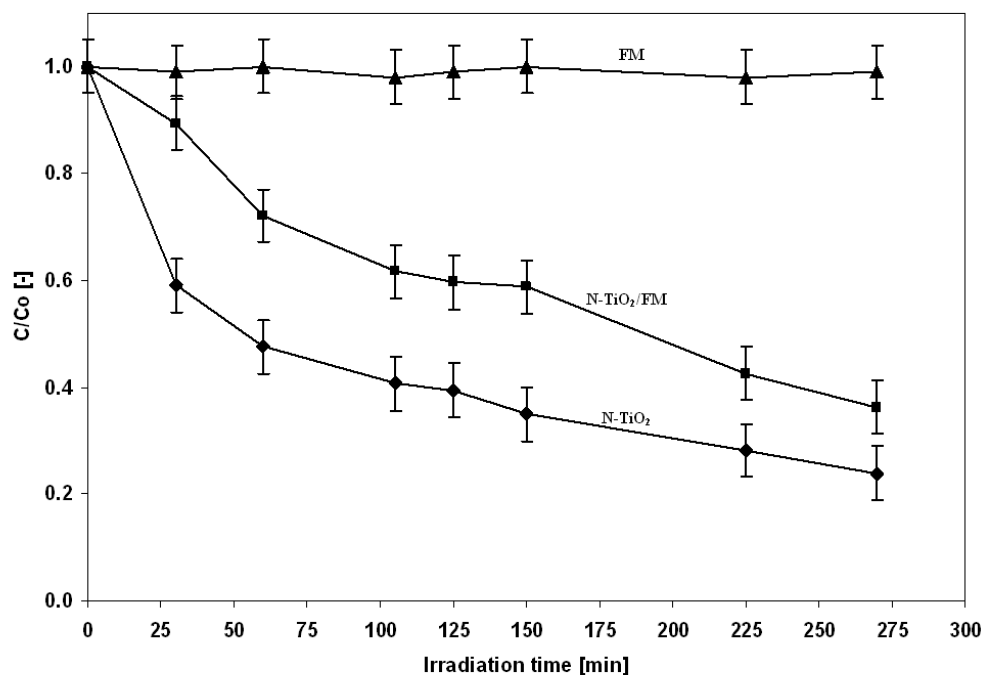


Figure 3: Photocatalytic degradation of phenol using N-TiO₂, FM and N-TiO₂/FM

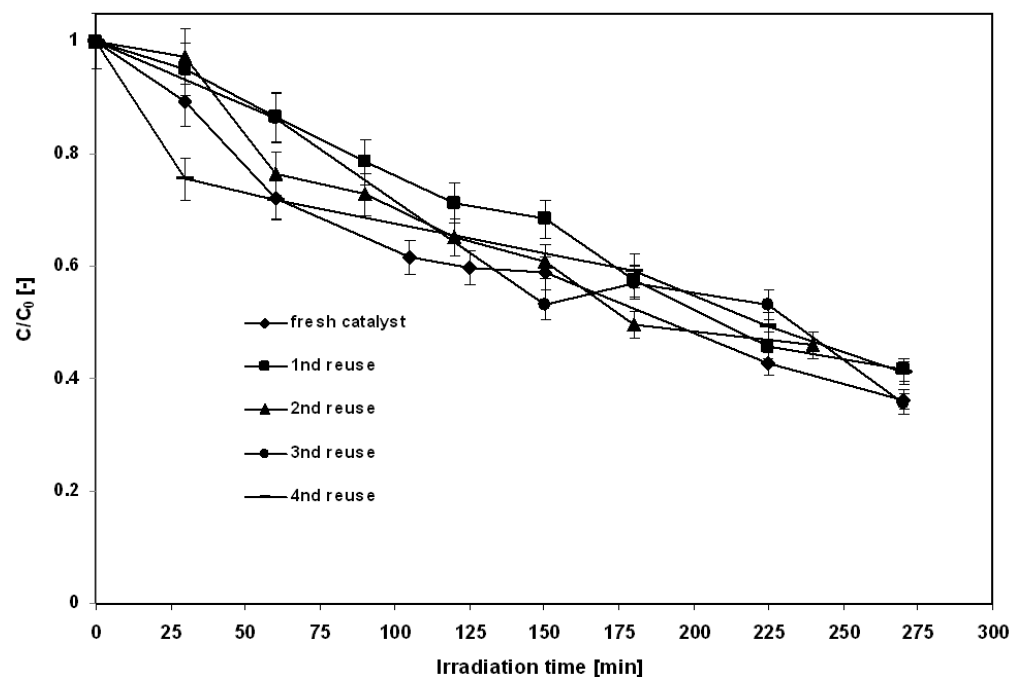


Figure 4: Photocatalytic degradation of phenol on N-TiO₂/FM after repetitive use

4. Conclusion

Visible-active magnetically separable nanocomposite N-TiO₂/SiO₂/Fe₃O₄ (N-TiO₂/FM) was successfully synthesized and tested in the photocatalytic removal of phenol under visible light irradiation. The XRD and Raman results confirmed the presence of crystalline magnetite, SiO₂, and TiO₂ in anatase phase and the average nanoparticle size of Fe₃O₄ magnetic core was about 20 nm.

The photocatalytic tests were carried out in a recirculating batch cylindrical photoreactor irradiated by a strip of white LEDs surrounding the external surface of the reactor and emitting in the visible region. The experimental results showed that N-TiO₂/FM nanoparticles are effective in the removal of phenol, reaching degradation and TOC removal of about 64 and 55%, respectively, after an irradiation time of 270 min. The results of visible-active magnetic catalyst reuse showed the effectiveness of prepared samples after four cycles of repetitive use, evidencing phenol degradation and TOC removal in the range 59-65 and 45-56%, respectively.

Acknowledgments

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