



# Degradation of nitro-aromatic explosives using recyclable magnetic photocatalyst: Catalyst synthesis and process optimization



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## HIGHLIGHTS

- Synthesis of a recyclable magnetic Titania nanoparticle with diameter of 22 nm.
- Modeling and optimization of the PNP degradation by photocatalytic method.
- Evaluation of kinetic, electrical energy consumption, and electrical energy cost.
- Study of redwater salts effect on the PNP degradation and redwater mineralization.

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## ABSTRACT

In this research, degradation of *P*-Nitrophenol (PNP) as a model nitro-aromatic compound was carried out by photocatalytic process using magnetic Titania nano particles (MTNPs). The recyclable MTNPs were synthesized with average diameter of 22 nm and a narrow size distribution. The process was modeled and optimized by a second order reduced polynomial model. Based on the model prediction, the process can be degraded PNP up to 90% under the optimum conditions of the initial pH = 4, [PNP] = 15 mg L<sup>-1</sup>, [MTNPs] = 85 mg L<sup>-1</sup>, and T = 25 °C. PNP mineralization was obtained 69%, at the optimum condition after 120 min of the process. The process kinetic was well fitted by pseudo first order kinetic model and electrical energy consumption of the process was obtained about 177.8 kWh/m<sup>3</sup>. Furthermore, the effect of sodium sulfite, sodium sulfate and sodium nitrite on the photocatalytic degradation process was assessed. The results showed that sulfite or sulfate ions decrease and nitrite ions increase the process efficiency. Also, a sample of redwater as a nitro-aromatic effluent was treated.

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## 1. Introduction

Nitro-aromatic compounds such as *P*-Nitrophenol (PNP), trinitrotoluene (TNT), dinitrotoluene (DNT), and nitrobenzene are valuable compound to manufacture explosives, drugs, dyes, and fungicides [1]. For example, in the TNT manufacture process a wastewater with a deep red color is produced which is known as redwater and is one of the important nitro-aromatic wastewaters. U.S. Environmental Protection Agency (USEPA) classified redwater as a reactive waste (number K047, 40 CFR, 261.32) that must be treated properly before disposal [2]. The wastewaters of these industries are toxic and their releasing in to the environment has crucial consequences. The oral LD<sub>50</sub> for PNP and TNT in rats is 250

and 795 mg/kg, respectively which confirm their toxicity [3,4]. Up to now, different methods such as biological, physical adsorption, and advanced oxidation processes (AOPs) have been utilized for the removal of nitro-aromatic compounds from aqueous media [5–8]. AOPs are in situ techniques which are able to oxidize and mineralize organic pollutants [1]. Considering to the mineralization of toxic organic material using AOP methods, they are preferred rather than physical and biological methods which produce secondary waste. Among the AOP methods photocatalytic process has been widely used by researchers [9–11]. In the process, application of Titania as a photocatalyst has been attracted, because of its chemical stability, low price, and non-toxicity [9]. It could successfully remove toxic organic pollutants especially nitro-aromatic compounds from aqueous media [10,12].

Also, the photocatalytic activity of Titania particles in the nano size scale is more than the larger size because of different physical and chemical properties of nanoparticles [11]. On the other hand, a serious problem can be caused for natural ecosystem by discharge

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of the nanoparticles into the environment. Since the nanoparticle size is similar to biological macromolecules and due to its antibacterial properties, it is toxic and has a crucial effect on the organisms [13]. Prevention is better than cure, hence ban of the nanoparticles entry into the environment is a vital task. Moreover, from the applied point of view, a valid nano-photocatalyst should be recycled and reused. To this aim, nano Titania, has been immobilized on the surface of different materials as fixed supporting beds such as glass fibers, polystyrene beads, quartz optical fibers, quartz raschig rings, and fiberglass cloth [14–18].

Application of the fixed bed types of reactors reduces the photocatalytic activity of Titania nanoparticles due to decrease of the available effective surface area. It is clear that the high catalytic surface area in slurry type of reactors cannot be ignored by researchers [19]. However, in these reactors separation of the Titania nanoparticles from treated effluent via a rapid and cost effective way is concerned. As a case of new and appealing method, photocatalytic nanoparticles have been combined with magnetic nanoparticles [19–21]. Therefore, the formed magnetic nano-photocatalysts can be easily separated from the effluent by a magnet and also be reused for further applications.

In this work, degradative removal of PNP molecule as a model nitro-aromatic explosive pollutant was surveyed by a synthesized magnetic Titania nanoparticles (MTNPs). The synthesis of MTNPs with average diameter of 22 nm and a narrow size distribution has been reported in details. Experiments were performed in a slurry type recycled batch photo-reactor. Effective operational parameters such as pH, dosage of the nanoparticles, and initial concentration of the pollutant were examined via response surface method (RSM) as a statistical experimental design. Under found optimum conditions, mineralization, kinetic, electrical energy consumption and its cost were investigated. Furthermore, the activity of recycled and reused MTNPs were tested. Also, ability of the photocatalytic process was examined for treatment of a redwater sample as a case of real wastewater.

## 2. Experimental

### 2.1. Reagents and instruments

P-Nitrophenol (PNP) with purity of 99% ( $C_6H_5NO_3$ ,  $M_w = 139.11$  g/mol) was prepared from Merck company.  $FeCl_3 \cdot 6H_2O$ ,  $FeCl_2 \cdot 4H_2O$ , tetraethyl orthosilicate (TEOS), tetrabutyltitanate (TBT), ethyl alcohol (EtOH, 99%), and ammonia solution (25%) were used to prepare MTNPs. Sulfuric acid and sodium hydroxide were used to adjust solution pH. All the chemicals were Merck and Fluka products. In all of the experiments, deionized water was used to prepare solutions.

Concentration of the PNP was measured by an UV–vis spectrophotometer (Shimadzu UV-3101PC). Total organic carbon (TOC) analysis was carried out by a multi N/C 3100 (Germany) instrument. The size of MTNPs was determined by Transmission Electron Microscope (TEM) (EM10C-100 KV- Germany). The crystal phases of the particles were evaluated by X-ray diffractometer (Philips PW 3710). Magnetic properties of the nanoparticles were assessed by a Vibrating Sample Magnetometer (VSM) (MDKFD-Iran). Also, a Fourier Transform Infrared Spectrometer (Nicolet 800) was used for determining created bonds in the synthesized MTNPs.

### 2.2. The slurry photo-reactor

To run the experiments a cylindrical pyrex container (1 l volume) was equipped with a cooling jacket to control the temperature and employed as reactor. An UV-C light source (150 W, Philips,  $\lambda_{max} = 254$  nm) was placed in a quartz tube and located in the cen-

ter of the reactor. Because of magnetic properties of the catalyst, stirring of the reactor content was done using a mechanical stirrer (Heidolph RZR 2041). An air compressor (RS-510) was used to blow air into the solution. Supplementary Fig. 1 shows a schematic view of the constructed photo-reactor.

### 2.3. Synthesize of the MTNPs

It is essential for a magnetic photocatalyst that easily can be collected and dispersed in the presence and absence of a magnetic field. Hence, the magnetic core of the photocatalyst should have intensive paramagnetic property. Hence, magnetite was chosen as the magnetic core of the photocatalyst for its superparamagnetic feature [22]. To synthesis the magnetite core nanoparticles, at first 40 ml deionized water was deoxygenated by purging nitrogen gas. After regulating of the temperature at 80 °C, 2.36 g of  $FeCl_3 \cdot 6H_2O$  and 0.86 g of  $FeCl_2 \cdot 4H_2O$  were added and mixed well by a mechanical stirrer to obtain a homogenous solution. Thereafter, 5 ml of ammonia solution (25 wt.%) was added dropwisely into the solution and continued stirring for 30 min. It is notable that the solution was bubbled with nitrogen gas in all of the synthesis stages. The obtained black precipitates of  $Fe_3O_4$  were washed by magnetic decantation for several times using deionized water and ethanol and dried under vacuum at 60 °C for 2 h [23].

In order to prevent incorporation of iron ions into the Titania crystal, which decreases the relevant photocatalytic activity, the synthesized  $Fe_3O_4$  nanoparticles were encapsulated by a nano layer of  $SiO_2$  [24]. In this regard, 1 g of the magnetite nanoparticles was dispersed into 20 ml deionized water by sonication. After that, 80 ml ethanol was poured into the suspension and mixed well by the mechanical stirrer. Then 2.5 ml of ammonia solution (25 wt.%) was added drop wisely while keeping the stirring speed. Finally, 1 ml TEOS was slowly added into the solution and the mixing was continued for 12 h. The obtained precipitate ( $Fe_3O_4@SiO_2$ ) was washed by magnetic decantation for several times using deionized water and ethanol and dried under vacuum at 60 °C for 2 h [24,25].

Lastly, 30 ml TBT was dissolved in 140 ml ethanol (99%). Then, 1 g  $Fe_3O_4@SiO_2$  nanoparticles were added into the solution and sonicated and mixed mechanically for 10 and 30 min respectively. Afterwards, 40 ml solution of water and ethanol (1:5) was added drop wisely into the suspension and continued stirring for 1 h at room temperature. Finally, the obtained nanoparticles were washed by magnetic decantation for several times using deionized water and ethanol and were dried at 105 °C for 1 h and calcinated at 500 °C for 1 h to form MTNPs ( $Fe_3O_4@SiO_2@TiO_2$ ) [19,26].

### 2.4. Characterization of the MTNPs

The synthesized MTNPs were characterized using TEM, XRD, FTIR, and VSM analyses. To approve the core-shell structure of the synthesized magnetic photocatalyst nanoparticles, the TEM analysis was performed that the relevant image has been demonstrated in Fig. 1. The TEM image illustrates formation of the core-shell structure well. Also, size distribution of the nanoparticles was evaluated based on the TEM image and its histogram was presented as Supplementary Fig. 2. It reveals a widespread size distribution in the range of 10–30 nm with mean diameter of 22 nm. It is notable that in this case, a particle size more than 300 nm has been reported in the previous related literatures [19,27].

The crystal phase and composition of the MTNPs were examined by XRD pattern. Fig. 2 shows XRD pattern of the synthesized nanoparticles in comparison with the anatase Titania and magnetite patterns. Formation of the MTNPs is confirmed via good accordance of the XRD pattern for the MTNPs with the anatase (Reference code: 01-089-4921) and magnetite (Reference code: 01-

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