

An Innovative and Easy Method for Iron-Doped Titania Synthesis

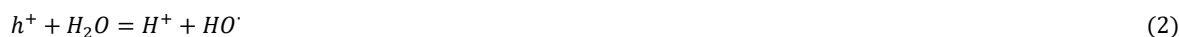
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In this work, photocatalytically active titanium oxide nanoparticles were synthesized for the treatment of contaminated water under visible light. Various Ag, Sr and Fe-based synthesis and doping techniques (mainly hydrothermal and sol-gel methods) were performed. Adsorptive and photocatalytic properties were studied by testing in batch mode for the decontaminating a synthetic methylene blue solution (used as a model contaminant) using a simple 13 W LED bulb as the light source. The best material in terms of both activity (high removal kinetics) and simplicity of synthesis was found to be titanium oxide doped with Fe via "solid-state" method. This method enabled the synthesis of titania nanoparticles about 70 nanometers in size with Fe³⁺ effectively substituting titanium atoms (Ti⁴⁺) in the crystalline bulk of titania. The pseudo-first-order kinetic model was found to represent the behavior of the experimental data.

1. Introduction

Population growth and industrialization led to increased production of contaminated water with emerging contaminants (Somma et al., 2021) that need to be removed for environmental protection (Akartasse et al., 2022). However, traditional techniques such as flocculation, filtration, and sedimentation cannot successfully remove the contaminant from water. Photocatalysis has proven to be an effective method for the degradation of organic pollutants due to its ability to mineralize several contaminants and, through radical oxidation (due to hydroxyl radicals, HO•), degrade them into CO₂. This phenomenon occurs when light radiation (of the appropriate wavelength) strikes the surface of the photocatalyst (a semiconductor) and photoexcites the electron, which from the valence band passes to the conduction band, generating a positive hole-electron pair. The excited electrons (e_{cb}) can react with dissolved oxygen in the water to form the superoxide radical (Eq. 1), while the positive hole (h^+) can oxidize a water molecule to form the hydroxyl radical (Eq. 2), which is more responsible for contaminant degradation due to its high oxidizing power (Eq. 3).



The most widely used photocatalyst is titanium oxide (TiO₂) because it is stable, chemically inert, inexpensive, non-toxic, and abundant. It has the disadvantage of a too high band gap (3.2 eV) thus working only under ultraviolet light (radiation at sufficient energy to photoexcite the electron) which is dangerous for human safety. To overcome this limitation, titania (TiO₂) doping is commonly employed as a successful method of decreasing the band gap thus allowing the catalyst to be active even under visible light. Titania doping involves enriching the crystalline bulk of titania with other chemical elements by forming lower-energy covalent bonds. Several synthesis techniques are already available to provide titania doping with several ions (Akerdi & Bahrami, 2019). The most widely used synthesis techniques are precipitation synthesis, the solvothermal method, and the sol-gel method (Kuriakose et al., 2013). In precipitation synthesis, the product obtained is controlled by solution concentration, pH, washing medium, and calcination temperature.

The advantages of this method are simple scalability, low cost, and nonrestrictive reaction conditions. The main disadvantage, however, is the difficulty in controlling particle size because of the high precipitation rate (Kuriakose et al., 2013).

The solvothermal method (hydrothermal if chemical reactions occur in aqueous solvents), through control of solution composition, reaction temperature, pressure, solvent type, and additives, provides efficient control of particle size, morphology, and crystallinity of the product. The disadvantages are the use of expensive equipment that is resistant to high pressures and temperatures and that the reaction usually proceeds without agitation, sometimes leading to an incomplete reaction and a non-uniform product. The sol-gel method is used for the synthesis of thin films and powders (Bokov et al., 2021), (Torres-Limiñana et al., 2022). The method provides excellent levels of purity, homogeneity, control of stoichiometry and composition, ease of processing, and the ability to make complex shapes (Mashuri et al., 2020). Disadvantages, however, include the possibility of particle agglomeration after calcination at high temperatures, which can cause a significant decrease in photocatalytic activity.

Among the most common doping agent, iron was selected, since, according to previous work (Ahmed et al., 2013) is an inexpensive but effective material therefore in this work different synthesis strategies have been attempted with this material and synthesis with silver and strontium has also been attempted for comparison.

2. Materials and methods

2.1 Chemicals

Titanium diisopropoxide bis-acetylacetonate (75% in isopropanol, Alfa Aesar), Titanium dioxide Degussa P25 (P25) with purity of 99.9% and particle size <41 nm Sigma Aldrich, ethanol (Honeywell, absolute, >99.8%), hexahydrated ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Honeywell), ferrous chloride (FeCl_2 , Honeywell), strontium hydroxide ($\text{Sr}(\text{OH})_2$, Sigma Aldrich), silver nitrate (AgNO_3 , Sigma Aldrich), hydrochloric acid (HCl 37% Honeywell) and sodium hydroxide (NaOH, Honeywell) Methylene Blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl} \cdot 3\text{H}_2\text{O}$, Sigma Aldrich). All the chemicals were used without any further purification. Demineralized water was used as a solvent for both solutions.

2.2 Photocatalyst synthesis

Titanium oxide (titania, sTiO_2) was synthesized starting with 7.1 mL of titanium diisopropoxide bis-acetylacetonate (75% in isopropanol) in 20 mL of ethanol mixed to form a homogenous solution. The solution was added dropwise to 40 mL of deionized water and stirred for 4 h at 80 °C. The solid was washed several times with deionized water using a centrifuge (10,000 rpm for 10 min) and then dried overnight in an oven at 60 °C. Finally, the solid was ground and calcined at 500 °C for 2 h.

Titania doping was performed with both sTiO_2 and P25 via hydrothermal and via "solid-state" methods: for this first type of doping, conducted via hydrothermal, titania and an iron precursor, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, dosed to meet the Ti:Fe ratio of 7:2, dissolved in water, was stirred to have a homogeneous suspension to which a 2M NaOH solution was added. The resulting product was placed in an autoclave at 160°C for 6 hours.

Finally, it was washed, dried in an oven (60 °C for one night), grinded, and calcined in a muffle at 500°C for 2 hours. Were then obtained the solids $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{P25}$.

For doping via solid state, titania (both sTiO_2 and P25) was grinded in a mortar with enough $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to obtain 1% iron by weight relative to titania. Once a homogeneous mixture has obtained the samples were calcined at 600°C for 3h. After calcination, they were grinded again for obtain the catalysts 1%Fe- TiO_2 and 1%Fe-P25.

The synthesis of titania doped with magnetite (Fe_3O_4) was carried out using bis(acetylacetonate) diisopropoxide of Ti at 75 wt% in isopropanol dissolved in ethanol, added dropwise in aqueous suspension with magnetite at 80 °C (to comply with the Ti:Fe ratio of 7:2) and kept in constant stirring for 4 hours.

Magnetite was previously synthesized by solubilizing 3 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.1 g of FeCl_2 in 150 ml of 0.2 M HCl and precipitating with 50 ml of 2 M NaOH.

However, such synthesis method was not successful because two separate solid phases were obtained.

The synthesis of titania doped with Ag and Sr (Ag/Sr- TiO_2) was carried out using solution of 7.1 ml Ti(IV) diisopropoxide and 50 ml absolute ethanol to which 200 ml water pH 1.5 (with hydrochloric acid) was added drop by drop under constant stirring. Then 5 ml of AgNO_3 and $\text{Sr}(\text{OH})_2$ 0.2 mol/L were added drop by drop under constant stirring. 5 ml of water containing 50 mmol hydrazine was added to the solution and stirred for 30 min. Then the suspension was sonicated at 80 MHz for 90 min and dried at 100 °C in an oven for 24 h. Finally calcined at 500 °C for 5 h.

Below is a table (Table 1) summarizing all the synthesis performed:

Table 1: All syntheses attempted

Catalyst	Titania (sTiO ₂)TiO ₂ /Fe ₃ O ₄		TiO ₂ /Fe ₂ O ₃	1%Fe-TiO ₂	Ag/Sr-TiO ₂
Reagents/Precursors	Titanium diisopropoxide	Titanium diisopropoxide/ FeCl ₂ FeCl ₃	P25/sTiO ₂ FeCl ₃ FeCl ₂	P25/sTiO ₂ FeCl ₃	Titanium diisopropoxide, AgNO ₃ Sr(OH) ₂
Reaction conditions	80 °C- 4 h	80 °C- 4 h	160 °C- 6 h	mechanical grinding	Room temperature, hydrazine
Molar ratio	-	Ti:Fe =7:2	Ti:Fe =7:2	Ti:Fe =100:1	Ti:Sr:Ag =7:1:1
Calcination step	500 °C – 2 h	-	500 °C – 2 h	600 °C- 3 h	500 °C – 3 h

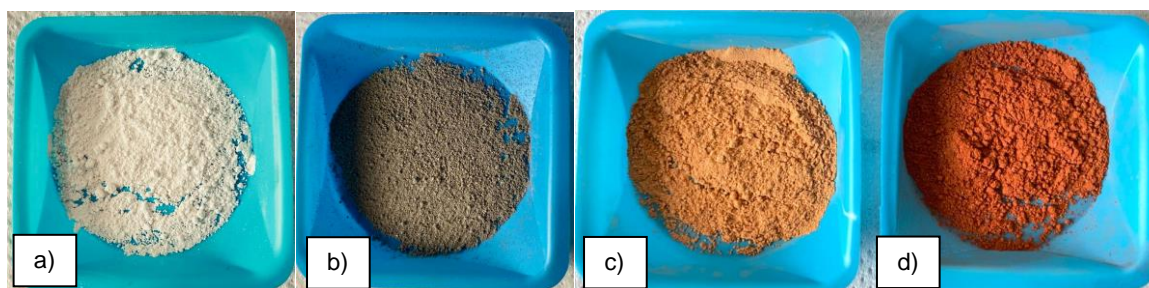


Figure 1: All synthesized materials: a) pure titania (sTiO₂), b) titania doped by strontium and silver (Ag/Sr-TiO₂), c) titania doped by iron (1%Fe-TiO₂), d) titania doped by hematite (Fe₂O₃/TiO₂)

2.3 Experimental setup

To evaluate the photocatalytic activity of the catalysts, batch experiments were performed with 20 mL of 5 ppm aqueous solution of methylene blue (MB) as a model contaminant and 20 mg of photocatalyst (1 g/L). A commercial 13 W Osram LED lamp (4000 K cool light) was placed 15 cm from the bottom of the beaker so that the irradiance of the sample was 9.4 W/m². The batches were stirred with a mechanical stirrer at a constant speed of 400 rpm. The aqueous suspension was kept in the dark for 30 min to reach MB adsorption-desorption equilibrium before starting the photocatalysis tests. The tests were also performed in the dark, to assess the adsorption capacity of the material and to appreciate the difference between the tests performed with and without using light radiation. MB concentration was determined by UV-vis spectrometric analysis (PG Instruments T80 + UV/Vis spectrophotometer) by measuring the absorbance at 664 nm of the supernatant after a specific time (0-180 min) after being centrifuged at 10000 rpm for 10 minutes.

The MB removal rate was calculated as follows:

$$\eta = \frac{A_0 - A(t)}{A_0} * 100 \quad (4)$$

where η is the MB removal efficiency, A_0 is the MB absorbance after the adsorption/desorption equilibrium was achieved and $A(t)$ is the MB absorbance of the solution at a specific time t .

3. Results and discussions

Tests were carried out both in the dark and under visible radiation to assess photocatalytic activity. The results of the tests are shown in Figure 2. From the data shown it was evident that pure titania did not show photocatalytic activity under visible light (Mohan et al., 2021) as the removal of the contaminant was the same under both visible light and in the dark. Therefore, contaminant removal was only due to the adsorption on the catalyst surface. This is true for both synthesized (sTiO₂) and commercial titania (P25). In addition, the sTiO₂ sample showed higher adsorptive capacity than P25 (they removed after 3 hours 50 and 9 % respectively). This could be attributed to the fact that sTiO₂ is richer in structural defects than 25, which makes it more reactive and less stable, inert, and more prone to contaminant adsorption (Barba-Nieto et al., 2020) in fact adsorption equilibrium was reached after 2 hours while for the other catalysts in less than 30 minutes.

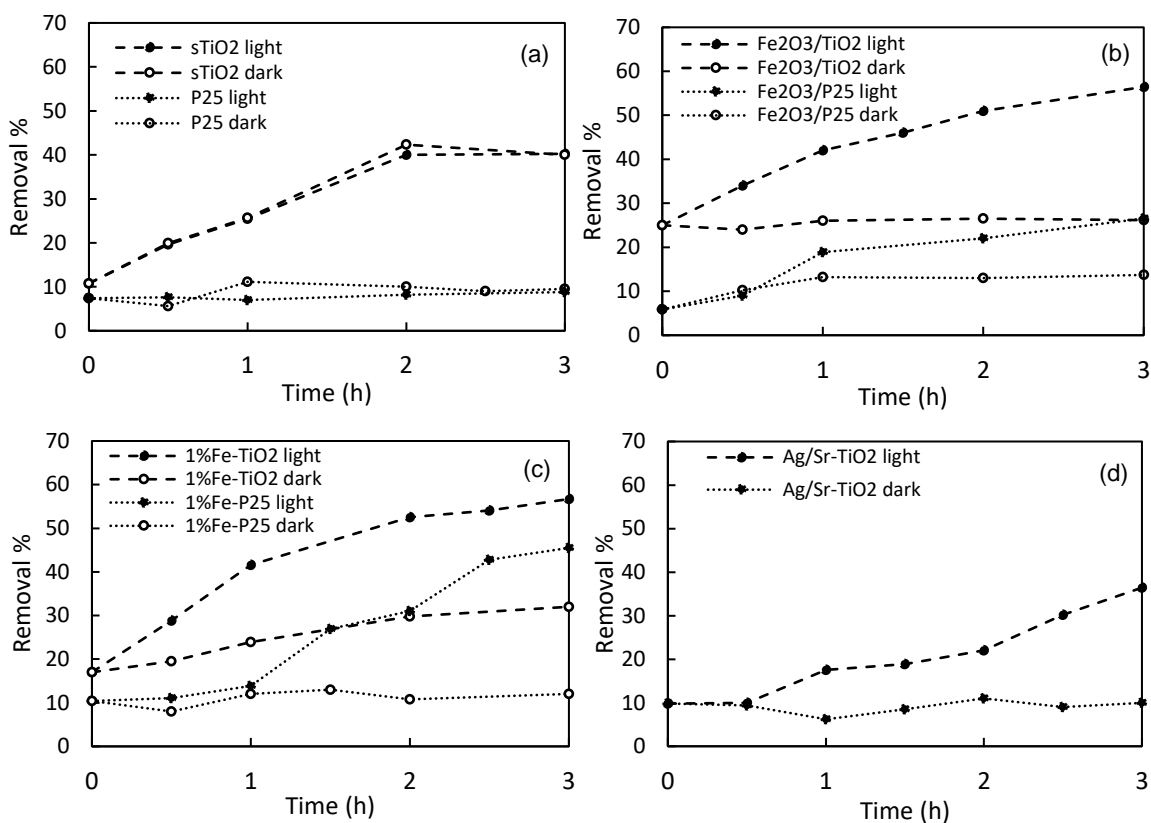


Figure 2: % removal as a function of time of MB 5 ppm solution using the amount of catalyst 1g/L at the irradiance of 9.4 w/m². All batches were kept in the dark for 30 minutes (which corresponds to time 0). The photocatalysts were tested both in the dark and under visible light and were (a) pure synthesized (sTiO₂) and commercial titania (P25), (b) Fe₂O₃/TiO₂ and Fe₂O₃/P25, (c) 1%Fe-TiO₂ and 1%Fe-P25, (d) Ag/Sr-TiO₂.

All other tested catalysts (Fe₂O₃/TiO₂, Fe₂O₃/P25, 1%Fe-TiO₂, 1%Fe-P25, Ag/Sr-TiO₂) showed good photocatalytic activity under visible radiation as significantly greater removal was observed when exposed to light as reported in Figures 2b, c, d, which means that doping was effective in order to sensitize titania by reducing its band gap and thus allowing it to produce hydroxyl radicals under visible radiation (Khasawneh et al., 2021). Furthermore, catalysts synthesized using P25 showed a lower % removals than the same catalysts synthesized with sTiO₂, as shown in Figure 2a. After 3 hours, a contaminant removal of 57 and 27 % was observed for Fe₂O₃/TiO₂ and Fe₂O₃/P25, respectively (Figure 2b). The same behavior was observed (Figure 2c) for the 1%Fe-TiO₂ and 1%Fe-P25 catalysts: after 3 hours, a removal of 57 and 46 % was respectively observed. Also in this case, the higher removal performance could be attributed to a higher presence of structural defects in the sTiO₂-based (Barba-Nieto et al., 2020) samples than in the P25-based samples, which contribute to an increased probability of formation of the photogenerated electron positive holes pair (Li et al., 2008) and thus to a higher production of hydroxyl radicals responsible for contaminant degradation. It also appeared evident how the Ag/Sr-TiO₂ catalyst poorly performed with respect to iron-based catalysts: after 3 hours, only a 36 % removal was observed. The poor photocatalytic activity shown could be due to the inhibitory effect on the recombination of the positive holes electron pair that Ag and Sr have (Wei et al., 2018). In any case, in this study, iron resulted to be the best doping agent: due to its similar ionic radius to titanium, it can effectively substitute for it in the crystal lattice of titania ensuring effective doping (Ti⁴⁺ is 0.68 Å⁺ and Fe³⁺ is 0.64 Å⁺) (Wang et al., 2005).

sTiO₂-based samples doped with iron (Fe₂O₃/TiO₂ and 1%Fe-TiO₂) showed comparable removal performance. In fact, after 3 hours of irradiation a removal of about 57 % of the contaminant was obtained with both catalysts. Iron substitution formed a Fe-O-Ti bond that allowed the material to absorb visible radiation, thus resulting in more effective production of hydroxyl radicals (Abbas et al., 2016). Moreover, coupling titania with hematite (or more in general, with lower band gap semiconductors) results in a physical separation of photogenerated charges since electrons tend to accumulate in the lower energy semiconductor and positive gaps do the opposite, so the probability of recombination decreases (Ola, 2014).

Although the two iron-based catalysts showed almost the same performances, considering the different synthesis strategies, the 1%Fe-TiO₂ material could be considered better than Fe₂O₃/TiO₂ because the simplicity of the synthesis via "solid-state" and, especially, the doping step does not involve the development of aqueous solutions to be processed.

4. Conclusions

In this work, the synthesis of different photocatalysts capable of working under visible light based on synthesized titania (sTiO₂) and commercial titania (P25) was carried out and their performance was tested by evaluating the removal of MB 5 ppm used as a model pollutant. In particular, sTiO₂, P25, Fe₂O₃/TiO₂, Fe₂O₃/P25, 1%Fe-TiO₂, 1%Fe-P25, Ag/Sr-TiO₂ were tested. It has been shown that pure titania does not exhibit photocatalytic activity under visible light as no difference in removals of the contaminant was observed between tests performed in the light and in the dark. Attempts of doping with different elements (Fe, Ag, and Sr) proved to be successful, since all the proposed photocatalysts exhibited a significant photocatalytic efficiency in contaminant removal when exposed to visible radiation.

The best performing materials were found to be sTiO₂-based materials doped with iron (Fe₂O₃/TiO₂ and 1%Fe-TiO₂) as both after 3 hours of irradiation removed 57% of the contaminant. However, it can be argued that 1%Fe-TiO₂ produced via "solid-state" synthesis is to be considered as the best catalyst, as the synthesis is easy, fast, and cheap to perform and does not produce wastewater.

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