Comparison of the Structural and Photo-catalytic Properties of Nanostructured Fe₃O₄/TiO₂ Core-Shell Composites Synthesized by Ultrasonic and Stöber Methods

Faezeh Parast¹, Mehdi Montazeri-Pour², Masoud Rajabi¹*, Fatemeh Bavarsih¹
¹Department of Materials Science and Engineering, Faculty of Technology and Engineering, Imam Khomeini International University (IKIU), Qazvin, Iran
²Department of Chemical and Materials Engineering, Buein Zahra Technical University, Buein Zahra, Qazvin, Iran

Abstract:
In the present research, Fe₃O₄/TiO₂ magnetic photo-catalytic nanocomposites with a core/shell structure were successfully synthesized using two techniques of ultrasonic and Stöber. In this way, iron oxide (II, III) nanoparticles as soft magnetic cores of this composite were prepared by utilizing a chemical method assisted by ultrasound with a Fe³⁺/Fe²⁺ molar ratio of 1.5 under the nitrogen atmosphere. Thereafter, titanium oxide coating was performed on Fe₃O₄ nanoparticles by using tetrabutyl orthotitanate (TBOT) and titanium isopropoxide (TTIP) precursors. The resultant nanostructures were characterized by means of X-ray powder diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, energy dispersive X-ray (EDX) analysis, vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Through findings obtained from TEM examinations, the formation of core/shell nanostructure was confirmed in the prepared Fe₃O₄/TiO₂ composites. Analysis of magnetic properties revealed that titanium oxide coating on iron oxide nanoparticles reduces saturation magnetization (Ms). The values of saturation magnetization for Fe₃O₄ powder and Fe₃O₄/TiO₂ nanocomposite powders achieved via ultrasonic and Stöber methods were 60, 23 and 9 emu/g, respectively. Photo-catalytic properties of Fe₃O₄/TiO₂ nanostructures were evaluated by the use of methylene blue dye under UV light. Results indicated that Fe₃O₄/TiO₂ composite obtained by the Stöber method has a better photo-catalytic property as well as a decreased but acceptable magnetic separation. Degradation of methylene blue dye in the presence of photo-catalytic powder prepared by ultrasonic and Stöber procedures was 61 and 69 %, respectively, within 90 minutes of UV light exposure.

Keywords: Photo-catalysts; Magnetite; Core/shell nanostructures; Magnetic materials; Nanocomposites.

1. Introduction

Due to the special properties and various potential use cases of composite nanoparticles with core/shell architectures, a large number of investigations have been devoted to prepare and study the properties of these nano-materials over the past decade [1,
Core/shell structured nanocomposites with magnetic cores are members of the family of these nano-materials, which have received a lot of scientific and industrial attention because of their numerous applications in diverse fields such as semiconductor photo-catalysts, selective separators, and biological or chemical sensors [3, 4].

In the case of semiconductor photo-catalysts which have been exposed to light with excitation energy higher than band gap energy, electron–hole pairs are generated [5, 6]. These charge carriers (electrons and holes) can perform the oxidation/reduction reaction with the compounds adsorbed on the semiconductor surface or lead to form radical groups. These radicals have a suitable oxidizing capability and can react with organic compounds such as aromatic groups, halogenated hydrocarbons, multivalent metals, organic dyes and even bacteria through different mechanisms [7-11].

Titanium oxide (TiO2) is a well-known semiconductor photo-catalyst which has attracted considerable interest, owing to its stabilized chemical structure and having outstanding physical and electrical properties, and biodegradability [5, 12-14]. The photocatalytic property of this material is applied in various environmental uses for the elimination of water contaminations and air pollutants. The titanium oxide-based photo-catalytic systems are utilized for various applications such as degradation of toxic organic compounds as well as destroying harmful bacteria and cancer cells [5, 15]. However, easy separation of titanium oxide particles from aqueous media is of great importance for photo-catalytic applications, but it needs complex and expensive processes. Also, titanium oxide separation might not take place completely; therefore, the remained titanium oxide results in toxicity and secondary contamination [5, 16, 17]. A wide variety of approaches have been utilized in order to solve these problems. A possible solution for overcoming these problems is the use of core/shell structured nanocomposites. In fact, magnetic particles can be used as cores, and coatings of titanium oxide on these particles can act as shells. By using this technique, control and gathering of these composite photo-catalysts can be achievable by the help of an external magnetic field [3, 18].

Iron (II, III) oxide nanoparticles (Fe3O4, magnetite) are among the most promising magnetic materials due to their appealing characteristics such as non-toxicity, chemical stability, high magnetic properties, and relatively low cost [19, 20]. Several wet chemical routes such as co-precipitation, sol-gel, and steam condensation methods have been used for the production of these nanoparticles. However, iron oxide nanoparticles are prone to agglomeration due to their high specific surface area and magnetization. Consequently, their surface is not suitable for fabrication of shell structures, and subsequent composite production. In order to establish stabilized solutions and to improve the distribution of these nanoparticles, several studies have used various protective agents to modify surface [20]. Some of these modifications are cheap and easy, such as chemical co-precipitation method, which usually needs surfactants in order to control particles size and their distribution. However, some other modifications are expensive and complex to perform, such as gamma ray exposure, which needs expensive precursors with special equipment [19]. Chemical ultrasonic is another way for preventing agglomerate formation which is applicable for the production of a wide range of nanostructured materials. Ultrasonic method is a technique for synthesis and layer deposition of metals and their oxides on various ceramics and polymers in nano scale. In this method, with a lower time and cost and without the use of a furnace for the production, powders with nano dimensions are achievable.

There are several techniques for the preparation of nanocrystalline titanium oxide including sol–gel, hydrothermal, solvothermal, electrodeposition, electrochemical anodization, etc. [21-24]; among which sol–gel method offers a number of unique features and is very common. Uniform nanostructures of titanium oxide can be obtained by a method known as Stöber, which is originated from the sol–gel process [25]. However, the time needed for production by this method is long and the developed precipitates are naturally amorphous. Therefore, heat treatment at high temperatures (500-800 °C) is needed for their
crystallization. Heat treatment can have destructive effects on photo-catalytic and magnetic properties. Furthermore, effective specific surface area decreases due to sintering and crystal growth. Accordingly, surface hydroxyl groups decrease. On the other hand, high calcination temperature of magnetic photo-catalysts with core/shell structure can persuade the reaction between the magnetic core and the titanium oxide shell. Moreover, heat treatment also results in the oxidation of the magnetic core followed by a reduction in the magnetic properties of prepared photo-catalysts [26, 27]. Hence, in order to produce such core/shell nanostructures, there is a need for a new method which does not require heat treatment. Sonochemical ultrasonic method is applicable for this purpose as it enables to synthesize a core/shell nanostructure without a need for a furnace; thus, the already explained problems get solved. Abbas et al. [20] synthesized \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) nanocubes by the single reaction sonochemical process without the use of surfactants. However, the quality of the titanium oxide coating formed as a layer around the core particles was not good. Xia et al. [28] obtained \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2 \) nanocomposites via ultrasonic and autoclave treatments by using poly (vinylpyrrolidinone) as the stabilizer. Fu et al. [29] fabricated the hybrid \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2 \) nanostructures via a facile but efficient synthesis route under mild conditions (\( \leq 100 \, ^\circ \text{C} \) in water) by using titanium (IV) butoxide as the precursor. They investigated the effect of increasing thickness of the titanium oxide shell of \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2 \) nanostructures on the methyl orange (MO) degradation. Their results showed that excessive increasing the thickness of the titanium oxide shell increased the photocatalytic degradation time. Recently, Lendzion-Bieluń et al. [30] prepared \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) magnetic nanostructures by microwave-assisted solvothermal method for phenol degradation.

Surface treatment of magnetic nanoparticles by surfactant can sharply decrease the saturation magnetization (\( M_s \)) of surface modified nanoparticles as compared to the native nanoparticles [31]. As far as the authors know, unlike previous similar works (two-step sonochemical methods) that use surfactants and stabilizers for the preparation of the \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) nanocomposite, in this study, the stabilizers were not used in the preparation of this nanocomposite. Therefore, by eliminating the stabilization step, the method of preparing these nanocomposites is easier and requires less time and cost. In addition, the use of ultrasonic waves (instead of magnetic stirring) reduces agglomeration and particle size [32] and consequently increases the photocatalytic properties of these nanocomposites.

In this study, firstly, \( \text{Fe}_3\text{O}_4 \) powder as the magnetic core was prepared by the use of precursors of iron chloride and sulfate via chemical co-precipitation under ultrasound. Following that, titanium oxide layer was directly deposited on the powder particles by utilizing two methods of ultrasonic and Stöber. Finally, investigations on the structural, magnetic, and photo-catalytic properties of these composites were carried out and findings across two synthesis procedure were compared.

2. Experimental Procedures
2.1 Materials

In order to prepare \( \text{Fe}_3\text{O}_4 \), starting materials including ferric chloride hexahydrate (\( \text{FeCl}_3.6\text{H}_2\text{O} \), Merck, \( \geq 99 \% \)) and ferrous sulphate heptahydrate (\( \text{FeSO}_4.7\text{H}_2\text{O} \), Merck, \( \geq 99\% \)) were respectively used as sources of trivalent and bivalent irons and sodium hydroxide (NaOH) was used as the precipitation agent in the co-precipitation solution. Also, ammonium hydroxide (28 wt.% NH\(_4\)OH), ethanol (C\(_2\)H\(_5\)OH), titanium isopropoxide (TTIP), tetrabutyl orthoformate (TBOT), and acetonitrile (C\(_2\)H\(_3\)N) were supplied by Merck and were reagent grade.
2.2 Synthesis of Fe₃O₄ nanoparticles

Firstly, a solution with a molar ratio of Fe³⁺/Fe²⁺ = 1.5 was prepared and exposed to ultrasound [19]. Afterward, sodium hydroxide (NaOH) was added in drops under ultrasonic vibration. During the addition, a black precipitate was rapidly formed. The main reaction under nitrogen atmosphere was:

\[ \text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (1) \]

Following that, in order to evaluate the effect of sonication time, the solution was exposed to ultrasound for 10, 15 and 20 min. The obtained products were placed in ultrasonic bath for 30 min under a temperature of 65 °C. Thereafter, in order to remove the excess amount of reactants, the reaction mixtures were centrifuged. The liquid in the centrifuge was separated and resultant Fe₃O₄ nano-particles were washed with ethanol and de-ionized water and then dried in a vacuum oven. The samples prepared under ultrasonic irradiation with various times of 10, 15 and 20 min were named as F10, F15 and F20, respectively.

2.3 Synthesis of Fe₃O₄/TiO₂ nanocomposites by Stöber method

In order to create a titanium oxide coating on Fe₃O₄ particles, the method of Behrad et al. [25] was utilized. Firstly, 2 wt.% of the prepared Fe₃O₄ powder (F20 optimum sample) was added to 70 ml ethanol and 2.5 ml ammonia, and the mixture was maintained under magnetic stirring. Afterward, the sample with 0.8 ml titanium isopropoxide (TTIP) and 5 ml ethanol was added to the solution as drop wise while stirring. Solution stirring was continued for 24 hours. After completion of the reaction, the obtained solution was centrifuged several times by the use of water and ethanol. The achieved precipitate was dried in a vacuum oven at a temperature of 74 °C. The attained powder was placed in the furnace with a temperature of 400 °C for 4 hours. This sample was coded as F20/TS.

2.4 Synthesis of Fe₃O₄/TiO₂ nanocomposites by ultrasonic method

Firstly, 40 mg of the prepared Fe₃O₄ powder (F20 optimal sample) was introduced to the ultrasonic reactor containing 70 ml ethanol and 20 ml acetonitrile. Then, 0.5 ml of ammonia solution (28 wt. %) was added at room temperature. Subsequently, the obtained suspension was put under magnetic stirring and a 0.7 molar alcoholic solution of tetrabutyl orthotitanate (TBOT) was added to it in drops. The mixture was stirred for 1.5 hours under ultrasonic. Finally, the suspension was centrifuged with help of ethanol and distilled water and the obtained solid precipitate was dried under vacuum in oven at a temperature of 80 °C. This composite sample was coded as F20/TU.

2.5 Photo-catalytic activity measurement

In this study, methylene blue (MB) discoloration under UV light (20 W Lamp) was used to evaluate the photo-catalytic property of the optimum nanocomposite. In this way, 0.03 gr of photo-catalyst samples prepared by two methods of Stöber and sonochemical were added to 30 ml aqueous solution (50 mg/l) of methylene blue, and it was stirred for about 30 min in a dark environment [33]. The solution obtained under these conditions was exposed to a UV-A lamp (20 W, Sylvania, Belgium). The wavelength range of UV irradiation was 320-400 nm and the emission spectrum energy was concentrated at 365 nm wavelength. The concentration of the non-degraded and remained methylene blue at different time periods was evaluated by an 1800 UV–Visible spectrophotometer. The percentage of MB degradation was estimated using the following equation:
\[ D(\%) = \frac{C_o - C_t}{C_o} \times 100 = \left( \frac{A_o - A_t}{A_o} \right) \times 100 \]  \tag{2} 

where, \( C_o \) and \( C_t \) are dye concentration before and after radiation at times of zero and \( t \), respectively. \( A_o \) and \( A_t \) are absorbance intensity before and after radiation at times of zero and \( t \), respectively.

### 2.6 Characterization

In order to identify the phase composition of the prepared samples, their X-ray diffraction patterns (XRD) were recorded by the use of a Philips PW-1730 X-ray diffractometer (40 kV, The Netherlands) using Cu-K\(_{\alpha}\) radiation (\( \lambda = 1.54 \) Å) with a step size of 0.05° in the 2θ range between 20 and 80°. The synthesized magnetic nanoparticles and the photo-catalytic nanocomposites were characterized by the use of field emission scanning electron microscopy (FESEM, TE-SCAN Company, model MIRA3), transmission electron microscopy (Philips model CM120 operating at 120 kV, TEM) and Fourier transform infrared spectra (Bruker, Tensor 27 FTIR). Magnetic properties of synthesized composites were also obtained by the use of vibrating sample magnetometer (VSM, Kavir Kashan Co.MDK6).

### 3. Results and Discussion

**Fig. 1.** XRD patterns of prepared Fe\(_3\)O\(_4\) samples: a) F10, b) F15 and c) F20.

Fig. 1(a) presents the X-ray diffraction pattern of F10 sample. As can be observed from the pattern of this sample, Fe\(_3\)O\(_4\) phase is formed as the main phase (COD card No. 96-900-2328). However, it appears that goethite phase (FeOOH with ICDD card No. 01-081-0464) is also present as impurity. Magnetite phase can be formed from used ferrous salts due to the following reactions (3), (4) and (5) [34):

\[
FeSO_4 + 2NaOH \rightarrow Fe(OH)_2^+ + Na_2SO_4 \tag{3}
\]
\[
FeCl_3 + 3NaOH \rightarrow Fe(OH)_3^- + 3NaCl \tag{4}
\]
\[
2Fe(OH)_3^+ + Fe(OH)_2 \rightarrow Fe_3O_4 + 4H_2O \tag{5}
\]
However, the formation of magnetite nanoparticles can be accompanied by the formation of the intermediate goethite phase \[35\]. Generally, in many reports, the formation of unwanted goethite is also possible in the synthesis of precipitated magnetite \[34, 36\]. The goethite phase may be obtained by oxidation \[34, 37\]:

\[
4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 4\text{FeOOH} + 2\text{H}_2\text{O} \quad (6)
\]

Therefore, a suitable crystal quality was not obtained in F10 sample. Precise control of size, shape and surface of particles is usually a challenging problem. In order to control the size and nature of particles in terms of their phase composition and crystallinity, variables and media parameters such as atmosphere, preparing conditions, reaction temperature, mixing rate, ion intensity of the medium, as well as the type of used salts (chlorides, nitrites, and sulfates) can be effective \[38\].

In this way, in order to improve the quality of obtained peaks of Fe$_3$O$_4$ powder, the effect of ultrasonic reaction time was investigated. For this purpose, F15 and F20 samples were respectively exposed to ultrasound for 15 and 20 minutes. Figs. 1(b) and 1(c) show the X-ray diffraction patterns related to F15 and F20 samples, respectively. As can be seen, increasing time results in the elimination of impurities and improvement in the peak intensity of crystalline phase. The as-obtained peaks of X-ray diffraction pattern for F15 sample (Fig. 1(b)) matched with the Fe$_3$O$_4$ and FeOOH phases corresponding to the COD card No. 96-900-2322 and ICDD card No. 00-018-0639, respectively. It seems that the impurities are removed by increasing the ultrasonic time up to 20 min, and sample yielded under this condition (F20) comprises approximately a single phase of Fe$_3$O$_4$ (Fig. 1(c)). In fact, as the ultrasonic reaction time prolonged, the possibility of further mixing of materials is increased \[39\] and consequently, this can lead to the formation of pure magnetic phase by the following reaction \[34\]:

\[
2\text{FeOOH} + \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (7)
\]

Morphology and particles size of prepared Fe$_3$O$_4$ were characterized by using FESEM images. FESEM micrograph of prepared iron oxide nanoparticles (F20 sample) is presented in Fig. 2. According to this image, the particles are almost spherical and their size distribution is relatively narrow. The mean size of prepared particles was estimated at 31 nm by the use of Image J metallography image analysis software. M. Abbas et al.\[20\] synthesized iron oxide nanoparticles with an average size of 80 nm by the use of ultrasound.
The typical transmission electron micrographs of the as-prepared F20/TU and F20/TS nanocomposite samples are shown in Fig. 3. According to these images, a layer is formed on the iron oxide particles which has resulted in the non-uniformity of nanoparticle surfaces [25]. Increasing time can be effective in particles coating and increasing photo-catalytic properties. On the other hand, there is a possibility that the value of magnetic properties has a direct relation with the level of coating in Fe₃O₄/TiO₂ nanostructures. The increase in the thickness of the photo-catalytic shell results in the reduction of magnetic properties, and consequently, decline in the recovery ability of these nanostructures [40].

The titanium oxide shell formed by Stöber apparently differs from TiO₂ shell made by ultrasonic by having a markedly rough or granular appearance rather than a relatively smooth morphology. It seems that core/shell composite particles consisting of multiple cores are formed via Stöber method because that a single shell material is coated onto some small core particles together [3], as shown in Fig. 3 (b).

The average thickness of titanium oxide shell in F20/TU and F20/TS samples was obtained as 7 and 18 nm, respectively, by the use of Image J software. The quality of coating of titanium oxide on the magnetic core, its thickness and particles distribution of photo-catalytic composite have an impressive effect on the photo-catalytic efficiency. As can be observed from the TEM image of the photo-catalytic composite synthesized by ultrasound (Fig. 3(a)), although it has been exposed to ultrasound for 1.5 hours, coating has not formed properly over all surfaces of the magnetic core, whilst titanium oxide coating in photo-catalytic composite prepared by Stöber method (Fig. 3(b)) has been performed very well. However, by comparison between the agglomeration degree in the two methods of ultrasound and Stöber (Fig. 3(a, b)), it can be observed that in ultrasonic method, particle distribution is much better than Stöber method. Comparison between the average sizes of photo-catalytic composite particles confirms this matter. The level of agglomeration of these nanostructures is related to ultrasonic time and presence of surfactants. Chio et al. [41] produced a Fe₃O₄/TiO₂ magnetic composite with an average particle size of 30 nm. As the average particle size gets smaller, the contact surface of particles with the photo-catalytic shell increases, and consequently the photo-catalytic efficiency increases. Herein, the average particle sizes of photo-catalytic composite particles prepared by ultrasonic and Stöber methods were obtained as 23 and 34 nm, respectively. Fig. 4 presents the EDS spectrum of F20/TU nanostructure, based on which, the presence of Fe, O, and Ti elements in the prepared nanostructure has been confirmed. The presence of these elements is consistent with previous obtained results.

![Fig. 3. TEM images of a) F20/TU sample and b) F20/TS sample.](image-url)
Fig. 4. EDS. spectrum of F20/TU sample.

Fig. 5 presents the hysteresis curves of F20, F20/TU, and F20/TS samples at room temperature under applied magnetic field of 1000 to 10000 Oe. Magnetic properties of nanoparticles also depend on their preparation conditions. As can be observed, the magnetization curve of particles passes through the origin, and no coercivity and remanent magnetization is observed in them. Therefore, it can be deduced that all of the prepared particles are superparamagnetic at room temperature [42]. During recent years, several groups have produced Fe3O4 nanoparticles via ultrasonic method by the use of FeSO4.7H2O precursor. Mizukoshi et al. [43] have used this precursor in a solution medium containing NaOH and polyethylene glycol monostearete (PEG-MS). The obtained nanoparticles were almost irregular with low saturation magnetization (32.8 emu/g). Chang et al. have also used this precursor in a solution of NaOH and sodium acetate (NaAc). However, particles obtained by their method have not uniform size and the saturation magnetization was reported to be low (54 emu/g) [44]. In this study, saturation magnetizations of Fe3O4 nanoparticles prepared by ultrasonic method were obtained as 60 emu/g.

The coating developed on the core particles affects their magnetic properties. As a result of the titanium oxide coating, saturation magnetization of F20/TU and F20/TS samples has obtained as 23 emu/g and 9 emu/g, respectively, in which the decrease in magnetic properties is due to titanium oxide coating on Fe3O4 nanoparticles. Behrad et al. [25] have produced a magnetic composite by titanium oxide coating and have reported that saturation magnetization of the prepared photo-catalytic composite is 3.7 emu/g. They have stated that the core/shell nanostructure of Fe3O4/TiO2 has a good magnetic recovery capability. As can be observed from the hysteresis curves of Fig. 5, a lower magnetization has been obtained for the photocatalyst nanocomposite prepared by Stöber method (F20/TU sample) compared with ultrasonic method (F20/TU sample) which indicates that Stöber method has provided a possibility for higher and better coating on the iron oxide nanoparticles in addition to its acceptable recovery ability. This is in agreement with the results of TEM images in Fig. 3. Therefore, the decrease in the magnetic properties obtained by Stöber method is possibly due to the decrease in the free surface of iron oxide after suitable layer deposition of the titanium oxide shell over long time duration (12 h). Thus, a higher decrease in saturation magnetization is expected after formation of more chemical bonds between cores and shells. However, in ultrasonic method, the surface of some of the magnetic cores may remain uncoated, and accordingly higher magnetic properties are obtained in this method.
Fig. 5. Magnetization loops for a) F20, b) F20/TU and c) F20/TS samples at room temperature.

Fig. 6. FTIR spectra of a) F20 sample, b) F20/TU sample.

Fig. 6 displays the spectroscopy results obtained by FTIR for optimum iron oxide and Fe$_3$O$_4$/TiO$_2$ nanostructured composite powders (F20 and F20/TU samples). As can be observed from FTIR spectrum of F20 sample, the absorption peaks around 430 cm$^{-1}$ and 591 cm$^{-1}$ as well as 627 cm$^{-1}$ are associated with tensile vibration mode of Fe–O bands which are related to Fe$^{2+}$ ions at octahedral sites and Fe$^{3+}$ at octahedral and tetrahedral sites of magnetite structure, respectively [45, 46]. These peaks confirm the formation of Fe$_3$O$_4$ structure. Furthermore, the frequency of Fe$^{3+}$–O band (Fe$^{3+}$O$_6$) shows a shift in comparison with Fe–O absorption band in Fe$_3$O$_4$ bulk (570 cm$^{-1}$) which is due to the increase in the surface band force constant originated from the refinement of grains to nano scale [47, 48]. The bands centered at 2923 cm$^{-1}$ and 1624 cm$^{-1}$ are related to bending vibrations of H–O–H of water molecules [49, 50], whilst the band at 3390 cm$^{-1}$ is attributed to the tensile vibration of O–H group [25, 50, 51]. According to the FTIR spectrum of F20/TS nanocomposite sample,
absorption at low frequencies of 500-900 cm\(^{-1}\) is associated with the tensile vibration of Ti–O–Ti bonds [10]. Due to the overlap between the peaks related to Ti–O and Fe–O, a relatively wide band is formed in this region, which results in a clear difference between Fe\(_2\)O\(_4\) and Fe\(_3\)O\(_4\)/TiO\(_2\) spectra. In addition, the presence of two peaks at 1120 cm\(^{-1}\) and 1341 cm\(^{-1}\) is due to tensile vibrations of Ti–O and Fe–O–Ti bands and is an evidence for TiO\(_2\) connected to the surface of magnetic particles [20]. The peak located at 1403 cm\(^{-1}\) is associated with the vibration of O–H bands which are existed in the components adsorbed on the surface of particles (Ti–OH) [52, 53].

The changes in the UV-Vis absorbance spectrum of methylene blue in a wavelength between 200 and 800 nm due to the addition of 0.03 g Fe\(_2\)O\(_4\)/TiO\(_2\) photo-catalyst powders obtained by ultrasonic and Stöber methods are presented in Figs. 7 and 8 for different time durations. The maximum absorbance intensity of methylene blue solution occurs in a wavelength of 664 nm.

The decrease of the MB concentration over the photo-catalyst is dependent on two factors of the adsorption and the photodegradation of the MB [54]. The efficacy of surface adsorption on the decolorization of methylene blue dye in the absence of illumination with the addition of photo-catalytic powders was evaluated. Fig. 7 presents the changes in the absorption spectra of MB dye solution with the addition of photo-catalytic powders after 30 min in darkness. The negative time indicates the approximate time required for the establishment of adsorption-desorption equilibrium in dark conditions. In the absence of UV irradiation, the concentration of MB slightly reduces with the presence of both samples. However, surface adsorption has not noticeable effect on the decolorization of MB dye solution, and concentration decrease was about 4.5 and 6.3 % after 30 min in the presence of F20/TU and F20/TS samples, respectively.

![Fig. 7. Effect of addition of different photo-catalytic powders on the absorption spectra of MB solution after 30 min in darkness (before UV-irradiation): a) F20/TU sample and b) F20/TS sample.](image)

The degradation percentage of methylene blue under UV light due to the addition of Fe\(_2\)O\(_4\)/TiO\(_2\) photo-catalyst powder prepared by ultrasonic method was obtained as 12, 27, 48 and 61 % for different times of 10, 30, 60, and 90 minutes, respectively, whilst the degradation percentages obtained for the composite photo-catalyst prepared by Stöber method were 13, 33, 52, and 69 %, respectively for same times (Fig. 8). Gradual omission of
methylene blue color confirms the presence of photo-catalytic TiO₂ layer on magnetic Fe₃O₄ particles. Maximum decomposition was also obtained as 69% by using Fe₃O₄/TiO₂ photo-catalyst powder resulted from Stöber method (F20/TS) during 90 minutes of UV radiation. The higher photo-catalytic efficiency of F20/TS sample can be due to the higher thickness of titanium oxide shell in this composite. On the other hand, the decrease in the agglomeration degree is effective on improving photo-activity. Lower agglomeration of photo-catalyst particles brings about increasing the contact surface with pollutants, and consequently can be an effective parameter in increasing photo-catalytic efficiency. However, it was observed that the Fe₃O₄/TiO₂ photo-catalyst sample prepared by ultrasonic method yields lower photo-catalytic efficiency despite its lower agglomeration. This may be attributed to the absence of calcination process in furnace through synthesis by ultrasonic, which results in lower formation of chemical bonds between titanium oxide and the surface of magnetic core. Furthermore, morphological characterization by TEM images demonstrated that the surfaces of the nanocomposites prepared by Stöber method were rough, which led to larger specific surface areas and more surface adsorption of MB dye on the photo-catalyst, while the surfaces of the nanocomposites synthesized by ultrasonic became smoother. The higher photo-catalytic efficiency resulted from Stöber method is consistent with results of VSM test and previous predictions about the better coating by this method.

![Figure 8](image_url)

**Fig. 8.** UV/Vis absorbance spectra of MB dye solution after different UV-irradiation times in the presence of different photo-catalytic powders: a) F20/TU sample and b) F20/TS sample.

The kinetic of methylene blue degradation by using composite powders has been studied under UV light. As it can be seen in Fig. 9, plotting LnC₀/C against UV light radiation time (t) yields almost linear relations by considering two wavelengths (664 and 617 nm). This indicates that photo-catalytic degradation of methylene blue probably followed Langmuir-Hinshelwood mechanism [55-57]. According to this mechanism, the kinetic of photo-catalytic reaction can be explained by following equation:

\[
\ln \frac{C_0}{C} = k_{app}t
\]  

where, \(k_{app}\) is the apparent rate constant of photo-catalyst degradation reaction and is considered to be dependent on wavelength. As can be observed, the values of rate constant (\(k_{app}\)) which is calculated in a wavelength of 664 nm for F20/TU and F20/TS sample are
0.0144 h\(^{-1}\) and 0.0148 h\(^{-1}\), respectively, which are slightly higher than the values at 617 nm (\(k_{\text{app}}=0.0107\) h\(^{-1}\) and \(k_{\text{app}}=0.0102\) h\(^{-1}\), respectively). This is in agreement with Fig. 8; because the absorbance intensity in a wavelength of 664 nm has reached its maximum and therefore, higher absorption has leads to increasing degradation reaction rate constant [57].

![Figure 9](image1.png)

**Fig. 9.** Kinetics of MB dye disappearance in the presence of a) F20/TU sample and b) F20/TS sample.

![Figure 10](image2.png)

**Fig. 10.** Sequential cycles of degradation of methylene blue using F20/TU and F20/TS samples.

For a further investigation on the photo-catalytic capability of recovered powders, the destruction cycles of methylene blue under UV radiation and time duration of 90 minutes was obtained for F20/TU and F20/TS samples. Because titanium oxide has made a chemical contact with Fe\(_3\)O\(_4\) particles; which is probably a divalent bond, by recovering the particles from solution through external magnetic field, it is expected that the particles have photo-catalytic properties again. Fig. 10 represents a comparison between the degradation degrees of methylene blue up to four successive cycles. The results imply that the recovered powders have a relatively good photo-catalytic capability. However, as can be observed, ability to maintain photo-catalytic performance for the sample prepared by Stöber is somewhat lower.
than that by ultrasound method. It may probably be due to the formation of more organic intermediate products during the photo-catalytic degradation and accumulation of them in the cavities and on the surface of the photocatalyst which affects the adsorption of MB dye [12, 58].

4. Conclusion

In this study, magnetic photo-catalysts with core/shell structure have been successfully prepared by utilizing two methods of ultrasonic and Stöber. The final prepared nanostructure includes Fe3O4 particles as the core and TiO2 as the photo-catalytic shell. Fe3O4 nanoparticles were produced by using ultrasonic chemical co-precipitation without performing calcination step in a furnace. The mean size of prepared Fe3O4 nanoparticles was about 31 nm.

Coating of TiO2 shell was carried out through applying tetrabutyl orthotitanate (TBOT) and titanium isopropoxide (TTIP) as the alkoxide in ultrasonic and Stöber techniques, respectively. TEM micrographs indicated that all synthesized particles are covered with a layer composed of titanium oxide. The average size of photo-catalytic composite particles for ultrasonic and Stöber methods were 23 and 34 nm, respectively. The results of VSM test showed that the values of saturation magnetization of composites prepared by ultrasonic and Stöber methods have decreased in comparison with Fe3O4 magnetic powder from 60 emu/g down to 23 and 9 emu/g, respectively. Measuring the photocatalytic properties of the final product by UV-Vis spectra also revealed that the efficiency of methylene blue removal in the presence of 0.03 g composite powders prepared by ultrasonic and Stöber methods is 61 and 69 % under 90 min UV radiation, respectively. The more rough morphology of coated titanium oxide layer, as demonstrated in the TEM images, as well as performing calcination process in furnace are believed to be responsible for a relatively good performance of photo-catalysts synthesized by Stöber technique. It was found that the kinetics of MB photo-catalytic degradation reaction obey Langmuir–Hinshelwood mechanism. Therefore, the obtained results confirm that the produced Fe3O4/TiO2 powders have good photo-catalytic activity; and due to the presence of magnetic core, they can easily be separated from solution and be recovered via an external magnetic field.

Acknowledgments

The authors would like to thank Iran National Science Foundation (INSF) for complete financially supporting this research work under Contract Number of 98/sad/42699 on 9/11/2019.

5. References

1. G. Li, Z. Wang, M. Yu, Z. Quan and J. Lin, Fabrication and optical properties of core–shell structured spherical SiO2@GdVO4: Eu3+ phosphors via sol–gel process. *Journal of Solid State Chemistry*, Vol. 179, pp. 2698-2706 (2006).
2. G. Liu, G. Hong and D. Sun, Synthesis and characterization of SiO2/Gd2O3: Eu core–shell luminescent materials. *Journal of Colloid and Interface Science*, Vol. 278, pp. 133-138 (2004).
3. R. Ghosh Chaudhuri and S. Paria, Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications. *Chemical Reviews*, Vol. 112, pp. 2373-2433 (2011).
4. Y. Jing, S.-H. He and J.-P. Wang, Magnetic nanoparticles of core-shell structure for recoverable photocatalysts. *Applied Physics Letters*, Vol. 102, pp. 253102 (2013).
5. W. Bahnemann, M. Muneer and M. M. Haque, Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions. *Catalysis Today*, Vol. 124, pp. 133-148 (2007).
6. F. Ghasemey-Piranloo, S. Dadashian and F. Bavarsihah, Fe$_3$O$_4$/SiO$_2$/TiO$_2$–Ag cubes with core/shell/shell nano-structure: synthesis, characterization and efficient photocatalytic for phenol degradation. *Journal of Materials Science: Materials in Electronics*, pp. 1-12 (2019).
7. I. Arslan, I. A. Balcioğlu and D. W. Bahnemann, Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UV-A and TiO$_2$/UV-A processes. *Dyes and Pigments*, Vol. 47, pp. 207-218 (2000).
8. S. Ahmed, M. Rasul, R. Brown and M. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. *Journal of Environmental Management*, Vol. 92, pp. 311-330 (2011).
9. Y. Sakatani, D. Grosso, L. Nicole, C. Boissière, G. J. de AA Soler-Illia and C. Sanchez, Optimised photocatalytic activity of grid-like mesoporous TiO$_2$ films: effect of crystallinity, pore size distribution, and pore accessibility. *Journal of Materials Chemistry*, Vol. 16, pp. 77-82 (2006).
10. V. Tizjang, M. Montazeri-Pour, M. Rajabi, M. Kari and S. Moghadas, Surface modification of sol-gel synthesized TiO$_2$ photo-catalysts for the production of core/shell structured TiO$_2$–SiO$_2$ nano-composites with reduced photo-catalytic activity. *Journal of Materials Science: Materials in Electronics*, Vol. 26, pp. 3008-3019 (2015).
11. J. Vujančević, A. Bjelajac, J. Ćirković, V. P. Pavlović, E. Horvath, L. Forró, B. Vlahović, M. Mitrić, D. Janačković and V. B. Pavlović, Structure and photocatalytic properties of sintered TiO$_2$ nanotube arrays. *Science of Sintering*, Vol. 50, pp. 39-50 (2018).
12. F. Bavarsihah, M. Rajabi and M. Montazeri-Pour, Synthesis of SrFe$_{12}$O$_{19}$/SiO$_2$/TiO$_2$ composites with core/shell/shell nano-structure and evaluation of their photo-catalytic efficiency for degradation of methylene blue. *Journal of Materials Science: Materials in Electronics*, Vol. 29, pp. 1877-1887 (2018).
13. M. Montazeri-Pour, N. Riahi-Noori and A. Mehdiikhan, Synthesis of single-phase anatase TiO$_2$ nanoparticles by hydrothermal treatment with application potential for photoanode electrodes of dye sensitized solar cells. *Journal of Ceramic Processing Research*, Vol. 14, pp. 595-600 (2013).
14. A. Golubović, B. Simović, S. Gašić, D. Mijin, A. Matković, B. Babić and M. Šćepanović, Sol-gel synthesis of anatase nanopowders for efficient photocatalytic degradation of herbicide Clomazone in aqueous media. *Science of Sintering*, Vol. 49, pp. 319-330 (2017).
15. J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, Understanding TiO$_2$ photocatalysis: mechanisms and materials. *Chemical Reviews*, Vol. 114, pp. 9919-9986 (2014).
16. M. Lapertot, "A strategy for xenobiotic removal using photocatalytic treatment, microbial degradation or integrated photocatalytic-biological process," Ed., Ecole Polytechnique Fédérale de Lausanne (EPFL), 2006.
17. Q. Yuan, N. Li, W. Geng, Y. Chi and X. Li, Preparation of magnetically recoverable Fe$_3$O$_4$@SiO$_2@$meso-TiO$_2$ nanocomposites with enhanced photocatalytic ability. *Materials Research Bulletin*, Vol. 47, pp. 2396-2402 (2012).
18. F. Ghasemey-Piranloo, F. Bavarsihah, S. Dadashian and M. Rajabi, Synthesis of core/shell/shell Fe$_3$O$_4$/SiO$_2$/ZnO nanostructure composite material with cubic...
magnetic cores and study of the photo-degradation ability of methylene blue. *Journal of the Australian Ceramic Society*, pp. 1-9 (2019)

19. S. Wu, A. Sun, F. Zhai, J. Wang, W. Xu, Q. Zhang and A. A. Volinsky, Fe$_3$O$_4$ magnetic nanoparticles synthesis from tailings by ultrasonic chemical co-precipitation. *Materials Letters*, Vol. 65, pp. 1882-1884 (2011)

20. M. Abbas, B. P. Rao, V. Reddy and C. Kim, Fe$_3$O$_4$/TiO$_2$ core/shell nanocubes: Single-batch surfactantless synthesis, characterization and efficient catalysts for methylene blue degradation. *Ceramics International*, Vol. 40, pp. 11177-11186 (2014)

21. D. V. Bavykin, J. M. Friedrich and F. C. Walsh, Protonated titanates and TiO$_2$ nanostructured materials: synthesis, properties, and applications. *Advanced Materials*, Vol. 18, pp. 2807-2824 (2006)

22. S.-J. Liu, X.-X. Wu, B. Hu, J.-Y. Gong and S.-H. Yu, Novel anatase TiO$_2$ boxes and tree-like structures assembled by hollow tubes: D, L-malic acid-assisted hydrothermal synthesis, growth mechanism, and photocatalytic properties. *Crystal Growth and Design*, Vol. 9, pp. 1511-1518 (2009)

23. X. Chen and S. S. Mao, Titania dioxide nanomaterials: synthesis, properties, modifications, and applications. *Chemical Reviews*, Vol. 107, pp. 2891-2959 (2007)

24. D. Wang, J. Liu, Q. Huo, Z. Nie, W. Lu, R. E. Williford and Y.-B. Jiang, Surface-mediated growth of transparent, oriented, and well-defined nanocrystalline anatase titania films. *Journal of the American Chemical Society*, Vol. 128, pp. 13670-13671 (2006)

25. F. Behrad, M. H. R. Farimani, N. Shahtahmasebi, M. R. Roknabadi and M. Karimipour, Synthesis and characterization of Fe$_3$O$_4$/TiO$_2$ magnetic and photocatalyst bifunctional core-shell with superparamagnetic performance. *The European Physical Journal Plus*, Vol. 130, pp. 144 (2015)

26. W. Jiang, X. Zhang, X. Gong, F. Yan and Z. Zhang, Sonochemical synthesis and characterization of magnetic separable Fe$_3$O$_4$–TiO$_2$ nanocomposites and their catalytic properties. *International Journal of Smart and Nano Materials*, Vol. 1, pp. 278-287 (2010)

27. D. Beydoun, R. Amal, G. K.-C. Low and S. McEvoy, Novel photocatalyst: titania-coated magnetite. Activity and photodissolution. *The Journal of Physical Chemistry B*, Vol. 104, pp. 4387-4396 (2000)

28. Y. Xia and L. Yin, Core–shell structured α-Fe$_2$O$_3$–TiO$_2$ nanocomposites with improved photocatalytic activity in the visible light region. *Physical Chemistry Chemical Physics*, Vol. 15, pp. 18627-18634 (2013)

29. H. Fu, S. Sun, X. Yang, W. Li, X. An, H. Zhang, Y. Dong, X. Jiang and A. Yu, A facile coating method to construct uniform porous α-Fe$_2$O$_3$–TiO$_2$ core-shell nanostructures with enhanced solar light photocatalytic activity. *Powder Technology*, Vol. 328, pp. 389-396 (2018)

30. Z. Lendzion-Bieluń, A. Wojciechowska, J. Grzechulska-Damszel, U. Narkiewicz, Z. Śniadecki and B. Idzikowski, Effective processes of phenol degradation on Fe$_3$O$_4$–TiO$_2$ nanostructured magnetic photocatalyst. *Journal of Physics and Chemistry of Solids*, Vol. 136, pp. 109178 (2020)

31. R. Y. Hong, B. Feng, X. Cai, G. Liu, H. Z. Li, J. Ding, Y. Zheng and D. G. Wei, Double-miniemulsion preparation of Fe$_3$O$_4$/poly(methyl methacrylate) magnetic latex. *Journal of Applied Polymer Science*, Vol. 112, pp. 89-98 (2009)

32. M. K. Poddar, M. Arjmand, U. Sundararaj and V. S. Moholkar, Ultrasound-assisted synthesis and characterization of magnetite nanoparticles and poly(methyl methacrylate)/magnetite nanocomposites. *Ultrasonics Sonochemistry*, Vol. 43, pp. 38-51 (2018)
33. X. Huang, G. Wang, M. Yang, W. Guo and H. Gao, Synthesis of polyaniline-modified Fe$_2$O$_3$/SiO$_2$/TiO$_2$ composite microspheres and their photocatalytic application. *Materials Letters*, Vol. 65, pp. 2887-2890 (2011)

34. A. Šutka, S. Lagzdina, I. Juhevanica, D. Jakovlevs and M. Maiorov, Precipitation synthesis of magnetite Fe$_3$O$_4$ nanoflakes. *Ceramics International*, Vol. 40, pp. 11437-11440 (2014)

35. A. Bell, V. Coker, C. Pearce, R. Patrrick, G. van der Laan and J. Lloyd, Time-resolved synchrotron X-ray powder diffraction study of biogenic nano-magnetite. *Z. Kristallogr.*, Vol. 26, pp. 423-428 (2007)

36. M. Ristić, T. Fujii, H. Hashimoto, I. Opačak and S. Musić, A novel route in the synthesis of magnetite nanoparticles. *Materials letters*, Vol. 100, pp. 93-97 (2013)

37. S. Alibeig and M. R. Vaezi, Phase Transformation of Iron Oxide Nanoparticles by Varying the Molar Ratio of Fe$^{2+}$:Fe$^{3+}$. *Chemical Engineering & Technology*, Vol. 31, pp. 1591-1596 (2008)

38. D. Maity and D. Agrawal, Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media. *Journal of Magnetism and Magnetic Materials*, Vol. 308, pp. 46-55 (2007)

39. J. Jing, J. Li, J. Feng, W. Li and W. Y. William, Photodegradation of quinoline in water over magnetically separable Fe$_2$O$_3$/TiO$_2$ composite photocatalysts. *Chemical Engineering Journal*, Vol. 219, pp. 355-360 (2013)

40. J.-W. Lee, K. Hong, W.-S. Kim and J. Kim, Effect of HPC concentration and ultrasonic dispersion on the morphology of titania-coated silica particles. *Journal of Industrial and Engineering Chemistry*, Vol. 11, pp. 609-614 (2005)

41. K.-H. Choi, S.-L. Oh, D.-Y. Kim and J.-S. Jung, Size dependent photocatalytic activity of photofunctional magnetic core–shell (Fe$_3$O$_4$@ TiO$_2$) particles. *Journal of Nanoscience and Nanotechnology*, Vol. 13, pp. 7134-7137 (2013)

42. R. Rahmawati, A. Taufiq, S. Sunaryono, A. Fuad, B. Yuliarto, S. Suyatman and D. Kurniadi, Synthesis of magnetite (Fe$_3$O$_4$) nanoparticles from iron sands by coprecipitation-ultrasonic irradiation methods. *Journal of Materials and Environmental Sciences*, Vol. 9, pp. 155-160 (2018)

43. Y. Mizukoshi, T. Shuto, N. Masahashi and S. Tanabe, Preparation of superparamagnetic magnetite nanoparticles by reverse precipitation method: contribution of sonochemically generated oxidants. *Ultrasonics Sonochemistry*, Vol. 16, pp. 525-531 (2009)

44. J. Cheng, R. Ma, D. Shi, F. Liu and X. Zhang, Rapid growth of magnetite nanoplates by ultrasonic irradiation at low temperature. *Ultrasonics Sonochemistry*, Vol. 18, pp. 1038-1042 (2011)

45. A. Jitianu, M. Raileanu, M. Crisan, D. Predoi, M. Jitianu, L. Stanciu and M. Zaharescu, Fe$_2$O$_3$–SiO$_2$ nanocomposites obtained via alkoxide and colloidal route. *Journal of Sol-Gel Science and Technology*, Vol. 40, pp. 317-323 (2006)

46. M. H. R. Farimani, N. Shahtahmasebi, M. R. Roknabadi, N. Ghows and A. Kazemi, Study of structural and magnetic properties of superparamagnetic Fe$_2$O$_3$/SiO$_2$ core–shell nanocomposites synthesized with hydrophilic citrate-modified Fe$_3$O$_4$ seeds via a sol–gel approach. *Physica E: Low-dimensional Systems and Nanostructures*, Vol. 53, pp. 207-216 (2013)

47. X. Huang, A. Schmucker, J. Dyke, S. M. Hall, J. Retrum, B. Stein, N. Remmes, D. V. Baxter, B. Dragnea and L. M. Bronstein, Magnetic nanoparticles with functional silanes: evolution of well-defined shells from anhydride containing silane. *Journal of Materials Chemistry*, Vol. 19, pp. 4231-4239 (2009)

48. L. Shen, Y. Qiao, Y. Guo, S. Meng, G. Yang, M. Wu and J. Zhao, Facile co-precipitation synthesis of shape-controlled magnetite nanoparticles. *Ceramics International*, Vol. 40, pp. 1519-1524 (2014)
49. M. Montazeri-Pour and A. Ataie, Synthesis of nanocrystalline barium ferrite in ethanol/water media. *Journal of Materials Science & Technology*, Vol. 25, pp. 465-469 (2009)
50. V. M. Vinosel, M. A. Janifer, S. Anand and S. Pauline, Structural and functional group characterization of nanocomposite Fe_{2}O_{3}/TiO_{2} and its magnetic property. *Mechanics, Materials Science & Engineering Journal*, Vol. 9, (2017)
51. M. Kari, M. Montazeri-Pour, M. Rajabi, V. Tizjang and S. Moghadas, Maximum SiO_{2} layer thickness by utilizing polyethylene glycol as the surfactant in synthesis of core/shell structured TiO_{2}–SiO_{2} nano-composites. *Journal of Materials Science: Materials in Electronics*, Vol. 25, pp. 5560-5569 (2014)
52. Y. Fan, C. Ma, W. Li and Y. Yin, Synthesis and properties of Fe_{3}O_{4}/SiO_{2}/TiO_{2} nanocomposites by hydrothermal synthetic method. *Materials Science in Semiconductor Processing*, Vol. 15, pp. 582-585 (2012)
53. H. Wang, H.-L. Wang, W.-F. Jiang and Z.-Q. Li, Photocatalytic degradation of 2, 4-dinitrophenol (DNP) by multi-walled carbon nanotubes (MWCNTs)/TiO_{2} composite in aqueous solution under solar irradiation. *Water Research*, Vol. 43, pp. 204-210 (2009)
54. R. Ahmad and P. K. Mondal, Adsorption and Photodegradation of Methylene Blue by Using PANi/TiO2 Nanocomposite. *Journal of Dispersion Science and Technology*, Vol. 33, pp. 380-386 (2012)
55. H. Hamad, M. A. El-Latif, A. E.-H. Kashyout, W. Sadik and M. Feteha, Synthesis and characterization of core–shell–shell magnetic (CoFe_{2}O_{4}–SiO_{2}–TiO_{2}) nanocomposites and TiO_{2} nanoparticles for the evaluation of photocatalytic activity under UV and visible irradiation. *New Journal of Chemistry*, Vol. 39, pp. 3116-3128 (2015)
56. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental*, Vol. 31, pp. 145-157 (2001)
57. N. Zhou, L. Polavarapu, N. Gao, Y. Pan, P. Yuan, Q. Wang and Q.-H. Xu, TiO_{2} coated Au/Ag nanorods with enhanced photocatalytic activity under visible light irradiation. *Nanoscale*, Vol. 5, pp. 4236-4241 (2013)
58. S. Gomez, C. L. Marchena, L. Pizzio and L. Pierella, Preparation and characterization of TiO_{2}/HZSM-11 zeolite for photodegradation of dichlorvos in aqueous solution. *Journal of Hazardous Materials*, Vol. 258, pp. 19-26 (2013)
добијени Штебер методом имају боља фотокаталитичка својства уз смањено, али прихватљиво, магнетно раздвајање. Добијене вредности фотодеградације метилен-плаве боје под ултраљубичастим светлом у присуству фотокаталитичких прахова композита су биле 61 %, односно 69 %, за ултрасоничну и Штебер методу после 90 минута под ултраљубичастим светлом.

Кључне речи: фотокатализ, магнетит, наноструктура језгро/омотач, магнетни материјали, нанокомпозити.

© 2020 Authors. Published by association for ETRAN Society. This article is an open access article distributed under the terms and conditions of the Creative Commons — Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0/).