SULFUR-DOPED-TITANIA COATED ON MAGNETITE AS MAGNETICALLY RECOVERABLE PHOTOCATALYST FOR THE UV-VISIBLE LIGHT-ASSISTED-DEGRADATION OF CONGO RED SOLUTION

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ABSTRACT

Novel magnetically recoverable photocatalysts of sulfur-doped-titania coated on magnetite, Fe₃O₄/TiO₂-S, were synthesized through the sono-coprecipitation method involving Fe₃O₄, titanium tetraisopropoxide and thiourea as the sulfur source. The synthesized photocatalysts were then employed in the photodegradation of Congo red at pH 5 for 90 min. The results showed that Fe₃O₄/TiO₂-S photocatalysts display very good photodegradation activity under UV light illumination. In addition, the sulfur doping strategy allows us to conduct the photodegradation of Congo red under visible light irradiation since it may reduce the photocatalyst bandgap energy and shift the wavelength to the visible light region. Moreover, the Fe₃O₄/TiO₂-S 5% and 10% photocatalysts demonstrate excellent visible light-driven-photocatalytic degradation of Congo red with the photoactivity of 96.25% and 98.75%, respectively.

Keywords: Fe₃O₄/TiO₂-S, Magnetic Photocatalyst, Photodegradation, Congo Red, Visible Light.

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INTRODUCTION

Water pollution remains the environmental global problem. The rapid growth of the human population and chemical industries may increase the release of dangerous contaminants to the aquatic environment. Not only improve the environmental burden, but water pollution may also give various severe health effects on humans. In this context, industrial dyes such as Congo red are relatively stable and, hence, cannot be easily degraded using conventional wastewater treatments. Among various technologies, photocatalysis has received considerable attention due to its effectiveness in the removal of harmful dyes from the environment.

In recent years, TiO₂ photocatalysts are widely used in water purification, as they are ideal for the degradation of organic and inorganic pollutants.¹⁻⁴ The physicochemical properties of TiO₂ semiconductors, such as high photoactivity, low toxicity, and relatively inexpensive, make TiO₂ be attractive photocatalyst used for environmental remediation.⁵ However, its application as a photocatalyst, un-modified TiO₂ is reported less efficient because the material is only active under exposure to ultraviolet light.⁶

The current challenge in the photodegradation technique is the exploitation of sunlight covering UV and visible light spectrum. In this case, the photo-response of TiO₂ can be improved in the visible light area. The improvement of photocatalytic activity can be performed by doping or inserting impurities into the semiconductor material with metal elements^{7,8} or non-metal elements.^{9,10} These elements can generate a new state or energy level between the valence band and the conduction band and act as electron donors or acceptors that cause absorption in the visible light region.¹¹ The doping of TiO₂ with metal elements, however, has several disadvantages, such as the increase of hole and electron recombination and low thermal stability.¹² Recently, several studies demonstrated that nonmetal doping can enhance the response of TiO₂ to visible light.¹³ Sulfur is a non-metallic element commonly used as a TiO₂ dopant, which can narrow the bandgap energy of the photocatalysts. In addition, sulfur has high stability when doped into TiO₂.⁹

From the practical point of view, the separation of the catalyst after the wastewater treatment is difficult and may increase the operational cost. The strategy to address this separation problem is by developing the

magnetically separable photocatalyst, where the photocatalyst may be easily recovered using the external magnet. Previous studies have introduced the magnetic property to the various photocatalysts by coating the catalysts on magnetite.^{4,14-18} In this study, we report herein the development of novel sulfur-doped-titania coated on magnetite ($\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$). The synthesized magnetically recoverable photocatalysts will be employed in the photodegradation of Congo red dye under the illumination of both UV and visible light.

EXPERIMENTAL

Material and Methods

The materials used in this study were chemicals with pro-analysis qualities and purchased from Merck including $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH, NH_4OH , $(\text{NH}_4)_2\text{SO}_4$, ethanol (96%), titanium tetraisopropoxide and thiourea. Some materials with the technical grade, such as sodium citrate, Congo red, and deionized water, were also utilized. All chemicals were used without further purification. The equipment employed in this research were X-Ray Diffractometer (XRD, Shimadzu XRD 6000), Specular Reflectance UV-Visible Spectrometer (SRUV, UV 1700 Pharmaspec UV-Vis Spectrophotometer Specular), Vibrating Sample Magnetometer (VSM, Oxford VSM 1.2H), Transmission Electron Microscope (TEM, JEOL-1400 120 kV), and Scanning Electron Microscope with Energy Dispersive X-Ray (SEM-EDX, JEOL JSM-6510LA).

Preparation of Photocatalysts

Preparation of Fe_3O_4

Into the solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (540 mg) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (280 mg) in 100 mL of deionized water, was added dropwise 25% of NH_4OH solution under sonication. After the precipitation of Fe_3O_4 , the aqueous solution of sodium citrate (0.5 M) was then introduced to the mixture and the sonication was continued for 10 min. The obtained precipitate was separated by an external magnetic bar, washed with distilled water until pH 7 and then dried at 100 °C for 1h.

Preparation of $\text{Fe}_3\text{O}_4/\text{TiO}_2$

The Fe_3O_4 particles (116 mg), $(\text{NH}_4)_2\text{SO}_4$ (100 mg) and TiO_2 (17,5 mg) were suspended in 20 mL of ethanol 96%. The suspension was sonicated for 10 min, and then added with titanium tetraisopropoxide (1,5 mL) and distilled water (1.7 mL). The sonication was carried out for 3 h. The external magnetic bar was used to separate the precipitate from the mixture. The magnetite precipitate was then washed until neutral and calcined at 500 °C for 3 h. The same procedure was conducted to produce $\text{Fe}_3\text{O}_4:\text{TiO}_2$ with a different molar ratio of 1:1, 3:1, 5:1, 10:1, and 15:1.

Preparation of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$

The suspension of Fe_3O_4 particles (116 mg) and $(\text{NH}_4)_2\text{SO}_4$ (100 mg) in 20 mL of ethanol was sonicated for 10 min. Then, titanium tetraisopropoxide with the optimum molar ratio of $\text{Fe}_3\text{O}_4:\text{TiO}_2$ and distilled water was introduced to the suspension, followed by the addition of the thiourea solution S: TiO_2 molar ratios of 1, 2, 5, 10, and 15%). The suspension was further sonicated for 3h. The precipitate was washed with distilled water, dried, and calcined at a temperature of 500 °C for 3h.

Photocatalytic Experiment

Photoactivity of $\text{Fe}_3\text{O}_4/\text{TiO}_2$

The photocatalytic experiment was conducted under the stirring condition in a closed vessel equipped with a UV and a visible lamp. As much as 25 mL of a Congo red solution (20 mg/L) and 10 mg of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ photocatalyst were placed in the glass vessel. The vessel was then irradiated at certain pH (3, 4, 5, 6, 7, and 8) and for a certain irradiation time (0, 30, 60, 90, 120, and 180 min). The photocatalyst was separated using an external magnet and the filtrate was analyzed using a UV-Vis spectrophotometer at 497 nm. The degradation yield of Congo red was calculated using Eq.-1.

$$\% \text{ Degradation} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

Where, C_i (ppm) and C_f (ppm) are the concentration of Congo red before and after the photocatalytic experiment.

Effect of Dopants on the Photoactivity of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$

As much as 20 mg of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ (with the dopant concentration of 0, 1, 2, 5, 10, and 15%) was introduced to 25 mL of Congo red solution (20 mg/L) at a pH 5. The photocatalytic degradation was performed for 90 min under UV and visible irradiation. After the process, the photocatalyst was separated and the filtrate was analyzed by a UV-visible spectrophotometer. The photocatalytic activity was evaluated using % degradation of Congo red based on Eq.-1.

RESULTS AND DISCUSSION

Preparation of Photocatalysts

Our endeavor was started by preparing two types of photocatalysts including sulfur-undoped- and doped-titania coated on magnetic. The first catalyst ($\text{Fe}_3\text{O}_4/\text{TiO}_2$) was prepared by coating TiO_2 on Fe_3O_4 surface with a variation of molar ratio of Fe_3O_4 to TiO_2 . The catalyst which provides the best magnetic property and high content of titania will be then doped with sulfur. The sulfur-doped-catalyst ($\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$) was produced by varying the concentration of sulfur dopant.

Figure-1 shows the XRD pattern as the function of the molar ratio of Fe_3O_4 to TiO_2 . The increase of TiO_2 concentration (Fig.-1) allows the increase of the intensity of the peaks at 25° , 38° , 48° and 53° , indicating that the anatase phase of TiO_2 has been coated on the magnetite surface.

Fig.-1: XRD Pattern of $\text{Fe}_3\text{O}_4/\text{TiO}_2$

Having prepared $\text{Fe}_3\text{O}_4/\text{TiO}_2$ with different molar ratios, we then simply evaluated the magnetic properties of the photocatalysts by determining the mass of photocatalyst attracted by the external magnet. Table-1 (entry 1-3) demonstrates that increasing the molar ratio of titania up to 1:5 does not change the magnetic property of the photocatalyst. However, further addition of titania (Table-1, entry 4-5) will, indeed, cover the surface of magnetite and hence reduce the number of photocatalysts attracted to the external magnet, which is not suitable in the magnetically photodegradation study. Therefore, the molar ratio $\text{Fe}_3\text{O}_4:\text{TiO}_2$ of 1:5 will be then used to synthesize the sulfur-doped-photocatalyst ($\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$).

Table-1: The % Magnetic attracted Mass of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ Photocatalyst with Different Molar Ratio

Entry	$\text{Fe}_3\text{O}_4:\text{TiO}_2$	Magnetic Attraction (%)
1	1:1	100
2	1:3	100
3	1:5	100
4	1:10	94
5	1:15	17

The synthesis of sulfur-doped-titania coated on magnetite ($\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$) was carried out using a similar method to that of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ photocatalyst. In this context, thiourea was employed as the source of sulfur dopant with the molar ratio of S to TiO_2 of 1%, 2%, 5%, 10%, and 15%. The doping of sulfur to $\text{Fe}_3\text{O}_4/\text{TiO}_2$ is expected to give photocatalyst with good photoactivity and response to visible light.

Fig.-2: Diffractogram of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$

Based on the XRD diffractogram of various $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ photocatalysts depicted in Fig.-2, the intensity of anatase TiO_2 characteristic peaks (25° , 38° , 48° , 53° , 62° and 75°) decrease along with the increase of sulfur dopant concentration, which indicates that the sulfur dopant enters the crystal lattice of TiO_2 . It should be also noted that the addition of dopant did not significantly damage the crystal structure of anatase TiO_2 . Compared with the non-doped photocatalyst, the sulfur-doped photocatalysts $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ relatively give the lower intensity of peak at 3400 cm^{-1} , indicating that hydroxyl group of titania is substituted with the sulfur group. The presence of sulfur in the photocatalyst is confirmed by the weak peak in around $1100\text{-}1040\text{ cm}^{-1}$ coming from the S-O and S=O bonds stretching vibration.

Fig.-3: FTIR Spectra of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$

The optical properties of the photocatalyst were determined using SR UV-Visible spectrophotometer (Fig.-4). Table-2 shows that the sulfur doping process may decrease the bandgap energy and increase the edge absorption wavelength (entry 2-6). This is probably because S^{4+} may enter the crystal lattice to replace Ti^{4+} , hence more new energy levels are formed under the conduction band resulting in a narrower bandgap.

The increase of bandgap energy was observed when 15% of dopant was used (Table-2, entry 7). According to the Burstein-Moss effect¹⁹, the doping process will push the fermi level closer to the conduction band. With higher dopant concentration, the fermi level is pushed above the conduction band which has been filled with electrons due to the doping effect, so that the excited electrons will occupy the higher fermi level.

Evaluation of the optical properties using SR UV-Visible spectrophotometer shows that $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ 10% display the smallest bandgap energy of 3.05 eV. It is interesting to highlight that the doping shifts the edge absorption wavelength to the visible light region, *i.e.*, 407 nm. Therefore, the photocatalyst of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ 10% will be employed in the photocatalytic experiment.

Fig.-4: SR UV-Visible Spectra of TiO_2 and $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$

Table-2: The Photocatalyst Bandgap Energy

Entry	Photocatalyst	Energy of Bandgap (eV)	Wavelength (nm)
1	TiO_2	3.27	380
2	$\text{Fe}_3\text{O}_4/\text{TiO}_2$	3.22	386
3	$\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 1\%}$	3.23	385
4	$\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 2\%}$	3.10	400
5	$\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 5\%}$	3.08	403
6	$\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 10\%}$	3.05	407
7	$\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 15\%}$	3.34	371

The morphology of the photocatalyst was investigated using TEM as displayed in Fig.-5. It is found that both photocatalysts ($\text{Fe}_3\text{O}_4/\text{TiO}_2$ 1:5 and $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 10\%}$) have the core-shell structure as indicated from the shape of the particles, which are spherical and black, covered in gray. While the black particle represents Fe_3O_4 , the gray particle shows the presence of TiO_2 . The TEM images also show that the sulfur dopants do not significantly change the shape and size of the material.

Fig.-5: TEM images of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ 1:5 (a) dan $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S 10\%}$ (b)

Based on the EDX spectrum (Fig.-6), the elements on the surface of the material include O, Ti, Fe, and S. Oxygen appears as the most abundant atom in the material since it binds both Ti and Fe atoms in the photocatalysts. Indeed, the order of atom composition of the rest atoms ($\text{Ti} > \text{Fe} > \text{S}$) (Table-3) can be explained from the molar ratio used in the preparation of the photocatalyst. These results also indicate that the sulfur doping of the material was successfully performed without other impurities.

Fig.-6: The EDX Spectrum of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S } 10\%$ Table-3: Composition of Elements on the Surface of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S } 10\%$

Entry	Element	% Mass	% Atom
1	O	50.27	75.18
2	S	1.44	1.07
3	Ti	43.06	21.51
4	Fe	5.23	2.24

The vibrating sample magnetometer (VSM) analysis was then carried out to determine the magnetization of the photocatalyst. Results show that there is a decline in the magnetic properties of Fe_3O_4 after coating with TiO_2 (Fig.-7). It is indicated that TiO_2 well coats the Fe_3O_4 particles. The reduction in the magnetic moment (M) of $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ nanoparticles is also observed (Table-4).

Fig.-7: VSM Curve of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{TiO}_2 \text{ 1:5}$ and $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S } 10\%$ Table-4: Magnetic Property of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{TiO}_2$, and $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$

Entry	Material	M (emu/g)
1	Fe_3O_4	76.03
2	$\text{Fe}_3\text{O}_4/\text{TiO}_2 \text{ 1:5}$	32.80
3	$\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S } 10\%$	13.15

Photocatalytic Experiment

The photocatalytic activity of the sulfur-doped-titania coated on magnetite photocatalysts is investigated by degradation of an anionic azo dye, namely Congo red, in an aqueous solution under UV and visible irradiation. After the experiment, the photocatalyst can be easily separated using the external magnet. The remaining solution was then analyzed using a UV-Vis spectrophotometer at 497 nm. The photoactivity of the catalyst can be represented by % degradation of the dye (Eq.-1). Initially, we evaluated the effect of solution of pH and degradation time on the % degradation of Congo red using $\text{Fe}_3\text{O}_4/\text{TiO}_2 \text{ 1:5}$ photocatalyst. Once the optimum conditions are obtained, we employed various $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ in the photocatalytic experiment under the exposure of UV and visible light.

Effect of pH on the Photodegradation of Congo Red

The photocatalytic study reveals that the degradation of Congo red using $\text{Fe}_3\text{O}_4/\text{TiO}_2$ 1:5 photocatalyst is pH-dependent. As depicted in Fig.-8, a high % degradation (88.42%) is obtained when the photodegradation is conducted at pH 3. The degradation efficiency slightly increases and reaches the optimum point at pH 5 (91.67%). Increasing the solution pH leads to the decrease of % degradation of Congo red. The phenomena can be explained by considering the species of both TiO_2 and Congo red in an aqueous solution under different pH values.

The TiO_2 surface will be protonated to give TiOH_2^+ in the acidic condition (less than pH 6). On the other hand, Congo red (pKa 4.1) will exist as its anionic form along with the increasing of pH. Therefore, the optimum pH was obtained at pH 5, where the electrostatic interaction between positively-charged-photocatalyst and anionic Congo red may optimally occur and may subsequently induce the photodegradation of the dye. Further increase of the solution pH (pH 6-8) will generate the negatively-charged- TiO_2 surface (TiO^-). As the consequence, there will be a repulsion interaction between these two anionic species, leading to the decrease of the % degradation of Congo red. Based on the previous explanation, the optimum pH of the $\text{Fe}_3\text{O}_4/\text{TiO}_2$ -catalyzed-degradation of Congo red is pH 5. From the operational point of view, this condition is not relatively extreme for wastewater treatment.

Fig.-8: Effect of pH on the Photodegradation of Congo Red catalyzed by $\text{Fe}_3\text{O}_4/\text{TiO}_2$ 1:5

Effect of Interaction Time on the Photodegradation of Congo Red

Interaction time is one of the important factors in wastewater treatment. In this context, the photoactivity of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ in the degradation of Congo red significantly increases during the first 60 min and reaches the optimum point at 90 min. The constant degradation percentage is observed as the optimum interaction time (Fig.-9). The longer irradiation time allows the generation of a higher amount of $\text{O}_2^{\bullet-}$ and $\text{OH}^{\bullet}$ as the active species in the photodegradation of Congo red. It is interesting to note that, more than 90% of Congo red dye photodegraded using $\text{Fe}_3\text{O}_4/\text{TiO}_2$ photocatalyst.

Figure-8 indicates that the longer the irradiation time in the photodegradation process, the greater the percentage of degradation. This is because of the longer contact time between the photocatalyst material and the Congo red molecule. The longer the irradiation time, the more radicals $\text{O}_2^{\bullet-}$ and $\text{OH}^{\bullet}$ degrade the dye molecules. This figure shows that the optimum irradiation time is 90 minutes. The degradation percentages at 120 and 180 minutes were relatively constant. After 90 minutes of irradiation, the number of electrons and holes generated in TiO_2 did not increase significantly so the percent degradation did not increase significantly.

Effect of Sulfur on the Photoactivity of $\text{Fe}_3\text{O}_4/\text{TiO}_2$ -S

With the optimum photodegradation conditions in our hand, we then turned our attention to study the effect of dopant concentration. We found that both the coating process on magnetite and the sulfur doping strategy may improve the performance of TiO_2 in the Congo red photodegradation underexposure of either UV or visible light (Fig.-10). The presence of magnetite may enhance the interaction between the photocatalyst and substrate, hence, improve the effectiveness of the coated photocatalysts. In addition, under visible light irradiation, we found that the unmodified TiO_2 photocatalyst display low photoactivity which is presumably due to the high band gap energy of TiO_2 .

Fig.-9: Effect of Time on the Photodegradation of Congo Red catalyzed by Fe₃O₄/TiO₂

As displayed in Fig.-10, all Fe₃O₄/TiO₂-S photocatalysts (0-15% S) give excellent photodegradation percentage (more than 85%) when the experiment is conducted under the exposure of UV light. Indeed, the UV light provides the excess energy to catalyze the photodegradation via the electron excitation from the valence to the conduction band.

To our delight, the sulfur doping technique allows us to enlarge the application of the photocatalyst for photodegradation under the visible light region. In general, the photodegradation activity is related to the catalyst band gap energy (Table-2). As previously explained, the presence of sulfur dopant on the magnetite-coated-titania may narrow the bandgap energy since a new energy level was generated below the conduction band. Therefore, energy provided by visible light is sufficient to promote the excitation of electrons in the photocatalytic process. Additionally, the edge absorption band might be shifted to the visible light region.

Fig.-10: Degradation of Congo Red catalyzed by Fe₃O₄/TiO₂-S Photocatalysts

It should be noted that both Fe₃O₄/TiO₂-S 5% (3.08 eV, 403 nm) and 10% (3.05 eV, 407 nm) catalysts show excellent performance in the degradation of Congo red with the photoactivity of 96.25% and 98.75%, respectively (Fig.-10). It is apparent that the lower the bandgap energy (Table-2), the more efficient the system in generating the active species of O₂• and OH• radicals for the degradation of Congo red.

CONCLUSION

The magnetically recoverable sulfur-doped-titania coated on magnetite (Fe₃O₄/TiO₂-S) photocatalysts have been successfully synthesized by facile sono-coprecipitation method and dispersion with ethanol followed by thermal treatment, where thiourea is employed as the source of sulfur dopant. The sulfur doping strategy allows us to obtain the photocatalysts with lower bandgap energy and shift the edge absorption band to the visible light wavelength. More importantly, we succeed to conduct the photodegradation of Congo red at pH 5 for 90 min under the illumination of UV and visible light. The Fe₃O₄/TiO₂-S photocatalysts also display good magnetic properties and can be recovered from the liquid medium by simply using the external

magnetic field. The results demonstrate that both $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$ 5% and 10% photocatalysts are very active for the visible light-promoted-photodegradation of Congo red with the photoactivity of 96.25% and 98.75%, respectively. The photodegradation study of Congo red using the magnetically recoverable sulfur-doped-titania coated on magnetite ($\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-S}$) under sunlight illumination is underway.

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