SYNTHESIS OF Mn(II)-LOADED $Ti_XSi_{1-X}O_4$ COMPOSITE ACTING AS A VISIBLE-LIGHT DRIVEN PHOTOCATALYST

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ABSTRACT

The synthesis and characterization of Mn-loaded $Ti_xSi_{1-x}O_4$ (x= 0.4-0.8) composites and a preliminary study of an activity testing their ability to work as photocatalysts for the degradation of methylene blue (MB) have been studied. Synthesis was conducted by the sol-gel method at room temperature using tetraethyl orthosilicate, titanium tetraisopropoxide, and manganese(II) chloride as precursors followed by thermal treatment at 500 °C. The characterizations were performed by X-ray diffraction, FT-IR spectrometry, UV-Vis diffuse reflectance spectrometry and a surface area analyzer. The photocatalytic activity test of composites for degradation of MB was carried out in a closed reactor equipped with UV and visible lights. In this test, the effects of ratio of Ti/Si composites, Mn^{2+} ion concentration, pH, and time of irradiation on the effectiveness of photodegradation of MB were studied. The results indicated that Mn-$Ti_{0.6}Si_{0.4}O_4$ composite could be synthesized through the sol-gel method followed by thermal treatment with a molar ratio of Ti/Si=60/40 and the optimum concentration of manganese was 2.5 wt%. The Mn-$Ti_{0.6}Si_{0.4}O_4$ composite significantly increased the photodegradation of MB at pH 10, with a percent degradation of 84.41% for 30 min under irradiation of visible light. The percent degradation of $Ti_{0.6}Si_{0.4}O_4$ was only 18.23% under irradiation of visible light.

***Keywords**: Mn-$Ti_xSi_{1-x}O_4$ composite; photocatalyst; photodegradation; methylene blue*

ABSTRAK

Telah dilakukan sintesis dan karakterisasi komposit Mn-loaded $Ti_xSi_{1-x}O_4$ (x= 0.4-0.8) serta uji aktivitasnya sebagai fotokatalis pada degradasi metilen biru. Sintesis dilakukan dengan metode sol-gel pada temperatur kamar menggunakan tetraetil ortosilikat (TEOS), titanium tetraisopropoksida (TTIP) dan mangan(II) klorida sebagai prekursor, dilanjutkan dengan perlakuan termal pada temperatur 500 °C. Karakterisasi dilakukan dengan metode difraksi sinar-X, spektrometri infra merah, spektrometri difusi reflektansi UV-Vis dan surface area analyzer. Uji aktivitas fotokatalitik komposit pada degradasi metilen biru dilakukan dalam reaktor tertutup yang dilengkapi dengan lampu Ultraviolet dan Tampak (Visible). Pada uji ini telah dipelajari pengaruh rasio Ti/Si komposit, konsentrasi ion Mn^{2+}, pH larutan dan waktu penyinaran terhadap efektivitas fotodegradasi metilen biru. Hasil penelitian menunjukkan bahwa komposit Mn-$Ti_{0,6}$-$Si_{0,4}O_4$ dapat disintesis dengan metode sol-gel pada temperatur kamar diikuti perlakuan termal dengan rasio molar Ti/Si 60/40 dan konsentrasi optimum mangan 2,5% berat. Komposit Mn-$Ti_{0,6}$-$Si_{0,4}O_4$ dapat meningkatkan efektivitas fotodegradasi metilen biru secara signifikan pada kondisi pH 10, dengan hasil persen degradasi sebesar 84,41% selama 30 menit pada paparan sinar tampak. Persen degradasi $Ti_{0,6}$-$Si_{0,4}O_4$ sebesar 18,23% pada paparan sinar Visible.

***Kata Kunci**: komposit Mn-$Ti_xSi_{1-x}O_4$; fotokatalis; fotodegradasi; metilen biru*

INTRODUCTION

Wastewater from the textile industry is one example of dye wastewater that is difficult to turn biodegradable because it contains unsaturated organic substance such as aromatic hydrocarbons with non-biodegradable functional groups and nitrogen-contained hydrocarbon [1]. Some conventional methods such as precipitation, adsorption, dissolved air floatation, coagulation, reverse osmosis and

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ultrafiltration were considered to be ineffective in removing dyes from textile wastewater. In addition, the adsorption method simply transfer non-biodegradable materials into the mud and created a new kind of pollution [2]. Therefore, the photocatalytic method using titanium dioxide (TiO_2) photocatalyst material with ultraviolet radiation sources was developed to decompose the dye into simpler components and in a way much better for the environment. TiO_2 is a semiconductor material that is often used as a photocatalyst because it has desirable optical and electronic properties including being very photoreactive, non-toxic, chemically stable in the long run and relatively inexpensive. However, TiO_2 is inactive under visible light irradiation, thus limiting their use in exposure to direct sunlight. If the visible-light driven TiO_2-photocatalyst can be developed, wide application of TiO_2 can be achieved.

Here, we developed visible-light driven TiO_2-photocatalyst by doping the manganese ion (Mn^{2+}) to TiO_2 and evaluated photocatalytic activity under visible-light irradiation.

EXPERIMENTAL SECTION

Materials

The Mn(II)-loaded $Ti_xSi_{1-x}O_4$ composite were prepared by sol gel method using tetraethyl orthosilicate (TEOS) 98% (Merck), titanium tetra-isopropoxide (TTIP) 97% (Merck), ethanol 99.99% pa, 37% hydrochloric acid (E-Merck), distillate water and manganese(II) chloride dihydrate ($MnCl_2.2H_2O$). The pure $Ti_xSi_{1-x}O_4$ composite also prepared for comparison.

Instrumentation

Infrared spectrophotometer of the $Ti_xSi_{1-x}O_4$ and Mn-$Ti_xSi_{1-x}O_4$ composite were measured using KBr pellet method at wave number 4000-400 cm^{-1} (FTIR 8201 PC Shimadzu, Universitas Gadjah Mada). The measurement of crystallinity of composite was performed with an X-Ray diffractometer (Shimadzu XRD 6000, UGM). Diffuse reflectance of $Ti_xSi_{1-x}O_4$ and Mn-$Ti_xSi_{1-x}O_4$ composites at a wavelength of 200-800 nm was measured using a UV-Vis spectrophotometer (UV 1700 type, UGM) to determine the adsorption edge which was used to determine the band gap energy (E_g) of the composite. Surface area, volume and pore diameter of the composites associated were determined by using surface area analyzer (Quantachrome Nova type, UIN Yogyakarta).

Procedure

Synthesis of Mn-$Ti_xSi_{1-x}O_2$ composite

The typical procedure for the preparation of the $Ti_{0.6}Si_{0.4}O_4$ composite was described as follows. Tetraethyl orthosilicate (TEOS, 1 mL) was mixed with 0.8 mL of ethanol and 0.3 mL of water, then 0.2 mL of 0.2 M HCl was added until the pH of the solution became about 2.0. The solution was stirred with a magnetic stirrer for 3 h to obtain a homogeneous SiO_2 sol. The molar ratio of TEOS:H_2O:ethanol:HCl became 1:4:3:0:01, respectively. Similarly, the TiO_2 sol was prepared by mixing 2 mL of TTIP (titanium tetraisopropoxide) with 1.2 mL of ethanol, 0.5 mL of water and then 0.3 mL of 0.2 M HCl was added until the pH of the solution became about 2.0. The TiO_2 sol was mixed with the SiO_2 sol. The mixture was stirred for 3 h to obtain a homogenous mixture. The Mn-$Ti_{0.6}Si_{0.4}O_4$ composite was made by rapidly mixing the $Ti_{0.6}Si_{0.4}O_4$ sol, then adding $MnCl_2.2H_2O$ (with a concentration of Mn 2.5 wt%) and stirring for 3 h to obtain a homogenous mixture. The mixture was allowed to form gels at room temperature, which was followed by thermal treatment at a temperature of 500 °C for 4 h. The dried gel (xerogel), a Mn-$Ti_{0.6}Si_{0.4}O_4$ composite, stored in a desiccator for characterization. In a similar manner, $Ti_xSi_{1-x}O_4$ sol was prepared by mixing SiO_2 and TiO_2 sol in a variety of molar ratios; Ti/Si= 50/50, 60/40 and 80/20 (x= 0.5, 0.6, and 0.8, respectively).

Procedure of methylene blue photodegradation under visible-light irradiation

The photocatalytic activity of $Ti_xSi_{1-x}O_4$ and Mn-$Ti_xSi_{1-x}O_4$ was examined using 50 mg composites and methylene blue (MB, 10 mL, 50 ppm). The mixture was stirred continuously under exposure to ultraviolet and visible light for 30 min. UV irradiation and visible light irradiation were performed using TUV lamp at 30 W and a bulb lamp at 60 W (Philips) respectively. The supernatants were then separated by centrifugation and analyzed using UV-visible spectrophotometry at the maximum wavelength of MB at 665 nm to determine the residual concentrations of MB.

RESULT AND DISCUSSION

Strategy to Develop the Visible-light Driven Photocatalyst

TiO_2 photocatalysts are generally used in powder form, which is some what ineffective because it requires TiO_2 in large amounts. These problems can be overcome by modifying the character of the surface area of the TiO_2, so it will be more effective and the

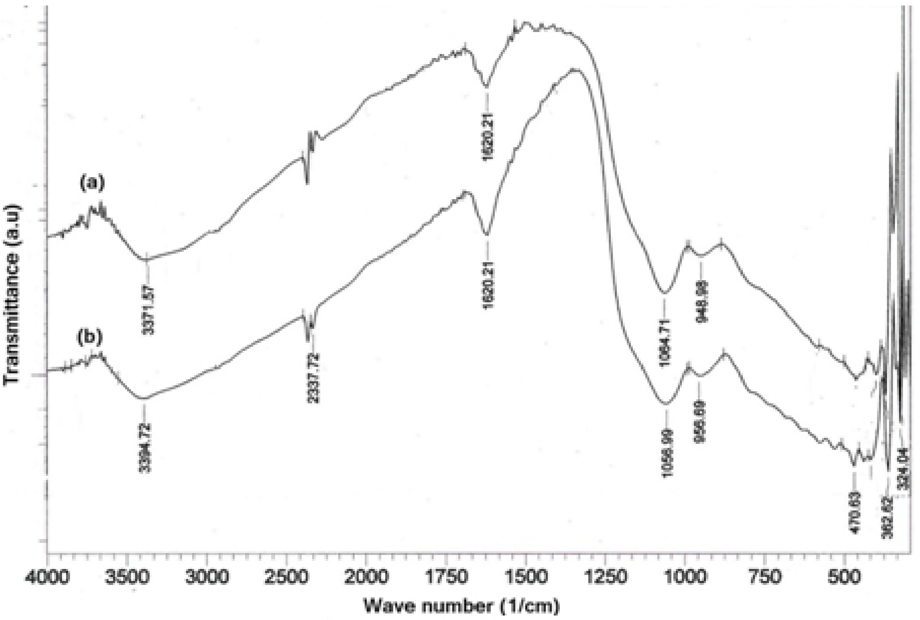

Fig1. FT-IR spectra of the composites: (a) $Ti_{0.6}Si_{0.4}O_4$ and (b) Mn-$Ti_{0.6}Si_{0.4}O_4$

amounts of TiO_2 required is small. In this research, TiO_2 was doped on silica by sol-gel method to form a $Ti_xSi_{1-x}O_4$ (x= 0.4-0.8) composite. Silica can restrict the growth of TiO_2 crystals by causing the TiO_2 particle size become smaller, thereby increasing the surface area of TiO_2. Supported by the research of Tang et al. [3], which explained that the TiO_2-SiO_2 composite has a greater mechanical strength, thermal stability and larger surface area compared to pure TiO_2. However, TiO_2 has band gap energy in the ultraviolet region which is owned in only 5-7% by sunlight, thus limiting its use in exposure to direct sunlight. Therefore, Wang et al. have postulated that TiO_2 can be modified by adding transition metal ions in order to absorb light in the visible region [4].

In this research, manganese ion (Mn^{2+}) was doped on a $Ti_xSi_{1-x}O_4$ (x = 0.4-0.8) composite via the sol-gel method to form the Mn-$Ti_xSi_{1-x}O_4$ composite. Mn^{2+} is very well capable of fluorescence in visible light, as evidenced by the emergence of the maximum absorption band at a wavelength of 450 nm [5]. The formation of the composite Mn-$Ti_xSi_{1-x}O_4$ is expected to have a high activity as a photocatalyst in the degradation of dyes by utilizing sunlight as a source of visible light. The preparation of Mn-doped TiO_2 immobilized on SiO_2 was firstly reported by Xu in 2008 [6]. However, visible-light photocatalytic activity was not clear. In this study, methylene blue (MB) was used to test the photocatalytic activity of composites under exposure to visible light. It support by Binas et.al. [7] explained that the photocatalytic activity on MB degradation using Mn doped TiO_2 showed a significant decolorization faster than undoped TiO_2 up to 70% on visible light exposure.

Characteristic of $Ti_xSi_{1-x}O_4$ and Mn-$Ti_xSi_{1-x}O_4$

Infrared spectroscopy

Fig. 1 showed the infrared spectra of $Ti_{0.6}Si_{0.4}O_4$ and Mn-$Ti_{0.6}Si_{0.4}O_4$ composite. Strong and broad absorption at wavenumber of 3394 cm^{-1} and 1620 cm^{-1} were assigned to be the stretching vibration and OH bending vibration of H_2O molecules that are trapped within the framework of the composite because it has a hygroscopic nature. The Ti-O absorption of TiO_2 appeared at 2337 cm^{-1}. This is similar to that presented by Nyquist [8]. Asymmetric stretching vibration of Si-O and Si-O bending vibration is shown of 1057 cm^{-1} and 471 cm^{-1}, originating from the bond Si-O-Si as it has been reported by Li et al. [9]. The peak at 957 cm^{-1} indicated the vibration of the Ti-O bond in silica. According to Pabon`s report [10], this wavenumber is characteristic of the bonds of Si-O-Ti, similar to that reported by Li et al. [9]. This infrared spectra showed that TiO_2 was immobilized into the silica structure.

The wavenumber shift from 1064.7 to 1057.0 cm^{-1} showed the vibrations characteristic of Si-O-Si bond in the TiO_2-SiO_2 composite before and after being immobilized with Mn^{2+} ion. A wavenumber shift can be observed from the changes in the Si-O system due to the addition of Mn^{2+} ion. The influence of the mass of the Mn atoms on the Si-O bond can be explained using the equation of Hooke's Law; the greater mass of an interacting atom can reduce the frequency of vibrations to smaller wavenumbers. This is evident from the decrease in the TiO_2-SiO_2 composite`s wavenumbers, immobilized using Mn^{2+} ion. It can be concluded that the composite Mn-TiO_2-SiO_2 has been synthesized.

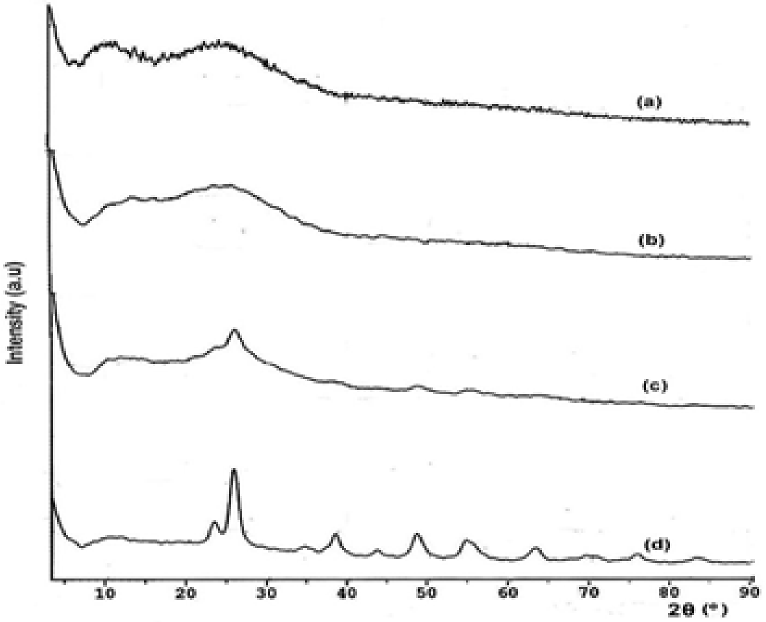

Fig 2. X-ray diffraction pattern of the $Ti_xSi_{1-x}O_4$ Composite ratio of Ti/Si: (a) 40/60, (b) 50/50, (c) 60/40 and (d) 80/20

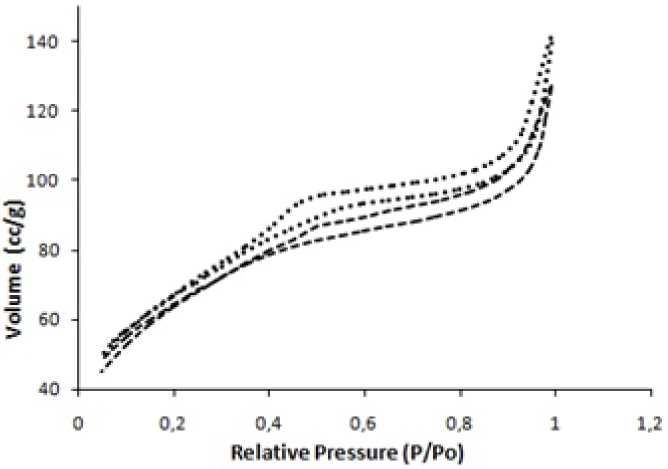

Fig 3. Adsorption/desorption Isothermal: (a) Mn-$Ti_{0.6}Si_{0.4}O_4$ and (b) $Ti_{0.6}Si_{0.4}O_4$

Table 1. BET Characterization of Composites

Characterization	$Ti_{0.6}Si_{0.4}O_4$	Mn-$Ti_{0.6}Si_{0.4}O_4$
Pore volume (cm^3/g)	0.100	0.122
Surface area (m^2/g)	225.987	235.661
Pore diameter (Å)	30.426	30.304

X-ray diffraction

The composites of $Ti_xSi_{1-x}O_4$ (x = 0.4, 0.5, 0.6, 0.8) were analyzed using X-ray diffraction to determine the degree of crystallinity of the samples (Fig. 2). Fig. 2 shows that the mole ratio of Ti/Si in the TiO_2-SiO_2 composite become greater, the TiO_2 anatase crystal displays pattern of diffraction with an increasingly sharp main peak at 2θ = 25° as the characteristic peaks. The growth of an anatase crystal size increases with an increasing composition of TiO_2 in $Ti_{0.6}Si_{0.4}O_4$, especially in composites with the $Ti_{0.8}Si_{0.2}O_4$ with an increasingly sharp peak. Conversely, as the mole ratio of Ti/Si in the TiO_2-SiO_2 composite becomes smaller, the TiO_2 diffraction pattern that appears in the diffractogram 2θ value will shift, becoming a greater and wider at 2θ = 23-27°, there by showing the amorphous nature of silica. This shift indicates that the size of TiO_2 in the composite decreased with increasing amount of silica. This is in accordance with the equation Brag: $n\lambda = 2d \sin\theta$, where the greater the value of θ, the smaller the value of d, which shows the distance between the field [11]. Increasing the amount of silica causes a species coordinated tetrahedral amorphous titania oxide, where the surface area of the silica gel helps TiO_2 particle dispersion in silica and inhibit crystal growth of anatase TiO_2.

Characterization of surface area and pore composite

The surface areas of $Ti_{0.6}Si_{0.4}O_4$ and Mn-$Ti_{0.6}Si_{0.4}O_4$ composites were shown in Table 1. The porosity curve isothermal study of the adsorption/desorption of nitrogen gas (N_2) in the composites are shown in Fig. 3. The addition of Mn^{2+} to the $Ti_{0.6}Si_{0.4}O_4$ composite causes an increase in pore surface area from 225.987 m^2/g to 253.661 m^2/g, pore volume from 0.100 cm^3/g to 0.122 cm^3/g and pore diameter from 30.426 Å to 30.304 Å.

Immobilized Mn^{2+} on a $Ti_xSi_{1-x}O_4$ framework will lead to changes in the bond that could change the structure with the arrangement of atoms to occur less

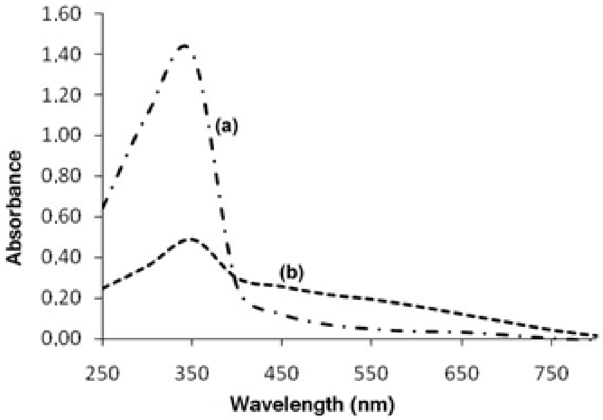

Fig 4. UV-Vis spectra measured by diffuse reflectance method (a) $Ti_{0.6}Si_{0.4}O_4$ and (b) Mn-$Ti_{0.6}Si_{0.4}O_4$

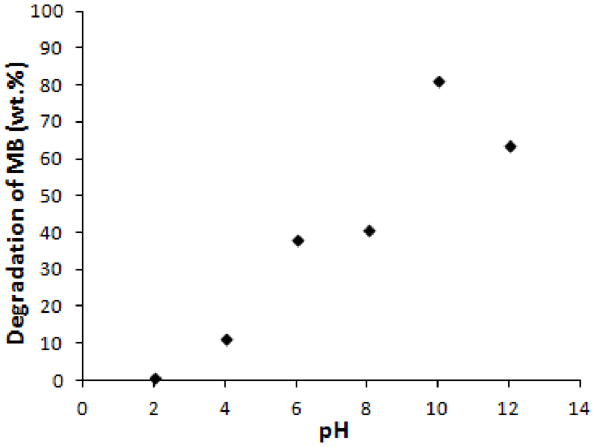

Fig 5. The degradation of MB at various pH

regularity so that the surface area increases. The amount of the surface area in Mn-$Ti_xSi_{1-x}O_4$ composite plays an important role in the visible-light photocatalyst. In addition, the adsorption of the substrate on the catalyst surface are quirement in the photodegradation process, so that with a large surface area that allows the photocatalytic activity is better because it facilitates the adsorption of organic matter and allows the transfer of adsorbate compounds towards the active site.

The pore properties of the composite were studied using the isothermal adsorption of nitrogen gas desorption shown in Fig. 3. The adsorption isothermal curves of N_2 gas of both composites are classified into IV type of the six types of isothermal adsorption/desorption curves given by Brenauer in accordance with the IUPAC, the pattern of the hysteresis curve shows that N_2 gas adsorption occurs on the adsorbent which has a pore size of mesopores with a diameter of 15-1000 Å. Therefore, it can be as certained that the composites have a bimodal pore size distribution as a material with pore size mesoporous and microporous.

Spectrophotometer UV-Vis diffuse reflectance

Fig. 4 showed the absorption spectra of the $Ti_{0.6}Si_{0.4}O_4$ composite and Mn-$Ti_{0.6}Si_{0.4}O_4$ in the wavelength range between 250-750 nm. The $Ti_{0.6}Si_{0.4}O_4$ composite provides a greater absorbance (1.404) compared to the Mn-$Ti_{0.6}Si_{0.4}O_4$ composite (0.489) at 350 nm. While in the visible wavelength region between 400-800 nm, the composite Mn-TiO_2-SiO_2 gave an absorbance greater than the $Ti_xSi_{1-x}O_4$ composite. From the Kubelka-Munk calculations of the wavelength edge of the composite [12], the band gap energies (E_g) were determined to be 3.1 eV (400 nm) for $Ti_{0.6}Si_{0.4}O_4$ and 1.77 eV (700 nm) for Mn-$Ti_{0.6}Si_{0.4}O_4$. This proves that the Mn-$Ti_{0.6}Si_{0.4}O_4$ can be used as a visible-light driven photocatalyst. When the Mn atoms interact as Mn^{2+} on the Ti^{4+}, Mn^{2+} has a valence electron which is higher than TiO_2, so it can fill the energy level above the valence band. Completion of this energy causes the electron levels to be close to the conduction band so that the band gap energy required to promote electrons into the conduction band becomes lower than it was the previously. The reduced value of E_g caused a shift of the absorption wavelength toward visible light (red shift).

Optimization of Reaction Condition

Influence of pH

The photodegradation of MB using $Ti_{0.6}Si_{0.4}O_4$ composites were conducted in various pH ranges between 2 to 12 on exposure to UV light in order to determine the optimum pH. The effect of pH on the percent degradation of MB is shown in Figure 5. The results showed an increase in percent degradation with increasing pH, reaching an optimum pH of 10 with a degradation yield of 78.9%. In general, pH gives a different effect on the TiO_2 photocatalyst surface species, a low pH of the TiO_2 in a TiO_2-SiO_2 composite are as a species $>TiOH^{2+}$ and $>TiOH$, whereas a high pH TiO_2 forms $>TiO^-$ and $>TiOH$. Species $>TiOH$ plays a role in the formation of •OH radicals after absorbing photons. The •OH radicals can degrade methylene blue; this supported by the presence of TiO^- dominant groups on the TiO_2-SiO_2 catalyst in alkaline pH conditions. It makes a cationic MB can interact strongly on the surface of $Ti_xSi_{1-x}O_4$ through electrostatic interactions between negatively charged TiO^- and positive charge of the cationic MB, therefore, increasing the activity of photodegradation.

Influence of mole ratio of Ti/Si in TiO_2-SiO_2 composite

The percent of degradation of MB under UV irradiation was shown in Table 2. The $Ti_{0.6}Si_{0.4}O_4$ composite provided the greatest value of percent degradation of 57.3%. TiO_2 dispered evenly within the

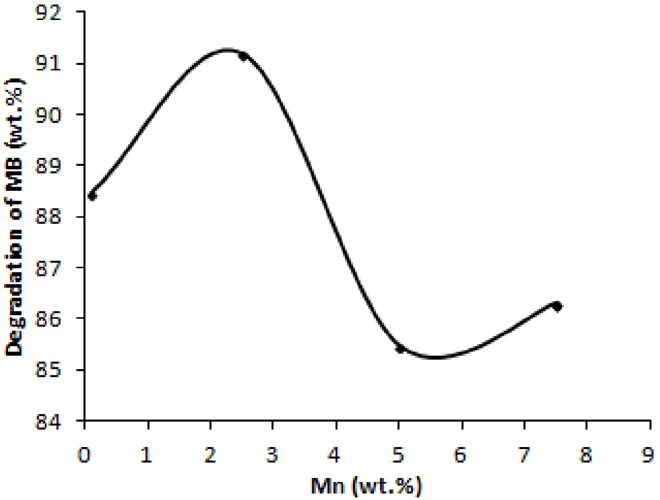

Fig 6. The effect of Mn^{2+} concentration in a Mn-$Ti_{0.6}Si_{0.4}O_4$ composite on the degradation of MB under visible light exposure

Table 2. Effect of the mole ratio of Ti/Si on the percent degradation of methylene blue under UV-irradiation

Molar ratio Ti/Si in $Ti_xSi_{1-x}O_4$ composite	% degradation of MB
40/60	52.7
50/50	40.5
60/40	57.3
80/20	29.0

silica effect on increasing the size of TiO_2 photoactivity for causing a smaller impact on increasing the surface area and band gap energy due to the quantum size effect [13]. The lowest percent degradation was found in the mole ratio of Ti/Si=80/20, resulting in only 29.0%. This was caused by the presence of TiO_2 in the composite being too large, jostling with the silica to form aggregate for clumps of TiO_2 thus decreasing the surface area as well as the effectiveness of photocatalyst. Thus *x* was optimized to be 0.6.

Influence of the doped contents of Mn^{2+}

Fig. 6 showed the percent of photodegradation of MB by the Mn-$Ti_{0.6}Si_{0.4}O_4$ composite with various concentrations of Mn^{2+} ion under exposure to visible light. In Fig. 6, the greater concentration of Mn^{2+} immobilized in the $Ti_{0.6}Si_{0.4}O_4$ composite caused degradation of MB growing up to optimum point of Mn^{2+} concentration; 2.5 percent weight by percent degradation of 91.2%. Further addition of Mn^{2+} can decrease the percent degradation of MB. The presence of excess Mn will form Mn clusters that can cover the surface of TiO_2, thus blocking the lights interaction with TiO_2.

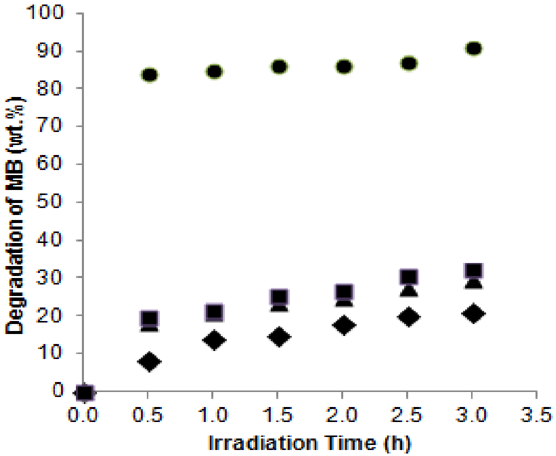

Fig 7. Time-course plots of photo-degradation of MB.Mn-$Ti_{0.6}Si_{0.4}O_4$ under visible-light irradiation (●), Mn-$Ti_{0.6}Si_{0.4}O_4$ under UV-irradiation (■), $Ti_{0.6}Si_{0.4}O_4$ under visible-light irradiation (▲), and Mn-$Ti_{0.6}Si_{0.4}$4O4 under dark (◆)

Photocatalytic Activity of Mn-$Ti_{0.6}Si_{0.4}O_4$ Composite for Degradation of Methylene Blue in Visible Light

Time-course plots of the degradation of MB by $Ti_{0.6}Si_{0.4}O_4$ and Mn-$Ti_{0.6}Si_{0.4}O_4$ composites under visible light irradiation were shown in Fig. 7. At first, we checked the adsorption of MB on $Ti_{0.6}Si_{0.4}O_4$, since these materials were porous to adsorb organic materials. Under dark conditions, the decrease in MB was only 20.94%. The presence of SiO_2 in the photocatalyst can act on the dye adsorption process causing a decrease in absorbance value not by the photocatalytic activity but by the adsorption process. Under visible-light irradiation, the addition of the photocatalyst $Ti_{0.6}Si_{0.4}O_4$ and Mn-$Ti_{0.6}Si_{0.4}O_4$ into the reaction system can increase the percent degradation of MB 29.5% and 91.0%, respectively, for 3 h. It was confirmed that the Mn-$Ti_{0.6}Si_{0.4}O_4$ acted as visible-light catalyst; however the photocatalytic activity under UV irradiation was inefficient.

When TiO_2 absorbs photon energy, the electrons in the valence band will be excited into the conduction band leaving a hole or holes in the valence band (H_{vb}^+). •OH radicals formed from the oxidation of the cluster titanol H_{vb}^+ (>TiOH) from the surface of TiO_2 [14]. The number of reactive species, •OH radical depends on the ease of TiO_2 to produce electrons to form holes (H_{vb}^+) (eq. 1). The release of electrons by TiO_2 is easier than it is for H_2O because TiO_2 is an n-type semiconductor with excess electrons [15], thereby increasing the effectiveness of photodegradation.

$$H_2O \xrightleftharpoons{hv} \bullet OH + H^+ + e^- \qquad (1)$$

As shown in Fig. 7, the photodegradation of MB by the Mn-$Ti_{0.6}Si_{0.4}O_4$ photocatalyst is much faster than the $Ti_{0.6}Si_{0.4}O_4$ photocatalyst upon exposure to visible light. The immobilization of Mn^{2+} affects the performance of the TiO_2 photocatalyst by establishing the energy level located in the band gap between the valence band and conduction band. This resulted in a decrease of energy band gap of the Mn-$Ti_{0.6}Si_{0.4}O_4$ composites and shifted the absorption to the visible wavelengths. When the energy band gap composite in accordance with the photon energy of visible light, the radical •OH is formed. Radical •OH will enter into the molecular structure of MB and disrupt conjugation system that leads to decomposition of MB completely. This clearly indicates that doping $Ti_xSi_{1-x}O_4$ with Mn^{2+} can be used as a potential photocatalyst and can work under exposure to visible light. On exposure using visible light, the effectiveness of the photodegradation increased significantly until the degradation reached 84.4%. Any further exposure provided no significant increase to the percent degradation of MB. Irradiation time described the time interaction between the photocatalyst with light in generating the radical •OH as well as the interaction of MB with the radical •OH. The longer time of irradiation, the more energy photons that are absorbed by the photocatalyst, so that the radical •OH formed on surface of the photocatalyst to a larger and larger extent. This can increase the effectiveness of the photodegradation property of MB. Any longer relegated more and more products, possibly preventing the interaction between the photocatalyst with light and photocatalyst with MB which is not degraded, so that the photodegradation reaction becomes less effective and tends to remain constant with any further increase time.

CONCLUSION

The photocatalytic method using Mn doped TiO_2-photocatalyst can be used as alternative technique to produce clean water by degradation of dyes wastewater on sunlight exposure. The effectiveness of photodegradation increased significantly up to an 84.41% at irradiation time of 30 min for a Mn-$Ti_{0.6}Si_{0.4}O_4$ composite under visible light exposure. It indicated that immobilization of Mn^{2+} ions on the $Ti_{0.6}Si_{0.4}O_4$ composite remarkably increased the photocatalytic activity under visible light exposure. This is evidenced by the decrease in the band gap energy from 3.1 eV for $Ti_{0.6}Si_{0.4}O_4$ and 1.77 eV for Mn-$Ti_{0.6}Si_{0.4}O_4$, which means an increase in the absorption spectrum towards larger wavelengths.

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REFERENCES

1. Joutey, N.T., Bahafid, W., Sayel, H., and Ghachtouli, N.E., 2013, “Biodegradation: Involved Microorganisms and Genetically Engineered Microorganisms” in *Biodegradation-Life of Science*, Intech, Morocco, 289–320.
2. Kansal, S.K., Singh, M., and Sud, D., 2006, *J. Hazard. Mater.*, 141(3), 581–590.
3. Tang, L., Li, B., Zhai, Z., Li, Junjie, Ou, E., and Wang, J., 2008, *Catal. Lett.*, 121(1-2), 63–69.
4. Wang J., Uma, S., and Klabunde, K.J, 2004, *Appl. Catal., B*, 48(2), 151–154.
5. Song, C.F., Lü, M.K., Yang, P., Gu, F., Xu, D., and Yuan, D.R., 2003, *J. Sol-Gel Sci. Technol.*, 28(2), 193–197.
6. Xu, Y., Lei, B., Guo, L., Zhou, W., and Liu, Y., 2008, *J. Hazard. Mater.*, 160(1), 78–82.
7. Binas, V.D., Sambani, K., Maggos, T., Katsanaki, A., and Kiriakidis, G., 2012, *Appl. Catal., B*, 113-114, 79–86.
8. Nyquist, R.A., Putzig, C.L., and Leugers, M.A., 1997, *Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts*, Academic Press, London, Vol. 1-3
9. Li, J., Liu, S., He, Y., and Wang, J., 2008, *Microporous Mesoporous Mater.*, 115(3), 416–425.
10. Pabón, E., Retuert, J., Quijada, R., and Zarate, A., 2003, *Microporous Mesoporous Mater.*, 67(2-3), 195–203.
11. Kunarti E.S., Wahyuni E. T., dan Hermawan, F.E., 2009, *Jurnal Manusia dan Lingkungan*, 16(1), 54–64.
12. Choudhury, B., Dey, M., and Choudhury, A., 2013, *Int. Nano Lett.*, 3(1), 25.
13. Ekimov, A.I., Efros, A.I.L., and Onushchenko, A.A., 1985, *J. Solid State Commun.*, 56(11), 921–924.
14. Hoffmann, M.R., Martin, S.T., Choi, W., and Bahnemann, D.W., 1995, *Chem Rev.*, 95(1), 69–96.
15. Smith, R.A., 1978, *Semiconductors: A thorough account of the basic theory of semiconductors*, Cambridge University Press, Cambridge.