PHOTOCATALYTIC ACTIVITY OF TiO₂/SiO₂ PREPARED FROM SILICA CONTAINED IN VOLCANIC ASH FOR AMMONIA REMOVAL

E.T. Wahyuni^{1,*}, S. Suherman¹, D. Setyawati², R. Puspita², and M. Mudasir¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences,

Gadjah Mada University, Yogyakarta, Indonesia 55284

²Master Students at Department of Chemistry, Faculty of Mathematics and Natural Sciences,

Gadjah Mada University, Yogyakarta, Indonesia 55284

*E-mail: endang_triw@ugm.ac.id

ABSTRACT

This paper presents a study on the improvement of TiO₂ photocatalytic activity by supporting it on SiO₂ purified from the volcanic ash of the eruption of Merapi Mt. standing in Yogyakarta, Indonesia. The preparation of TiO₂/SiO₂ was conducted by the sol-gel method at various pH. The photocatalyst prepared were characterized by using XRD, FTIR, SEM, and DRUV spectrometry methods. The photocatalytic activity was examined for ammonia removal. The research results reveal that silica gel from the volcanic ash can be used for supporting TiO₂ photocatalyst to successfully form nanoparticles with anatase type and to enhance its photocatalytic activity in the ammonia removal. The highest activity of TiO₂/SiO₂ was shown by photocatalyst prepared at pH 4. The ammonia removal was found to be controlled by photocatalysts dose, pH and the UV irradiation time, wherein the maximum ammonia removal (65%) from 50 mg/L in 100 mL solution was obtained by applying 50 mg of the photocatalyst dose, at pH 9, and 24 h of time. The ammonia removal was believed through oxidation reaction to form NO₃⁻ ion and/or degradation to form N₂ gas, but it has not been proved yet that needs to be further studied.

Keywords: Volcanic Ash, Silica Source, TiO₂/SiO₂, Nanoparticles, Ammonia.

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INTRODUCTION

Volcanic ash is found abundantly in some areas in Indonesia since many active volcanos frequently erupt by throwing the ash out in a very large amount. The main component in the ash is SiO₂ (ranging from 55-60%w)¹⁻² accompanied by several oxides such as Al₂O₃, Fe₂O₃, CaO, MgO, K₂O and Na₂O with a lower fraction.¹ Due to the fine particle size,³ the ash can contaminate air, water and soil that can further create the health and environmental problems.¹ Volcanic ash has been used as a silica source for silica-based adsorbent,² that has been examined for Cd(II) removal, as well as a modified silica-based adsorbent for Cr(VI) anionic removal,⁴ with promising results.

On the other side, titanium dioxide (TiO₂) well known as a photocatalyst semiconductor has been frequently studied to solve environmental problems due to its superiorities in term of high activity, good stability toward chemical and biological effects, low price, and environmentally benign.⁵⁻⁶ The environmental problems that have been overcoming by the photocatalytic method were contamination of persistent organic pollutants (POPs) in water, including dyes,⁷ phenols,⁸ alkylbenzene sulfonate surfactant,⁹ antibiotic of amoxicillin,¹⁰ and ammonia.¹¹ The photodegradation of organic pollutants is stimulated by OH radicals that are released by TiO₂ under UV illumination.⁵⁻⁶ Most of TiO₂ used in the reported researches above was in powder form, due to the practical reason. However, photocatalyst in powder form could arise problems including recovery difficulties and low effectiveness when it is used in low dose.¹² Increasing the effectiveness can be carried out by using TiO₂ powder in a higher dose, but the high TiO₂ dose may cause dense suspension that can inhibit the light exposure.⁹ The less light-transmitting to the suspension leads to the low effectiveness of the photodegradation.

The problem of using TiO_2 powder has been solved by supporting TiO_2 on several materials such as zeolite,¹³ clay,¹⁴ resin,¹⁵ and SiO_2 .¹⁶⁻¹⁹ It has been concluded that the higher activity of TiO_2 was observed when it was supported on the materials mentioned above. The improvement of the photocatalytic activity of TiO_2 supported on a matrix material was resulted by enlargement of the surface area and the elevation of the band gap energy (E_g), due to the reducing TiO_2 particles size which falls in nanoparticle dimension (1-10 nm).¹³⁻¹⁹

Among the supporting materials, SiO_2 is the most interesting because of its high stability, high hydrophilicity, inertness, and transparency.¹⁶⁻²⁰ The starting materials of SiO_2 for supporting TiO_2 photocatalyst mostly used were tetra ethoxy silane (TEOS),¹⁶⁻¹⁹ but it is known as high in price. Replacement of the expensive TEOS by the cheaper silica gel purified from waste, such as from rice husk ash,²⁰ mud,²¹ and fly ash,²² will be a benefit for providing supporting materials. However, it is a lack of reports regarding the use of volcanic ash as a silica source for supporting TiO_2 .

In this present study, the use of volcanic ash of Merapi Mt, one of the most active volcanic mountains in Indonesia, as a silica source for supporting material of TiO_2 photocatalyst is addressed. In the preparation of $\text{TiO}_2/\text{SiO}_2$ photocatalyst, one of the plausible factor determining the photocatalyst formation is pH, that motivates us to evaluate the influence of preparation pH on the photocatalyst characters and activity. The activity $\text{TiO}_2/\text{SiO}_2$ prepared is examined for the removal of ammonia in water under UV irradiation.

Ammonia is used as a subject for testing the photocatalyst activity since ammonia is the commonest water contaminant.^{11, 23-24} The ammonia pollution in the water can originate from the biodegradation of crop residues^{11,23} as well as wastewater and industrial effluents of fertilizers, dyes, metal plating, herbicides, pesticides, industrial solvents, chemical, industrials and petrochemical²⁴. Ammonia has notable as a major threat both to the environment and human health when it is in the presence of excess amounts.²³⁻²⁴ The environmental problems created by excessive ammonia are eutrophication, depletion of dissolved oxygen and toxicity to fish and other aquatic organisms.²³ Thus, the prevention of ammonia environmental pollution by eliminating the ammonia in wastewater before entering the rivers is urgently required.

Ammonia removal has been conducted by photocatalytic degradation,¹¹ that is an interesting method because of its preferences characteristics such as minimal generation of secondary waste, simple operation, inexpensiveness and high-efficiency.⁵⁻⁶ A study has reported that TiO_2 supported on light expanded clay aggregate (LECA) could degrade ammonia into harmless N_2 and H_2 gases.²⁴ However, ammonia removal by TiO_2 supported on SiO_2 from volcanic ash, under UV irradiation has not been explored yet. In this present research, the photodegradation efficiency of ammonia by $\text{TiO}_2/\text{SiO}_2$ was evaluated by optimizing the operating parameters including solution pH, degradation time and photocatalyst dose to reach the maximum efficiency in the ammonia removal.

EXPERIMENTAL

The chemicals used were sodium hydroxide pellet, titanium tetra isopropoxide, ethanol, hydrochloride acid, and ammonium hydroxide in PA grade purchased from E, Merck and were used without any purification. Volcanic ash used as a subject material was taken from the ash that was collected in January-February 2019 from Merapi's eruption in November 2010 that was distributed widely in some areas around Yogyakarta, Indonesia. The instrumentations used for analysis and characterization were GBC Atomic Absorption Spectrometer, X-Ray Diffraction of 6000X Shimadzu, Fourier Transform-Infrared Shimadzu type, Variant Diffuse Reflectance Spectrophotometer, and GBC Visible spectrophotometer machines.

Purification of silica (SiO_2) from the volcanic ash was conducted by referring the procedure reported previously by Wahyuni et al.⁴ For that purpose, about 1 gram of volcanic ash was mixed with 100 ml of the concentrated NaOH solution, then it was heated at around 100 °C while being stirred for 2 h. The silicate solution that was formed, then acidified with 1M HCl solution to form a white gel, named as silica gel.

Preparation of $\text{TiO}_2/\text{SiO}_2$ by using silica gel from the volcanic ash was conducted by mixing the silica gel with TTIP solution in various pH (2, 4, 6 and 9), giving mole ratio of Ti: Si = 1:1 and was stirred for 1 h, to form dense solutions. When the solid phase in the dense solution, was settled down, then it was

separated from the filtrate by filtering through Whatman Paper 41. The solid samples were dried at 70 °C for 1 h, then the heating was continued at 400 °C for 2h. The dried solid samples were noted as $\text{TiO}_2/\text{SiO}_2$ (pH2), $\text{TiO}_2/\text{SiO}_2$ (pH4), $\text{TiO}_2/\text{SiO}_2$ (pH6) and $\text{TiO}_2/\text{SiO}_2$ (pH9), corresponding to the preparation pH.

Then the photocatalysts prepared were characterized by using XRD, FTIR, DRUV, and AAS machines. In the XRD analysis, the fine powder of $\text{TiO}_2/\text{SiO}_2$ was placed in the sample compartment, then it was scanned with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at a scanning rate of 4 °/minute in 2 θ mode between 5 and 50°. The IR spectra were taken at 4000-400 cm^{-1} of the wavenumber, wherein the sample was pelleted with KBr matrix. The DRUV spectrophotometer was operated from 200-800 nm of the wavelength to get corresponding spectra. To get the SEM images, the samples were coated with carbon technique.

The photoactivity of $\text{TiO}_2/\text{SiO}_2$ materials was tested for the removal of ammonia in synthetic wastewater. The process was carried out in a closed compartment equipped by a UV-A lamp and magnetic plate, shown by Fig.-1. A series of ammonia solutions with various concentrations, as much as 100 mL, that have been added with $\text{TiO}_2/\text{SiO}_2$ powder with a certain weight, were exposed by UV light accompanied by stirring as long as 24 h. The mixtures then were filtered through Whatman paper 41 to obtain clear solutions. The concentrations of ammonia left in the clear solutions were determined by using UV/VIS. Spectrophotometer. The same procedure with 50 mL of ammonia 50 mg/L was repeated for various photocatalyst doses (10, 20, 30, 40, and 50 mg), pH alteration (1, 3, 5, 7, 9 and 11), and the time of illumination (30, 60, 120, 180, 240, and 300 min). When one parameter was varied, the others were set to be constant.

Fig.-1: A Set of Apparatus for Ammonia Photodegradation

The ammonia in the solution was analyzed by visible spectrophotometry method based on the complex compound of indophenol blue by following procedure of Indonesia National Standard (SNI No 06-6989.30-2005): 25 mL of the ammonia solution with a certain concentration was added with 1 mL of the phenol solution 90%, 1 mL of sodium nitroprusside 0.5%, and 2.5 mL of the oxidizing agent (alkaline citrate + sodium hypochloride). The solution was stirred to get homogeneous solution, then it was kept for 1 h until the stable blue color was obtained. The absorbance of the solution then was observed at 640 nm of the wavelength. The concentration of the ammonia was calculated by plotting its absorbance on the corresponding standard curve.

RESULTS AND DISCUSSION

The $\text{TiO}_2/\text{SiO}_2$ photocatalyst resulted from the interaction between TTip and silica from volcanic ash in the solution. At the beginning of the preparation, when TTip, $(\text{Ti}(\text{OC}_3\text{H}_7)_4)$, was dissolved in ethanol ($\text{C}_2\text{H}_5\text{OH}$), the propoxide groups of TTip was replaced by ethoxy groups of ethanol to result in titanium isoethoxide $(\text{Ti}(\text{OC}_2\text{H}_5)_4)$ and propanol ($\text{C}_3\text{H}_7\text{OH}$). The reaction is presented as eq.(1). Then titanium isoethoxide reacted with water to form titanium tetra-hydroxides $(\text{Ti}(\text{OH})_4)$ and ethanol ($\text{C}_2\text{H}_5\text{OH}$), as seen in eq.(2). In the acid condition, the titanium tetra-hydroxides reacted with hydrogen ion to form cation of titanium di-hydroxides, as written as eq.(3). In the solution with neutral pH, $\text{Ti}(\text{OH})_4$ was dominantly found. At the high pH or in the basic solution, the large amount of hydroxyl ion was available, which would react with $\text{Ti}(\text{OH})_4$ to form of $(\text{TiO}_4)^{4-}$ anion. The reaction is displayed as eq.(4).²⁵

In the case of silica, in the solution with pH lower than 3, the syanol group (-SiOH) was protonated by hydrogen ion to form $-\text{SiOH}_2^+$ ion (eq.5). In the pH range of 4-8, the species found was -SiOH. The anion of $-\text{SiO}^-$ was formed at a pH higher than 8, (eq.6). The respective reactions are presented bellow:²⁶

X-ray diffraction (XRD) analysis was performed to investigate the structural phases and crystallite sizes of the samples. The XRD patterns of all samples are shown in Fig.-2. In the figure, a broad peak at about 21-25° is assignable to SiO_2 implying the amorphous typical pattern. The figure also reveals the presence of the peaks at 25.25°, 37.52°, 48.02°, 53.58°, 54.88°, 62.61°, and 75.07° which are attributed to TiO_2 anatase, as filed by JCPDS no: 21-1272. The same findings have been also reported.¹⁶⁻¹⁹ From these XRD data, it is evident that TiO_2 crystalline from TTip and the amorphous SiO_2 from volcanic ash have been formed.

The XRD patterns of the prepared $\text{TiO}_2/\text{SiO}_2$ are seen similar to the characteristic pattern of TiO_2 anatase, with lower intensities compared to the intensities of the unsupported TiO_2 . It is confirmed that TiO_2 in $\text{TiO}_2/\text{SiO}_2$ was formed in the anatase crystalline phase.¹⁶ The assignable lower intensities may represent the smaller TiO_2 fraction in the $\text{TiO}_2/\text{SiO}_2$ samples. Furthermore, it is observable in the XRD patterns of all the $\text{TiO}_2/\text{SiO}_2$ samples, that the increase of the preparation pH from 2 to 4 gives the intensities plausible raised, then the intensities slightly decrease when the pH was elevated from 4 to 6. The interesting trend appears at pH 9, that the intensities are drastically declined. The alteration of the intensities showing the various amount of $\text{TiO}_2/\text{SiO}_2$ was yielded. This data can be explained based on the speciation of both TTip as TiO_2 precursor and silica gel as the starting material of SiO_2 during the preparation.

Based on the speciation of both Ti(IV) and Si(IV) in the solution as presented above, it can be explained as follow. At pH 2, the species of $(\text{Ti}(\text{OH})_2)^{2+}$ and $-\text{SiOH}_2^+$ that were in the same charges, were inhibited to interact, which resulted in a small amount of $\text{TiO}_2/\text{SiO}_2$. At solution pH of 4-6, the species of Ti(IV) and Si(IV) were present as $\text{Ti}(\text{OH})_4$ and $-\text{SiOH}$ respectively, enabling them to easily interact one with each other, which resulted in more amount of $\text{TiO}_2/\text{SiO}_2$. In the solution with pH 9, TiO_4^{4-} and $-\text{SiO}^-$ were found that were in the same charges, consequently, they were prevented from the interaction, yielding lower amount of $\text{TiO}_2/\text{SiO}_2$.

Fig.-2: Influence of the Preparation pH on their XRD Patterns. The XRD Patterns of : (a) SiO_2 , (b) TiO_2 , (c) $\text{TiO}_2/\text{SiO}_2$ (pH2), (d) $\text{TiO}_2/\text{SiO}_2$ (pH4), (e) $\text{TiO}_2/\text{SiO}_2$ (pH6), and (f) $\text{TiO}_2/\text{SiO}_2$ (pH9)

The average crystalline sizes of the TiO_2 in $\text{TiO}_2/\text{SiO}_2$ were estimated from XRD line broadening using Scherrer's equation,¹⁸⁻¹⁹ by considering the full width and half maximum (FWHM) value. The Scherrer's formula is expressed as; $D = (k\lambda) / \beta \cos\theta$, where D is the mean crystallite size, k the shape factor, λ the wavelength of the X-ray radiation, β the line broadening at half the maximum (FWHM) and θ the Bragg angle. The calculated crystallite sizes of the different samples are illustrated in Table 1, demonstrating that the crystallite size of $\text{TiO}_2/\text{SiO}_2$ was smaller than the bare TiO_2 . The decrease in the particle size of TiO_2 resulted from the inhibition of the particle growth by SiO_2 matrix.¹⁶⁻¹⁹ It is confirmed that TiO_2 nanoparticles have been successfully produced by supporting it on SiO_2 purified from the volcanic ash.

Table-1: The Average Particle Size of TiO_2 based on their XRD Patterns Calculated by Using Scherrer's Equation

No	Photocatalyst	Average Particle Size of TiO_2 (nm)
1	TiO_2	12.028
2	$\text{TiO}_2/\text{SiO}_2$ (pH2)	8.983
3	$\text{TiO}_2/\text{SiO}_2$ (pH4)	8.459
4	$\text{TiO}_2/\text{SiO}_2$ (pH6)	10.814
5	$\text{TiO}_2/\text{SiO}_2$ (pH9)	12.311

It also can be seen in the table, the preparation of $\text{TiO}_2/\text{SiO}_2$ at alteration pH has resulted in $\text{TiO}_2/\text{SiO}_2$ with the different average particle sizes. The lowest particle size of TiO_2 was obtained in $\text{TiO}_2/\text{SiO}_2$ prepared at pH 4. It is implied that the growth confinement was maximum at pH due to the proportional amount of $\text{Ti}(\text{OH})_4$ and $-\text{SiOH}$ that were mutually interacted. At pH 2, the amount of $-\text{SiOH}$ may be very view because most of them were in $-\text{SiOH}^+$ form, causing less limitation of the particle growth, that was why the larger particle size was produced. At the higher pH (6 and 9), the particle size is seen to be larger, due to the less prevention of the particle growth, that was caused by the less amount of $-\text{SiOH}$, where the most amount was formed as $-\text{SiO}^-$ during the preparation.

FTIR analysis was performed to detect an interaction between TiO_2 and SiO_2 in $\text{TiO}_2/\text{SiO}_2$ prepared. The FTIR spectra of $\text{TiO}_2/\text{SiO}_2$ prepared from silica gel at various pH are displayed in Fig.3. It is seen in the figure that SiO_2 has several typical absorption bands at 800, 1095, 1635, and 3448 cm^{-1} of the wavelengths. The absorption bands at 800 and 1095 cm^{-1} assigned the presence of symmetric and asymmetric vibration of Si-O-Si bond respectively. The broad absorption at 3429 cm^{-1} and 1635 cm^{-1} attributed of the bend vibration of O-H group from water adsorbed by the silica as well as from syanol of Si-OH bond.¹⁶⁻¹⁷

In the spectra of TiO_2 it is observed that the strong band at 570 cm^{-1} was associated with the characteristic vibrational modes of TiO_2 .¹⁸ The absorption in the range from 3,425 cm^{-1} may be related to the presence of O-H stretching vibration (Monomer, intermolecular, intramolecular and polymeric). The absorption band at 1,635 cm^{-1} was due to the presence of O-H bending vibration which is probably because the reabsorption of water from the atmosphere has occurred.¹⁶

The spectra of all $\text{TiO}_2/\text{SiO}_2$ samples exhibit absorption peaks appearing at 570, 1095-1076, 1630, and 3425 cm^{-1} , that are a combination of the peaks that belonged to TiO_2 and that are of SiO_2 . The peak at about 900-1000 cm^{-1} , that is associated with Si-O-Ti is not observed. indicating no Si-O-Ti bond occurred in $\text{TiO}_2/\text{SiO}_2$ photocatalyst.¹⁶⁻¹⁷ The absence of the bond defined that $\text{TiO}_2/\text{SiO}_2$ was not formed as composite. This finding well agreed with their respective XRD data.

Also, it is attributable that the intensity of Si-O-Si peaks at 1095 cm^{-1} decreases as the preparation pH increases. The decrease in intensity of the peaks was due to the increase of TiO_2 formed and covering the surface of SiO_2 and thus inhibiting the vibration of the Si-O-Si group. The same findings were also reported by previous studies.¹⁶⁻¹⁷

The SEM images were taken to find out the morphology of $\text{TiO}_2/\text{SiO}_2$ prepared. The images are displayed in Fig.4. In the figure, it is observable that SiO_2 is featureless and TiO_2 is in larger and aggregate forms, while TiO_2 in $\text{TiO}_2/\text{SiO}_2$ are looked at as smaller size and more dispersed. The smaller and dispersion of the smaller size and dispersed resulted from the limitation of the particle growth through interaction of TiO_2 with $-\text{SiOH}$ during the preparation. Further, $\text{TiO}_2/\text{SiO}_2$ prepared at pH 4 seems to be the densest

compared to that of prepared at pH 2 and pH 9. It is implied that the most amount of $\text{TiO}_2/\text{SiO}_2$ was yielded from the preparation at pH4. This data is in good agreement with the XRD data.

Fig.-3: Influence of Preparation pH. The IR spectra of : (a) SiO_2 , (b) TiO_2 , (c) $\text{TiO}_2/\text{SiO}_2$ (pH2), (d) $\text{TiO}_2/\text{SiO}_2$ (pH4), (e) $\text{TiO}_2/\text{SiO}_2$ (pH6), and (f) $\text{TiO}_2/\text{SiO}_2$ (pH9)

Fig.-4: The SEM Images of : (a) SiO_2 , (b) TiO_2 , (c) $\text{TiO}_2/\text{SiO}_2$ (pH2), (d) $\text{TiO}_2/\text{SiO}_2$ (pH4), and (e) $\text{TiO}_2/\text{SiO}_2$ (pH9)

The DRUV spectra were recorded to determine band gap energy (E_g) as a character of a photocatalytic semiconductor, that is illustrated as Fig.-5.

Fig.-5: The DRUV Spectra of : (a) TiO_2 , (b) $\text{TiO}_2/\text{SiO}_2$ (pH2), (c) $\text{TiO}_2/\text{SiO}_2$ (pH4), and (d) $\text{TiO}_2/\text{SiO}_2$ (pH9).

The figure demonstrates that TiO₂ has strong absorption of about 380 nm. It is generally seen that the absorption wavelength of TiO₂ formed in the TiO₂/SiO₂ samples shifts into the shorter region and enters to the UV range. The shift of the optical absorption into a shorter wavelength known as a blue shift represents the smaller particle size classified as nanoparticles. The absorption wavelength was converted into band gap energy (Eg) by following the relationship of $E_g \text{ (in eV)} = 1240/\lambda \text{ (in nm)}$, and the Eg values were displayed in table 2. The Eg of TiO₂ in TiO₂/SiO₂ is found to be higher than that of TiO₂, implying that the supported TiO₂ can absorb the UV light stronger than the unsupported one. Since the Eg value is associated with the photocatalytic activity, it is strongly hoped that TiO₂/SiO₂ to get enhancement in its activity as photocatalyst.

Table-2: The Absorption Wavelength and their Respective Bandgap Energy

Photocatalyst	TiO ₂	TiO ₂ /SiO ₂ (pH2)	TiO ₂ /SiO ₂ (pH4)	TiO ₂ /SiO ₂ (pH9)
λ (nm)	387	370.15	359.4	375.76
Eg (eV)	3.20	3.35	3.45	3.30

To examine the activity of TiO₂/SiO₂ photocatalyst, it was employed for the removal of ammonia in water under UV light irradiation. The reactions that may be occurred between ammonia and the UV light in the presence of the TiO₂ based photocatalyst, can be presented below as eq.(7) to eq.(14).²⁴

or

It is found that the degradation of ammonia can yield N₂ and/or NO₃⁻ ions that are safe for humans and the environment. According to the previous research²⁴, the most results of the degradation ammonia was N₂ and H₂, along with the low level of NO₂⁻/NO₃⁻. The opposite results of the degradation were also reported elsewhere that the major was NO₂⁻/NO₃⁻ accompanied by minor N₂ gas.²³ Fig.6 illustrates that supporting TiO₂ on SiO₂ can improve its activity in the removal of ammonia over TiO₂. The improvement was a result of the increasing Eg and decreasing particle size. The higher Eg represents more light absorption by the photocatalyst, providing more number of OH radicals that promote more effective oxidation. The smaller particle size provides a larger active surface on the photocatalyst that facilitates the more effective contact between ammonia and OH radicals on the photocatalyst surface, in turn to produce more degradation or oxidation of the ammonia. Also, SiO₂ matrix of TiO₂/SiO₂ can provide a more active area for ammonia to adsorbed and contact OH radicals of TiO₂ surface. It is worthy to remind that a photocatalysis process is initiated by adsorption of the substrate on the photocatalyst surface,⁹ continued by OH radicals attacking to the substrate to stimulate degradation reaction.

It is also seen in the figure that the activity of TiO₂ in TiO₂/SiO₂ was controlled by the preparation pH. The activity of TiO₂/SiO₂ prepared at pH 2-4 is observable to enhance and reaches a maximum, but that of the photocatalysts prepared with pH exceeds 4 and up to 9, the activity is revealed to decline. The activity of TiO₂/SiO₂ is dependent on the amount of TiO₂ loaded, and the surface area corresponding to their particle size and Eg value. The activity of TiO₂/SiO₂ (pH2) with low TiO₂ loaded, smaller particle size and high Eg, is found to be low. Based on the particle size, and Eg the activity should be high but the opposite result was obtained. It is clear that the low activity is due to the low TiO₂ loaded, that only released OH radical in a small number. In this case, the role of TiO₂ amount seems to be more dominant. The photocatalysts that were prepared at pH 4 with the smallest particle size and highest Eg shows the

strongest activity or gives the highest ammonia removal. In this condition, a synergic effect of TiO_2 amount, E_g , and particle size play an important role in the ammonia removal. $\text{TiO}_2/\text{SiO}_2$ that was prepared at pH 6 and pH 9, show a decrease in the activity because they possessed lower TiO_2 loaded, larger particle size and smaller E_g value, which can depress the reaction to occur.

Fig.-6: The Effect of Supporting TiO_2 on SiO_2 towards the Ammonia Removal. (1) TiO_2 , (2) $\text{TiO}_2/\text{SiO}_2(\text{pH}2)$, (3) $\text{TiO}_2/\text{SiO}_2(\text{pH}4)$, (4) $\text{TiO}_2/\text{SiO}_2(\text{pH}6)$, and (5) $\text{TiO}_2/\text{SiO}_2(\text{pH}9)$.

The influence of the photocatalyst dose on the ammonia removal is displayed as Fig.-7. In the figure, the improvement of the ammonia removal is assignable as the increase of the photocatalyst dose, and it reaches a maximum at using 30 mg in 50 mL of the ammonia solution. The use of the photocatalyst dose higher than 30 mg, the removal is seen to be slightly decreased. With the enlargement of the photocatalyst mass, more OH radical was provided, which should result in more effective ammonia removal, but the opposite data is observed. It is because the further increase of the photocatalyst dose may elevate the turbidity of the solution that can give a screening effect on the light penetrating light into the solution. Consequently, the less number of OH radicals is released from the TiO_2 , which results in the low effectiveness of the ammonia removal.

Fig.-7: The Influence of the Dose of $\text{TiO}_2/\text{SiO}_2(\text{pH}4)$ Photocatalyst on the Ammonia Removal

The efficiency of the ammonia removal is attributable to increase, as the reaction time was extended up to 180 mins (3 h), and the efficiency slightly reduces for the longer than the optimum time, as exhibited by Fig.-8. The longer irradiation time might give more effective contact between light and TiOH , which produced more OH radicals. The longer time also enabled the OH radicals and ammonia to contact in more effectively. It is implied that the maximum releasing OH radicals and so the photocatalysis process, was reached in 180 mins.

Since the pH of the solution has an important role in the effectiveness of the degradation, in this research the influence of the pH on the ammonia removal is evaluated and the results are displayed as Fig.-9. The

effectiveness of the removal is improved, then it reduced with the alteration pH. At pH 3, TiOH representing TiO_2 that is solvated by water was protonated to form TiOH_2^+ . This positive charge of the titania inhibits it to release OH radicals¹² so that only a few number OH radicals might be provided. It is similar, that NH_3 can also be protonated to form NH_4^+ , that prevents it to be adsorbed on the surface of TiOH_2^+ . The low adsorption causes the low NH_3 oxidation.

Fig.-8: The Influence of the Reaction Time on the Ammonia removal

Elevating pH up to 7 can raise the removal and reaches the maximum level. In such pH range, the neutral charge of TiOH fraction should increase (based on its $\text{pzc} = 6.8$), which promotes more OH radicals. Similarly, the fraction of NH_3 in the solution should also improve, is ready to be adsorbed on the TiOH surface, that turns to greatly induce the ammonia removal. When the pH was further elevated up to 11, the depletion ammonia removal is attributed. In the basic condition, TiO^- was present prominently, that is prevented for releasing the OH radicals. At the same pH, NH_3 is maximally present that can be completely oxidized. But because the less OH radicals were available, and the adsorption of NH_3 by TiO^- may be inhibited, the photocatalysis removal of ammonia is observed to decline. The optimum pH is detected as 7. This finding is different from some previous Authors. Gong, et al.²³ found that the optimum pH in the ammonia photocatalytic degradation was 3, while Zenderzaban et al.²⁴ reported that 9 was the optimum pH for the same process.

Fig.-9: Influence of the Solution pH on the Ammonia removal

CONCLUSION

It can be concluded that by using SiO_2 purified from volcanic ash as a supporting material, TiO_2 nanoparticles with anatase type have been successfully formed in $\text{TiO}_2/\text{SiO}_2$ photocatalyst. The supported photocatalyst was found to have higher bandgap energy (E_g) compared to the E_g of the bare TiO_2 . It is also observed that the best characters of $\text{TiO}_2/\text{SiO}_2$ in term of particle size and E_g was obtained when the preparation was conducted at pH 4. By photocatalysis process over $\text{TiO}_2/\text{SiO}_2$, the ammonia concentration

in the solution could be decreased as much 40-65%, and the decrease was more effective than was shown by the bare TiO_2 (15%). The ammonia diminish was found to be controlled by photocatalysts dose, pH and the illumination time. The maximum ammonia removal (65%) from 50 mg/L in 100 mL solution was reached when 50 mg of the photocatalyst, at pH 7, and 180 mins were employed. The ammonia removal was believed to take place through degradation into N_2 gas, that is safer in the environment.

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REFERENCES

1. E.T. Wahyuni, S. Triyono and S.Suherman, *Journal of People and Environment* (in Indonesian), **19(2)**, 150(2012)
2. L. Simatupang, R. Siburian, P. Sitanggang, M. Doloksaribu, M. Situmorang and H. Marpaung, *Rasayan Journal of Chemistry*, **11(2)**, 819(2018), DOI:10.31788/RJC.2018.1122091
3. P. Delmelle, F. Villiras and M. Pelletier, *Bulletin of Volcanology*, **67**, 160(2005), DOI:10.1007/s00445-004-0370-x
4. E.T. Wahyuni, R. Roto, F.A. Nissah, M. Mudasir and N. H. Aprilita, *Indonesian Journal of Chemistry* **18(3)**, 428 (2018), DOI:10.22146/ijc.26905
5. R. Renugadevil, T. Venkatachalam1, R. Narayanasamy, S. Prabahar and P. Krishnamurthi, *Rasayan Journal of Chemistry*, **9(2)**,125 (2016)
6. H. M. Mateus, J. Bautista-Ruiz, J.Barba-Ortega and M. R. Joya, *Rasayan Journal of Chemistry*, **12(3)**, 1304 (2019), DOI:10.31788/RJC.2019.1235265
7. M. Z. B. Mukhlis, F. Najnin, M. M. Rahman and M. J. Uddin, *Journal of Scientific Research*. **5**, 301 (2013), DOI:10.3329/jsr.v5i1.11641
8. N. Barka, I. Bakas, S. Qourzal, A. Assabbane and Y. Ait-Ichou, *Oriental Journal of Chemistry*, **29**, 1055 (2013), DOI:10.13005/ojc/290328
9. E. T. Wahyuni, R. Roto, M. Sabrina, V. Anggraini, N. F. Leswana, A. C. Vionita. *American Journal of Applied Chemistry*. **4**, 174 (2016), DOI:10.11648/j.ajac.20160405.13
- 10.D. Dimitrakopoulou, I. Rethemiotaki, Z. Frontistis, N. P. Xekoukoulotakis, D. Venieri and D. Mantzavinos, *Journal of Environmental Management*, **98**, 168(2012), DOI:10.1016/j.jenvman.2012.01.010
- 11.M.A. Kebede, M. E. Varner, N.K. Scharko, R.B. Gerber and J. D. Raff, *Journal of American Chemical Society*, 8606 (2013)
- 12.S. Arul and T. Senthilnathan, __*Rasayan Journal of Chemistry* **12(2)**, 891(2019), DOI:10.31788/RJC.2019.1225175
- 13.M. Mahalakshmi, S.V. Priya, B. Arabindoo, M.Palanichamy and V.Murugesan. *Journal of Hazardous Materials*, **161**, 336 (2009), DOI:10.1016/j.jhazmat.2008.03.098
- 14.N. Todorova, T. Giannakopoulou, S. Karapati, D. Petridis, T.Vaimakis and C.Trapalis. *Applied Surface Science*, **319**, 113(2014), DOI:10.1016/j.apsusc.2014.07.020
- 15.H. A. Al-Turaif, *Progress in Organic Coating*, **69**, 241(2010), DOI:10.1016/j.porgcoat.2010.05.011
- 16.D.A. Kumar, J.M. Shyla and F.P Xavier, *Applied Nanoscience*, **2**, 429 (2012)
- 17.A. Nilchi, S. Janitabar-Darzi and S. Rasouli-Garmarodi, *Materials Sciences and Applications*, **2**, 476 (2011), DOI:10.4236/msa.2011.25064
- 18.O. Kesmez, H. E. Camurlu, E. Burunkaya and E. Arpac, *Solar Energy Materials & Solar Cells.*, **93**, 1833 (2009)
- 19.T. Ohno, S. Tagaw, H. Itoh, H. Suzuki and T. Matsuda, *Materials Chemistry and Physic* **113**, 119 (2009), DOI:10.1016/j.matchemphys.2008.07.034
- 20.I. Fatimah, S. Fadhilah, Y. Yulan and S. A. Mawardani _*Rasayan Journal of Chemistry*, **11(2)**, 544 (2018), DOI:10.31788/RJC.2018.1122067

- 21.W. Trisunaryanti, I.I. Falah, D.R. Prihandini and F.Marsuki, *Rasayan Journal of Chemistry*, **12(3)**, 1523 (2019), [DOI:10.31788/RJC.2019.123597](https://doi.org/10.31788/RJC.2019.123597)
- 22.H. Akbar, G. Krishan, S. D. Prajapati and R. Saini. *Rasayan Journal of Chemistry*, **9(1)**, 27 (2016)
- 23.X. Gong, H. Wang, C. Yang, Q. Li, X. Chen and J. Hu. *Future Cities and Environment*, **1**, 12 (2015), [DOI:10.1186/s40984-015-0012-9](https://doi.org/10.1186/s40984-015-0012-9)
- 24.M. Zendezhaban, S. Sharifnia and S. N. Hosseini. *Korean Journal of Chemical Engineering*, **30**, 574 (2013), [DOI:10.1007/s11814-012-0212-z](https://doi.org/10.1007/s11814-012-0212-z)
- 25.P. Klankaw, C. Chawengkijwanich, N. Grisdanurak and S. Chlarakorn, *Superlattices and Microstructures*, **51**, 343 (2012), [DOI:10.1016/j.spmi.2011.12.004](https://doi.org/10.1016/j.spmi.2011.12.004)
- 26.D.J. Belton, O. Deschaume, S.V. Patwardhan and C.C. Perry, *Journal of Physical Chemistry B.*, **114(31)**, 9947 (2010), [DOI:10.1021/jp101347q](https://doi.org/10.1021/jp101347q)

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