Acta. Chim. Asiana., 2023, 6(1), 295 – 300
e-ISSN/p-ISSN 2550-0503/2550-049x
Available online at: www.aca.unram.ac.id

RESEARCH PAPER

Synthesis and characterization of TiO_2-Fe for photocatalytic applications of domestic waste

Annisa Rahmadhani, Hasmalina Nasution*, Prasetya, Novialis Dayumita, Sri Hilma Siregar

Department of Chemistry, Muhammadiyah University of Riau
Jl. KH. Ahmad Dahlan No. 88 Kp. Melayu, Kec. Sukajadi, Kota Pekanbaru, Riau 28156, Indonesia
*hasmalinanst@umri.ac.id

DOI: 10.29303/aca.v6i1.140

Article info:

Received 27/12/2022

Revised 07/02/2023

Accepted 10/02/2023

Available online 25/02/2023

Abstract: Wastewater originating from household, industrial, and public places that contains materials can endanger human life and living things and disrupt environmental sustainability. Various methods have recycled domestic wastewater. One is through the photodegradation process utilizing ultraviolet light in the photocatalytic process. Inorganic materials are semiconductors with photocatalyst activity that can absorb photons and simultaneously carry out material interface transformation reactions. The research aimed to determine the effect of adding Fe metal dopants on TiO_2 photocatalyst activity in simulated methylene blue and domestic waste treatment. The precursor used was TiO_2 P25 Degussa Anatase. Fe dopant was added using the hydrothermal method with variations of 2%, 4%, and 6%. The XRD characterization results show that TiO2 has a high degree of crystallinity, so the overall process of electron diffusion and electron transfer in SSPT is higher to increase its efficiency. SEM-EDX characterization results show that TiO_2-Fe particles are scattered in a spherical shape with a size of less than (<)100 nm and tend to agglomerate. Test results of simulated methylene blue (MB) waste with a UV-Vis spectrophotometer at variations in mass, concentration, pH, and time showed that the addition of doping could increase photocatalytic activity and optimum conditions at 6% (F6) were used in the analysis of parameters pH, COD and TSS of domestic wastewater. The pH value increased from 5 to 6, % COD degradation was 59.17%, and TSS was 23.07%. This research showed that TiO_2-Fe was effective enough for domestic wastewater treatment.

Keywords: TiO2-Fe, Photocatalyst, Methylene blue, Domestic wastewater

Rahmadhani, A. Nasution, H., Prasetya, Dayumita, N., Siregar, S. H. (2023). Synthesis and characterization of TiO_2-Fe for photocatalytic applications of domestic waste. *Acta Chimica Asiana 6*(1), pp 295 – 300, DOI: 10.29303/aca.v6i1.140

INTRODUCTION

Household wastewater has been recycled using various methods. One is using the photodegradation method, namely utilizing ultraviolet light for the photocatalyst activity to absorb photons and simultaneously carry out transformation reactions at the material interface [1, 2].

Titanium dioxide has a band gap energy of (3.0 – 3.2) eV which is equivalent to the wavelength of UV light (< 380 nm), limiting its application [3]. Only about 5% of UV rays that reach the earth are visible rays. Several attempts have been made to shift the absorption towards visible light by reducing the band gap energy using metal cation doping. One of the metal cations used as dopants is Fe^{3+}. Fe^{3+} metal can be used as a dopant because it has an ionic radius of 0.064 nm which is almost the same as the radius value of Ti^{4+}, which is 0.068 nm so that Fe^{3+} will more easily substitute some Ti^{4+} ions in the TIO_2 structure [4].

This research was conducted to provide a solution for handling and processing domestic wastewater, namely degrading domestic waste with TiO_2-Fe photocatalysts, so that it meets the requirements for quality standards for domestic waste referring to the minister of environment and forestry regulation No.68 of 2016 with the hydrothermal method for the synthesis of TiO_2-Fe.

MATERIALS AND METHODS

Synthesis of Fe-TiO_2 by Hydrothermal Method

The synthesis begins by weighing 2%, 4%, and 6% $Fe(Cl)_3$ by weight of TiO_2, which is 10g, and adding 5 mol L^{-1} 50mL NaOH to the mixture. The mixture was transferred into a 100 mL steel autoclave, heated at 140^0C for 14 hours, and cooled in the reactor to 80^0C. The results were washed with hot water; then, the slurry was stirred while adding HCl slowly for 10 minutes and centrifuged at 900 rpm for 10 minutes. Washed with hot deionized water until the pH of the liquid is close to 7, then baked for 12 hours at 80^0C. The final process is that the material is calcined at 550^0C for 5 hours. After finishing material, the results are characterized using XRD and SEM-EDX.

Methylen Blue Waste Degradation

Effect of Mass, Time, pH, and Concentration of Fe-TiO_2 Catalyst on MB

Take 25 mL of MB wastewater and 75 mL of distilled water with a volume pipette, then put it into a 250 mL beaker glass, add 2%, 4%, and 6% Fe-TiO_2 material with four variations, namely 0.1 gr, 0.3 gr, 0. .5 gr and 0.7 gr (For mass variations). The same thing was done with the mass; only the difference was in the concentration variations, namely 20 ppm, 40 ppm, 60 ppm, and 80 ppm. For effect on pH with variations 1, 3, 5, 7, 9, and 11. For time variations of 10 minutes, 30 minutes, 60 minutes, and 90 minutes. They then stirred with a hotplate stirrer for 90 minutes using and without a photoreactor. Furthermore, MB levels were tested with a UV-Vis spectrophotometer at a wavelength of 663 nm.

Effect of Catalyst on Domestic Liquid Waste Parameters

Take 500 mL of domestic liquid waste with a volume pipette. Then it was put into a 1000 mL beaker, 0.07 gram of 6% Fe-TiO2 was added, then stirred with a hotplate stirrer for 90 minutes using a photoreactor. Then tests were carried out on the parameters of Chemical Oxygen Demand (COD) (SNI 6989.73: 2009), Total Suspended Solid (TSS) (SNI 6989.3: 2019), and pH (SNI 6989.11:2019).

RESULTS AND DISCUSSION

Results of Synthesis of TiO_2-Fe

The yield of the synthesis of TiO_2-Fe material was obtained at 78% for A2 material, 57% for A4 material, and 86% for A6 material (Table 1). The most percentage of this yield is found in A2 and A6 materials. Less A4 material may be due to the human factor. According to references, the more Fe, the better this material is for the degradation process.

Table 1. The yield of TiO_2-Fe Synthesis

No	Sample	Initial Mass	Final Mass	Yield (%)
1	A2	10.2	8	78
2	A4	10.4	5.93	57
3	A6	10.6	9.16	86

Characterization

X-Ray Diffraction (XRD)

The results of the XRD characterization of the TiO_2-Fe photocatalyst material can be seen in the image below:

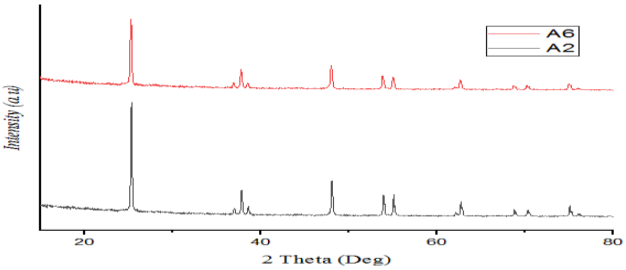


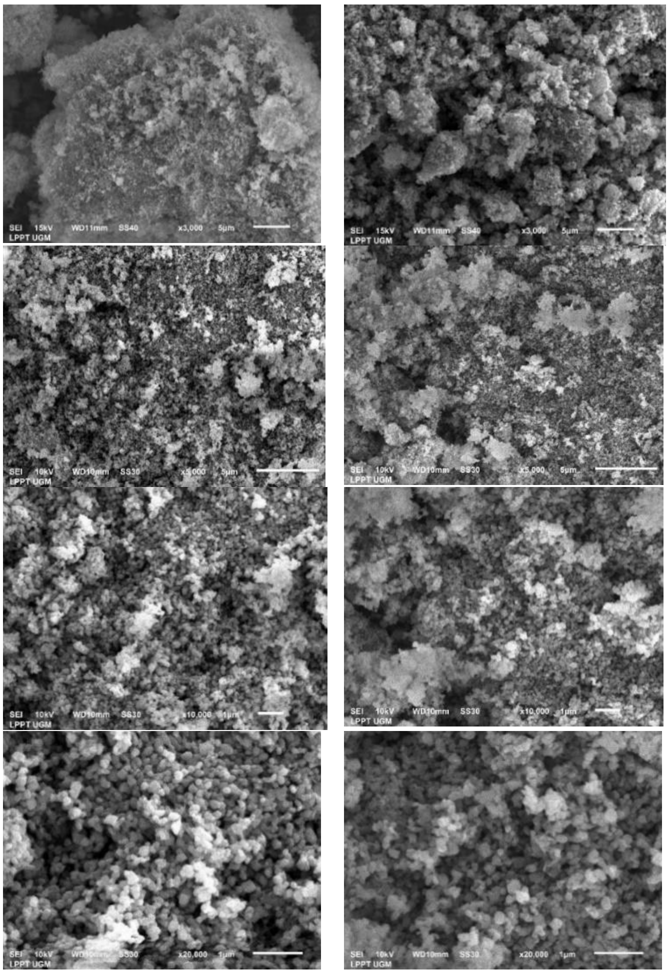
Figure 1 XRD pattern black peak (A2) TiO_2-Fe 2% and red peak (A6) TiO_2-Fe 6%

Figure 1 shows that TiO_2-Fe has a high intensity. This shows that TiO_2 has a high degree of crystallinity, so the electron diffusion process will be faster so that the overall electron transfer process in SSPT is higher so that it can increase its efficiency [5]. From the results of the diffraction pattern obtained, the TiO_2-Fe samples appeared peaks of 2θ 25°, 36°, 37°, 38°, 47°, 53°, 54°, 62°, 68°, 70°, 74° and 82° which corresponds to the peaks of the anatase phase based on JCPDS No. 21-1276 in the appendix. The determination of the TiO_2 crystal phase was strengthened by the results from the analysis using the Match program. From the program, it was found that all the peaks corresponding to the sample diffraction results were TiO_2 with an anatase crystal phase [6].

According to Wen et al. (2012), the shift in the 2θ diffraction peak occurred due to the influence of the Fe dopant concentration. When the Fe concentration increases, the diffraction field distance becomes larger because more and more Fe cations are doped on it TiO_2 and vice versa. This is because the radius of the Fe cation is smaller than the Ti cation, so the widening of the field spacing indicates that some Fe cations may be substituted in the TiO_2 lattice. The diffraction peaks with the highest intensity were then processed to determine the size of the crystallites and the distance between the sample lattices.

Scanning Electron Microscopy-Energy Dispersive X-ray **(SEM-EDX)**

Figure 2 shows the morphology of TiO$_2$-Fe particles analyzed using SEM. The TiO$_2$-Fe particles are scattered in a spherical shape with a size of less than (<100) nm and tend to agglomerate. In general, the process of forming nanoparticles occurs through several stages of the mechanism [7] Rahman, T 2014. The process of synthesis of monodisperse particles is divided into two main stages, namely the nucleation stage and the growth stage. At the nucleation stage, the formation of a particle nucleus occurs, which then becomes the place for the joining of other particles in the core. This stage will depend on the reaction system and the parameters that control the reaction. The more TiO$_2$-Fe nuclei formed, the collision and coalescence rates will increase[8].



TiO$_2$-Fe 2% TiO$_2$-Fe 6%

Figure 2 Material morphology magnification a) 3,000 x b) 5,000 x C) 10,000 x d) 20,000 x

Effect of Catalyst Mass TiO$_2$-Fe 2%, TiO$_2$-Fe 4% and TiO$_2$-Fe 6%

Table 2. Degradation (%) of Mass Variation Without Photoreactors

Variation of masa	TiO$_2$-Fe 2 %	TiO$_2$-Fe 4 %	TiO$_2$-Fe 6 %
0.01	84.59	83.15	81.43
0.03	93.85	92.17	89.30
0.05	93.67	96.24	91.35
0.07	93.64	96.90	96.56

Table 3. Degradation (%) of Mass Variation With Photoreactors

Variation of masa	TiO$_2$-Fe 2 %,	TiO$_2$-Fe 4 %	TiO$_2$-Fe 6 %,
0.01	92.34	88.27	88.62
0.03	96.20	90.82	94.26
0.05	96.81	92.85	96.72
0.07	96.88	95.42	97.00

The degradation ability can be observed. Tables 2 and 3 show the degradation ability of the A2 material with an optimum mass variation at 0.07 g is capable of degrading MB dyes up to 93.64% without a photoreactor, and A2 material using an optimum mass photoreactor of 0.07 g is capable of degrading MB up to 96.88%. The optimum condition for the mass of the A4 catalyst is that at a mass of 0.07 g, it can degrade up to 96.90% without a photoreactor. Using a photoreactor is able to degrade A4 material by 95.42%, catalyst A6, which is at a mass of 0.07 g with a degradation capability of 96.56% without a photoreactor. Whereas for the A6 catalyst using a photoreactor, it can degrade by 97.00%.

Effect Chatalyst Consentration TiO$_2$-Fe 2%, TiO$_2$-Fe 4% dan TiO$_2$-Fe 6%

From the conditions of the three materials, it can be seen that the higher the concentration of MB, the rate of degradation of MB decreases. The greater the initial concentration of MB, the smaller the final concentration remaining after 120 minutes [9]. From the results of the ability of the catalyst to degrade MB, this catalyst has the potential to be used in high concentrations and can be used in treating other industrial wastes (Tables 4 and 5).

Table 4. Degradasi (%) of Concentration Variation Without Photoreactors

Variation Of Concentration	TiO_2-Fe 2 %	TiO_2-Fe 4 %	TiO_2-Fe 6 %
20 ppm	94.41	95.26	96.47
40 ppm	88.05	88.69	90.62
60 ppm	69.63	69.25	78.50
80 ppm	48.25	50.05	60.93

Table 5. Degradation (%) of Concentration Variation With Photoreactors

Variation Of Concentration	TiO_2-Fe 2 %	TiO_2-Fe 4 %	TiO_2-Fe 6 %
20 ppm	96.01	96.68	95.63
40 ppm	89.02	80.28	94.65
60 ppm	73.61	83.17	58.01
80 ppm	56.39	61.64	43.37

Effect of Catalyst pH TiO_2-Fe 2%, TiO_2-Fe 4% dan TiO_2-Fe 6%

The pH value of the MB solution affects the degradation process. The results of the optimum pH conditions can be seen in Tables 6 and 7. The three materials have the optimum pH condition in an acidic atmosphere, namely at pH 1 and 3. It can be seen that the ability to degrade the three materials reaches 99%. From the result of the optimum pH conditions, it can be co concluded that the three materials have good degradability under acidic conditions. However, at alkaline pH the catalyst is also able to degrade up to 80%.

The optimum conditions for a material at various pH variations are because a catalyst will have its own optimum conditions when it is contacted with pH. At low pH, the absorption efficiency and capacity of MB play an important role in the adsorption mechanism [10]. The cationic nature of the new MB will appear at an acidic pH, so that the positively charged MB will bind to the negatively charged side of the adsorbent capacity to tend to increase when the pH of the solution is lowered [11].

Table 6. Degradation of pH Variation Without Photoreactors

Variation of pH	TiO_2-Fe 2 %	TiO_2-Fe 4 %	TiO_2-Fe 6 %
pH 1	98.79	98.01	98.58
pH 3	98.39	97.12	98.37
pH 5	95.84	96.14	96.25
pH 7	85.85	85.78	298
pH 9	35.97	80.56	
pH 11	24.45	78.58	81.01

Table 7. Degradation of pH Variation With Photoreactors

Variation of pH	TiO_2-Fe 2 %	TiO_2-Fe 4 %	TiO_2-Fe 6 %
pH 1	98.86	98.78	98.24
pH 3	99.43	98.39	99.33
pH 5	98.21	95.81	93.48
pH 7	92.78	85.78	85.85
pH 9	41.54	81.84	81.93
pH 11	51.65	81.01	81.11

Effect of Time Variation TiO2-Fe 2%, TiO2-Fe 4% dan TiO2-Fe 6%

The results of time variation can be concluded which catalyst is the best and which will be used in the application of domestic waste. Catalysts A4 and A6 are the best catalysts, which have the highest degradation percentage and faster degradation time than the other catalyst.

Table 8. Degradation of Time Variation Without Photoreactors

Time Variation	TiO_2-Fe 2 %	TiO_2-Fe 4 %	TiO_2-Fe 6 %
10 minute	81.27	82.04	90.72
30 minute	93.38	92.54	93.34

60 minute	95.75	96.03	95.04
90 minute	97.67	98.39	98.57

Table 9. Degradation of Time Variation With Photoreactors

Time Variation	TiO_2-Fe 2 %	TiO_2-Fe 4 %	TiO_2-Fe 6 %
10 minute	90.37	82.27	84.25
30 minute	93.58	89.67	92.38
60 minute	96.43	95.14	96.21
90 minute	98.48	99.08	99.40

The relationship between the results of material characterization influences the degradation results. In the degradation process, the level of crystallinity of the material will greatly affect the degradation process. The more crystalline a material is, the faster the degradation process will be and increase its degradation ability. The material process breaks down the structure into a simpler one. If using an adsorbent, the waste will be trapped in the material and produce new waste again (Tables 8 and 9).

The influence of Catalyst on COD Value

The results of the analysis of chemical Oxygen Demand (COD) levels in domestic wastewater samples by titrimetry showed that the control or initial waste domestic wastewater sample was 343.56 mg/L, and after degradation using a photocatalyst, it became 140.26 mg/L (Table 10).

Table 10. COD Analysis Result of Domestic Waste Water

Catalyst	COD (mg/L)	%Degradation	%RPD	%R
control	343.56	-	6.43	-
A6	140.26	59.7	0	0

The high level of COD in the waste is due to the large amount of organic and inorganic substances contained in the waste. Thus it can be stated that the high COD content in the waste is proportional to the number of contaminants contained in the waste. The higher the COD level, the greater the potential hazard that can be caused by the waste. Because the high levels of COD in the waste can damage the ecosystem in the surrounding waters, cause a foul, and can produce pathogenic bacteria that can interfere with the health of the surrounding community [11].

The Influence of Catalyst on TSS Value

Table 11. TSS Analysis Result of Domestic Waste Water

Catalyst	TSS (mg/L)	%Degradation	%RPD
Control	52	-	15%
A6	40	23.07	15%

Table 11 shows that the total suspended solids content obtained before degradation was 52 mg/L, and after degradation using photodegradation was 40 mg/L. This is due to a large number of suspended particles, such as dissolved organic materials, bacteria, plankton, and other organisms in the wastewater, causing high levels of total suspended solids [12]. We can see that 6% TiO_2-Fematerial is able to degrade waste with a TSS parameter of 23.07%.

The Influence of Catalyst on pH Value

Table 12. pH Analysis Result of Domestic Waste Water

catalyst	Initial pH	Final pH	%RPD
Kontrol	5	5	0
A6	5	6	0

The pH value is an important supporting parameter for analysis because it is an indicator of the sustainability of the decomposition process by microorganisms in a waste treatment system [13-16]. The table above shows that in all samples of wastewater, the pH complies with the established liquid waste quality standard, which is six according to government recommendations, with a limit of 6.0-9.0. before degradation 5.0 and after degradation 6.0 (Table 12).

Conclusion

Based on the results of the research, it can be concluded that the TiO_2-Fe catalyst is able to degrade domestic waste through COD, TSS, and pH parameters, although it does not meet the quality standards set by the government.

References

[1] Wulandari, M., Astuti and Muldarisnur. 2018. Synthesis of porous TiO2-SiO2 nanoparticle as photocatalysts for household wastewater purification. Andalas University Physics Journal. 7(1):33.

[2] Cahyanti, R., Sumari, S., Fajaroh, F., Asrori, M. R., & Fajar, Y. (2023). Fe-TiO2/zeolite HA photocatalyst for degradation of waste dye (methylene blue) under UV irradiation. AIMS Materials Science, 10(1), 40-54.

[3] Wen, L., Liu, B., Zhao, X., Nakata, K., Murakami, T., & Fujishima, A. (2012). Synthesis, characterization, and photocatalysis of Fe-doped: a combined experimental and theoretical study. International Journal of Photoenergy, 2012.

[4] Pratiwi, E., Anthoni, H., and Aritonang. 2020. Synthesis of Fe3+-doped TiO2 for Rhodamine B Degradation by Photocatalysis with the Assistance of Visible Light. Positron. 10(1).

[5] Imani, S., Alizadeh, A., Roudgar-Amoli, M., & Shariatinia, Z. (2022). Bi-layered photoelectrodes of TiO2/activated carbon modified with SrTiO3 films boosted sunlight harvesting of dye-sensitized solar cells. Inorganic Chemistry Communications, 145, 110045.

[6] Kiswanti, E and Pratapa, S. 2013. Synthesis of Titanium Dioxide (TiO2) Using the Acid-Dissolved Metal Method. Journal of Science And Arts Pomits. 3(2).

[7] Rahman, T., Fadlulloh, A., Nandiyanto, A., dan Mudzakir, A. 2014. Review: Sintesis Titanium Diokasida Nanopartikel. *Jurnal Integrasi Proses*. 5 No. 1.

[8] Kumalasari, M. 2013. The use of TiO2 nanoparticles synthesized on a water-based basis using the sol-gel method on cotton as an application for anti-UV textiles.

[9] Pratiwi, E., Anthoni, H., and Aritonang. 2020. Synthesis of Fe3+-doped TiO2 for Rhodamine B Degradation by Photocatalysis with the Assistance of Visible Light. Positron. 10(1).

[10] Marey, A. (2020). Synthesis composite of TiO2/chitosan and TiO2/bentonite for removing turbidity from Ismailia canal as water treatment plant. African Journal of Chemical Education, 10(1), 124-133.

[11] Silalahi, I. 2019. Analysis of Cod (Chemical Oxygen Demand) Levels in Domestic Liquid Waste by Titrimetry at Pt. Shafera Enviro Laboratory. Essay. University of Northern Sumatra. Medan.

[12] Ramadhani, D. 2017. Analysis of Total Suspended Solids (Tss) Content from Domestic Wastewater Using the Gravimetric Method at the Tirtanadi Cemara PDAm Wastewater Treatment Plant, Medan. Essay. University of Northern Sumatra. Medan.

[13] Nilasari, E., Faizal, M., and Suheryanto. 2016. Household Wastewater Treatment Using a Combined Strainer Process and Bioremediation of Water Hyacinth (Eichornia crassipes), (Case Study at Griya Mitra 2 housing, Palembang). Journal of Science Research. 18(1).

[14] Delhiraja, K., & Philip, L. (2020). Characterization of segregated greywater from Indian households: part A—physico-chemical and microbial parameters. Environmental monitoring and assessment, 192, 1-23.

[15] Sohouli, E., Irannejad, N., Ziarati, A., Ehrlich, H., Rahimi-Nasrabadi, M., Ahmadi, F., & Luque, R. (2022). Application of polysaccharide-based biopolymers as supports in photocatalytic treatment of water and wastewater: a review. Environmental Chemistry Letters, 1-21.

[16] Sumarlan, I., Fatimah, I., & Wijaya, K. (2020). Indonesian Modified Clay for Dye Waste Treatment. *Acta Chimica Asiana*, *3*(1), 122-126.