Synthesis of Double Layer ZnO/ZnO : Fe by Coating Method for Tetracycline Degradation

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ABSTRACT

The results of the experiment by using the sol - gel method showed that the ZnO/ZnO:Fe thin layer was deposited on the glass preparations. This research intends to deteriocin tetracycline by using a double layer thin film ZnO/ZnO:Fe which is added with Fe compounds of 2%, 4%, 6%, 8%, and 10%. In giving the concentration, it is known that the results obtained are 3.104; 3.116; 3.117; 3098; and 3.117 eV. The depiction of the optical character shows that the best absorption is at ZnO/ZnO:Fe with a concentration of 2% with a value of 0.402. Meanwhile, the lowest absorption value of ZnO/ZnO:Fe was 8% with a value of 0.272. The use of ultraviolet for declination showed the highest results, namely thin film ZnO/ZnO:Fe thin film ZnO/ZnO:Fe

Keywords: Thin Film, Double Layer, Zno/Znofe, Degradation

I. INTRODUCTION

Tetracycline is one of the most widely used drugs for treatment. Tetracycline is widely used in the food industry, aquaculture, and agriculture [1]. Mutagens in humans and animals can be caused by tetracycline contamination in water, it causes permanent damage to the human body. So it is necessary to test the degradation of tetracycline in waste and water sources [2].

Adsorption, sedimentation, activated sludge treatment, and photocatalyst are methods that can be used to treat tetracycline-contaminated waste in the pharmaceutical industry. The method that is often used is photocatalyst, this method can be said to be an efficient way to treat tetracycline waste. The advantages of this method are that it is relatively inexpensive, constant, and safe for the surrounding environment [3]. Decomposition of wastewater often uses ZnO, which is an n-type element with a range of 3.4 eV and a large stimulant of 60 mV [4]. Used to optimize the photocatalytic work of ZnO include widening the optical absorption range of *ultraviolet light* into the visible region, preventing the unification of electron pair elements and photogenerating holes [5],[6],[7]. Iron or Fe is a metal that is believed to be efficient in minimizing the band gap and changing the character of ZnO [8]. *Double layer thin films* were analyzed by *sol-gel*. The advantages of this method are chemical homogeneity, small molecular size, high purity, no interaction with the container, energy saving, and reduced evaporation [9]. *Research* aims to understand the effect *doping* iron (Fe) *Thin Film Double Layer* ZnO/ZnO:Fe for

the declination of tetracycline waste. Furthermore, the *Ultra Violet Spectrophotometer* was used to personify the results of the synthesis with the aim of understanding the optical properties.

II. METHODS AND MATERIAL

Instruments and Materials

In this study using several instruments, namely: Compressor (Krisbow, AS 186), Spray Gun (Krisbow HS-80 KW1 (200333), UV lamp, Hotplate, *Magnetic stirrer*, Digital Scales (model VMC, VB 304), and UV-Vis Spectrophotometer (Shimadzu, 1240 SA).

While the materials in this study used, among others: Glass preparations, Zinc Nitrate Dehydrate ($Zn(NO3)2.4H2O$), Acetone ($CH3COCH3$), Methanol ($CH3OH$), Tetracycline, Aquades, and Iron (III) Nitrate Nonahydrate ($Fe(NO3)39H2O$).

Research and Variables

The independent variable in this test was the amount of iron (Fe) added to ZnO/ZnOFe, namely 2%, 4%, 6%, 8%, and 10%. As well as a light source in UV light which is a parameter for degradation. The control variables in this study were material, *hotplate* (60°C), time of degradation (3 hours) and deposition temperature (500°C). the dependent variable is the value of the effectiveness of *tetracysline*.

Sol-Gel Synthesis ZnO/ZnO:Fe

Technique *The sol-gel* useful for creating *thin films* ZnO/ZnO:Fe *Sol-gel* ZnO/ZnO:Fe is made by preparing $Zn(NO_3)_2.4H_2O$ or *Zinc Nitrate Dehydrate* then mixed in 13 ml of distilled water for further stirring using a *magnetic stirrer* at 60°C within 1 hour until the solution is completely mixed. This process is also useful in making ZnO:Fe solutions, but given the addition of *doping* iron (Fe) derived from $Fe(NO_3)_3.9H_2O$ or *Ferrite nitrate* which has various concentrations *doping* , namely ZnO: Fe solution is made in the same way as the previous process, but

with additional *doping* sourced from *Ferrite nitrate* ($Fe(NO_3)_39H_2O$) with variations *doping* 2%, 4%, 6%, 8%, and 10% and then stirred using a *magnetic stirrer* at a temperature of 60°C for 1 hour until homogeneous.

Degradation and Characterization

Making a tetracycline solution of 25 ppm by preparing 25 mg of tetracycline powder and then dissolving it in 1 liter of distilled water. A thin layer of ZnO/ZnO: Fe in accordance with the concentration value was added to the solution and the degradation was carried out using UV light for a period of 3 hours. The thin layer and the obtained degradation results were specified by means of UV-Vis spectrophotometry (Shimadzu UV-Vis 1240 SA).

III. RESULTS AND DISCUSSION

ZnO/ZnO:Fe thin layers were successfully crystallized (deposition) on the preparation plate using the *spray coating* with the addition of 2%, 4%, 6%, 8%, and 10% Fe concentrations in the sample. Although the effect (Fe) is not significant, it can still be observed by moving *the film* from white to yellowish as shown in Figure 1.
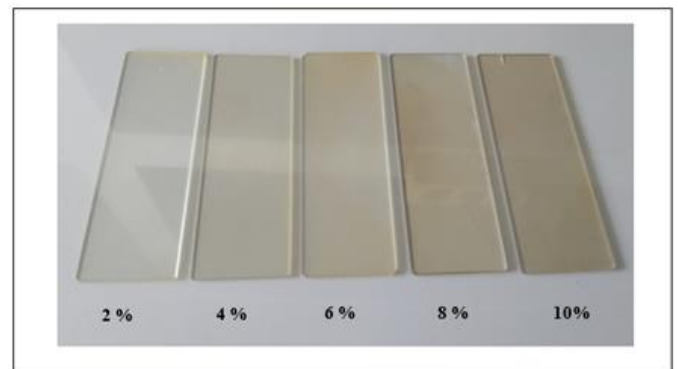

Figure 1: ZnO/ZnO:Fe thin film deposition results with concentrations of 2%, 4%, 6 %, 8%, and 10%

Observation of the absorbance of the ZnO/ZnO:Fe thin layer at a wavelength of 300-800 nm can be seen in Figure 2. Where the largest lift is ZnO:Fe with a concentration of 2% (0.402), and the lowest value is ZnO:Fe with a concentration of 8% (0.272).
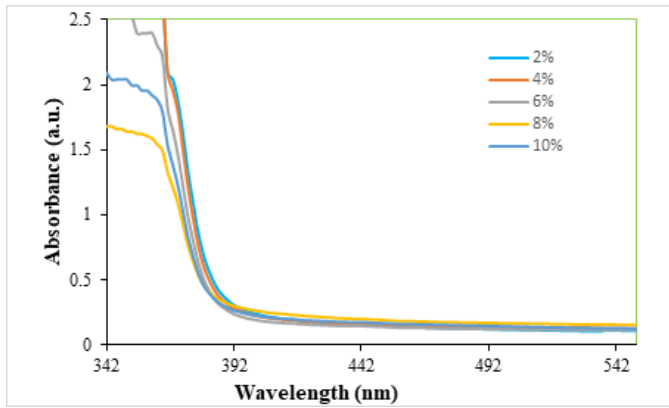
Figure 2. Absorbance spectrum of ZnO/ZnO:Fe thin film.

An increase in iron (Fe) concentration usually causes an increase in absorbance. This happens because the Zn atom is replaced with an iron atom (Fe) which creates a distance for each adjacent particle. The high concentration of Fe dopant allows for even greater agglomeration, where the layer (*film*) will also thicken. The thickening *film* proves that more molecules are involved in receiving light and less light (light) is transmitted. The *tauch plot* can be used to determine the minimum energy required to excite electrons from the valence band to the conduction band (band gap) of ZnO/ZnO:Fe thin films with a concentration variation of 2% (3.104); 4% (3,116); 6% (3,117); 8% (3,098); and 10% (3.117 eV) which can be seen in Figure 3.
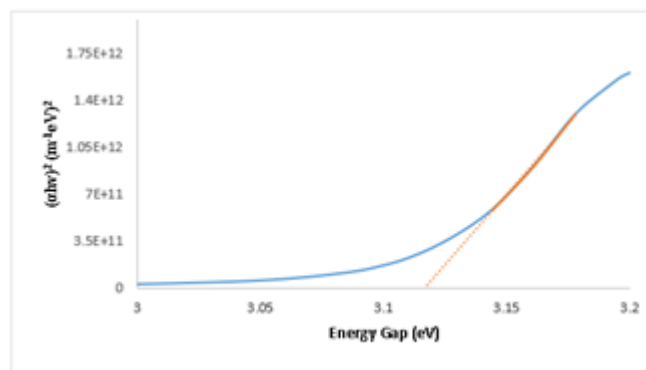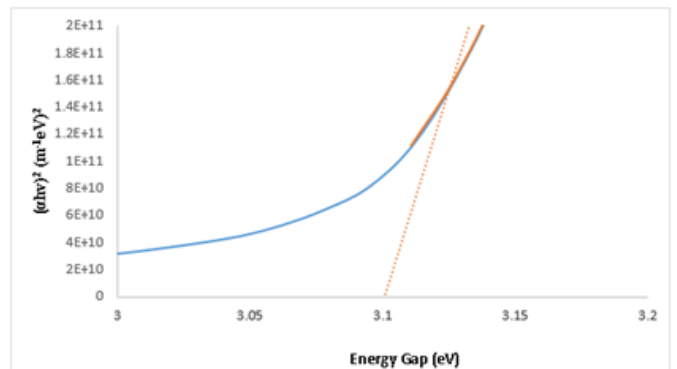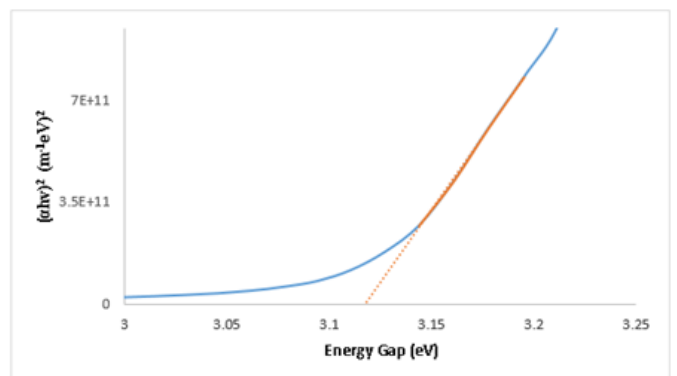

(a)
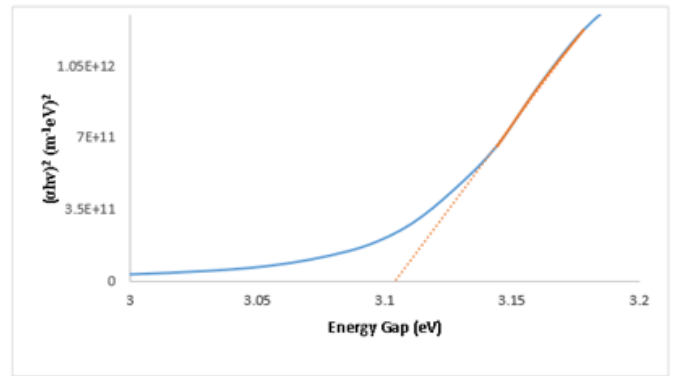
(b)
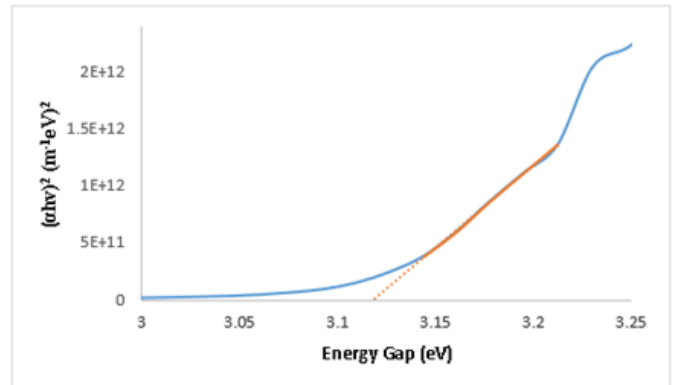
(c)

(d)

(e)

Figure 3. Determination of band gap (a) ZnO: Fe 2% (b) ZnO: Fe 4% (c) ZnO: Fe 6% (d) ZnO: Fe 8% (e) ZnO: Fe 10%

The decrease in the band gap with the addition of doping was due to a shift in the red spectrum. The decreasing band gap number due to the doping shift of the transition metal II-VI semi-conductor is associated with the sp-d spin reaction of the electron band and the d electrons of the sd and pd transition metals interact, which causes a space in the narrow energy band of hydroxyl compounds (OH*) [10][11].Compound radicals and hydroxyl radicals are useful in the degradation of tetracyclines. However, the arrangement of holes and electron pairs is an unstable state and will instinctively undergo a recombination. Doping iron (Fe) in ZnO serves as an inhibitor on the continuity of recombination. This can happen because the Fe3+ dopant produces a new energy level where it is able to capture electrons so they don't fall directly in the valence band and the degradation process can run quickly [12,13] The rate of irradiation degradation was determined by analyzing the optical properties of the sample every thirty minutes. Can be seen in Figure 4.
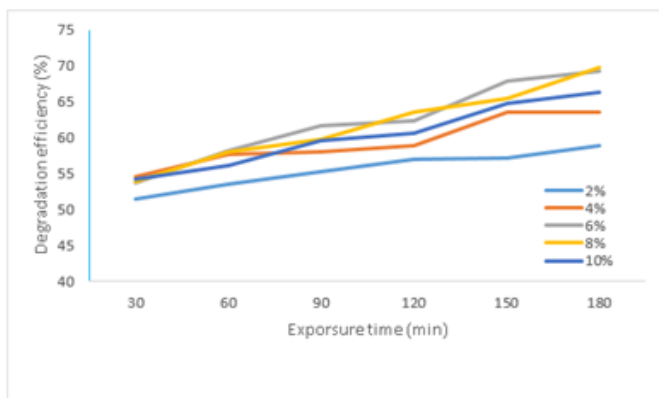

Figure 4. Degradation efficiency under UV irradiation

The greatest degradation with an efficiency value of 69.744% was in the *ultraviolet light* of a thin layer of ZnO/ZnO:Fe with a concentration of 8%. While the smallest value with a value of 55.283% is ZnO:Fe with a concentration of 2%. The relationship between visible light absorption and the potential of the valence band is related to the level of photocatalytic efficiency at each increase in the concentration of the dopant [14]. Concentration of ZnO:Fe 4% with the lowest power efficient for degradation in visible light.

Meanwhile, ZnO:Fe films with 2% and 10% concentrations in the band gap have the highest energy efficiency for degradation under UV light. The catalytic efficiency of the ZnO:Fe film is influenced by the size of a crystal and the light absorption factor [15], so further research is needed.

IV. CONCLUSION

The conclusion that can be drawn from this research is that the sol-gel technique with *psray coating* causes *a double layer of* ZnO/ZnO:Fe thin film to be deposited on the preparation plate. Degradation of tetracycline using *a double layer thin film* ZnO/ZnO:Fe with various concentrations of Fe solution, namely 2% (3,104 eV); 4% (3.116 eV); 6% (3,117 eV); 8% (3,098 eV); and 10% (3.117 eV). The optical characteristic specification shows that the largest absorbance value is ZnO/ZnO:Fe with a concentration of 2% (0.402) and the smallest absorbance is ZnO:Fe with a concentration of 8% (0.272). The effectiveness of using UV light degradation is the greatest at *of thin film* , valued at 69.744% and the smallest effectiveness is to *thin film* ZnO/ZnO:Fe with 2% concentration of 55.283%.

V. REFERENCES

[1]. Y. Xie , C. Liu , D. Li , Y. Liu," In situ-generated H2O2 with NCQDs/MIL-101(Fe) by activating O2: A dual effect of photocatalysis and photo-Fenton for efficient removal of tetracyline at natural pH" Applied Surface Science, vol. 592 , 2022.

[2]. L. Feyzi , N. Rahemia , S. Allahyaria, "Efficient degradation of tetracycline in aqueous solution using a coupled S-scheme ZnO/g-C3N4/zeolite P supported catalyst with water falling film plasma reactor", Process Safety and Environmental Protection, vol.161, P 827-847,2022.

[3]. Z. XuChuan, Z. Yang, Z. Yingying Gu, Y. An,"BiOCl-based photocatalysts: Synthesis

methods, structure, property, application, and perspective" Inorganic Chemistry Communications, vol. 138, 2022.

[4]. X. Wang,Y. Zhou, F. Feng, Y. Guo, Z. Hao, C. Lu, X. Li," Synthesis of high photoreactive flower-like ZnO nanoneedles assembly with exposed nonpolar {1010} facets oriented by carbon spheres" Applied Surface Science, vol. 598, 2022.

[5]. P. Jia, H. Tan, K. Liu, W. Gao," Synthesis, characterization and photocatalytic property of novel ZnO/bone char composite" Materials Research Bulletin, vol. 102 p. 45–50, 2018.

[6]. J. Wang, G. Wang, J. Jiang, Z. Wan, Y. Su, H. Tang," Insight into charge carrier separation and solar-light utilization: rGO decorated 3D ZnO hollow microspheres for enhanced photocatalytic hydrogen evolution", Journal of Colloid and Interface Science. vol. 564, p. 322–332, 2020

[7]. X. Zhang, X. Zhang, X. Wang, L. Liu, J. Ye, D. Wang, "Enhancing the photocatalytic activity and photostability of zinc oxide nanoneedle arrays via graphitic carbon mediation", Chinese Journal of Catalysis. Vol. 39, p.973–981, 2018.

[8]. H.Sutanto, I.Alkian, V. J. Pramunditya, Mukholit, E. Hidayanto, I. R. Duri, and Priyono," Effect Of Fe Addition On Zno Thin Films For Photodegradation Under UV And Halogens Light" International Journal Of Scientific & Technology vol. 9, 2020.

[9]. W. Bousslama, H. Elhouichet, and M. Férid M,"Enhanced Photocatalytic Activity of Fe Doped ZnO Nanocrystals Under Sunlight Irradiation", Optik, vol. 134, p. 88-98, 2017

[10].S. Yakout, and A. El-Sayed,"Enhanced Ferromagnetic And Photocatalytic Properties InMn or Fe Doped P-CuO/NZnO Nanocomposites", Advanced Powder Technology, 2019.

[11].N. Khalid, A. Hammad, M. Tahir, M. Rafique, T. Iqbal, and G. Nabi,"Enhanced Photocatalytic Activity of Al And Fe CoDoped Zno Nanorods For Methylene Blue Degradation", Ceramics International, 2019.