



Study of Sonocatalytic Activity ZnO-WO₃ Composite on Degradation Phenol in Aqueous Solution

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Abstract

Sonocatalysis was used to study phenol degradation using a ZnO/WO₃ composite. The degradation was assisted by ultrasonic waves at 40 KHz and conducted using the sonocatalysis technique. The degradation percentage was calculated using data from the UV-Vis spectrophotometer. The composite characterization results showed that the samples containing WO₃, ZnO and also contained a new structure ZnWO₄. The morphological length and width of the composites were revealed by SEM examination. Furthermore, heterogeneous particle sizes were discovered. The surface area of composite was bigger than before combined. The optimum condition in degradation of phenol by ZnO-WO₃ composite are 0,4 g of catalyst at 30 ppm of phenol, 7 min reaction time with the greatest phenol degradation at 92,5%. The catalyst can be reused 5 times to degrade phenol at 85%. The composite catalyst and assisted with ultrasonic as the sonocatalytic technique are one of the most environmentally and cost effective.

INTRODUCTION

The expansion of the industrial sector results in an increase in polluting chemicals in the environment (Chung & Chen, 2009). Herbicides, fungicides, coal gasification, paper mills, coke factories, resin polymer manufacturing, oil refining, paint industries, textile, food processing industry, and biotechnology all produce phenol, a hazardous hydroxyl benzene compound (Borji et al., 2014). Phenol can induce skin burns, central nervous system paralysis, and a significant drop in body temperature, as well as damage to internal systems such as the kidneys, liver, spleen, lungs, and heart (Rappoport, 2003). At quantities of 5-25 mg/L, phenol toxicity can harm aquatic microorganisms and kill fish. The content of phenol in drinking

water should not exceed 1 g/L, and in waterways should not exceed 1 mg/L, according to World Health Organization rules (Yunus et al., 2017). Therefore, it is necessary to develop an effective and efficient organic waste treatment method.

Organic contaminants in liquid waste have been degraded using a variety of methods. In particular, there are three different types of traditional ways for dealing with liquid waste. Physical, chemical, and biological techniques are the three types. Adsorption, filtration, and reverse osmosis are physical techniques. Ion exchange and extraction are chemical techniques, whereas aerobic and anaerobic processes are biological ones (Mozia et al., 2005). These three techniques, however, each have their own set of drawbacks. These three approaches generate waste and are not

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cost-effective (Kumar et al., 2012). Several studies have investigated that *Advanced Oxidation Processes* (AOPs) having the potential to oxidize organic pollutants without producing *secondary waste* (Azbar et al., 2004).

The sonocatalytic technique is one of the most environmentally benign AOPs, because it generates CO₂ and H₂O. Typically, this technique uses ultrasonic vibrations and a catalyst to breakdown organic compounds in aqueous medium. The cavitation effect bubbles produced by the liquid under ultrasonic radiation are the basis for this technique. It has the ability to collect sound energy and collapse to release energy in a very short amount of time, while also having a high temperature and pressure (Li et al., 2018).

TiO₂, ZnO, CdS, Fe₂O₃, and WO₃ are some of the most often used catalysts. Tungsten trioxide (WO₃) is a semiconductor material that can accelerate the degradation process under visible radiation. Tungsten (VI) oxide, also known as tungsten trioxide or tungstate anhydride, is a chemical compound containing oxygen and tungsten. Tungsten trioxide (WO₃) has a very good ability under visible light irradiation with better absorption ability than other semiconductors because WO₃ has a band gap of about 2.7 – 2.8 eV which makes it more sensitive to visible light (Sajjad et al., 2018). Meanwhile, zinc oxide (ZnO) is known as an ideal and suitable catalyst because it is stable, inexpensive and environmentally friendly (Hunge et al., 2018). The combination of these two components has a beneficial role in increasing the charge separation and ZnO response in ultrasonic radiation so that high catalyst efficiency can be obtained in the separation of organic particles (Meng et al., 2014). Thus, the goal of this study is to create a ZnO-WO₃ composite material with increased sonocatalytic activity against phenol degradation.

MATERIALS AND METHODS

Materials

The materials used in this research are ZnO, WO₃, K₃Fe(CN)₆, NH₄OH, phosphate buffer, 4-Aminoantipyrine, Ethanol, Phenol (All chemicals were purchased from Sigma-Aldrich), distillate water, Whatman paper.

ZnO-WO₃ Preparation and Characterizations

10 mL of ethanol is added to a solid mixture of 5g ZnO and 14,2g WO₃. This combination was allowed to sit for 3 hours till it turned into powder. It was then dried for 24 hours at 100°C in an oven. Crushed in a mortar and then filtered through a 150-mesh filter and furnace in 800°C for 8 hours. After that, this sample was characterized. The structure of material characterizes using X-ray diffraction (Rigaku) with Cu K α X-ray as a source. The morphology of catalyst was observed by JEOL JSM-6700F SEM and surface analysis of the catalyst was examined by using Micromeritics ASAP 2000.

Maximum Wavelength Determination

50 mL of Phenol solution was added with 2.5 mL of 0.5N NH₄OH then added phosphate buffer solution, 1 mL of 8% aminoantipyrine and 1 mL of K₃Fe(CN)₆. It was then analyzed by using a UV-Vis spectrophotometer in a range 200-800 nm wavelength in order to obtain the maximum Phenol wavelength.

Standard Curve of Phenol

1000 ppm phenol solution was diluted to 100 ppm. Then the 100 ppm Phenol solution was diluted with various concentrations of 2, 4, 6, 8 and 10 ppm. The solution is then measured its absorbance using a UV-Vis Spectrophotometer at the optimum wavelength (664 nm) that has been obtained.

Phenol Degradation By Sonocatalytic Test Using ZnO-WO₃ Catalyst

Variation Weight of ZnO-WO₃ Catalyst

ZnO-WO₃ as much as 0.1, 0.2, 0.3, 0.4 and 0.5g were put into 50 mL of 30 ppm Phenol. They were then placed into the sample container and exposed to ultrasonic wave. After that, they were filtered and taken as much as 1 mL. The absorbance was measured using a UV-Vis Spectrophotometer at the maximum wavelength (664 nm). The percentage of degradation is calculated.

Effect Reaction Duration

A total of 0.4 grams of ZnO-WO₃ was put into 50 mL of 30 ppm Phenol. It was placed into the sample container before being placed in a sonicator

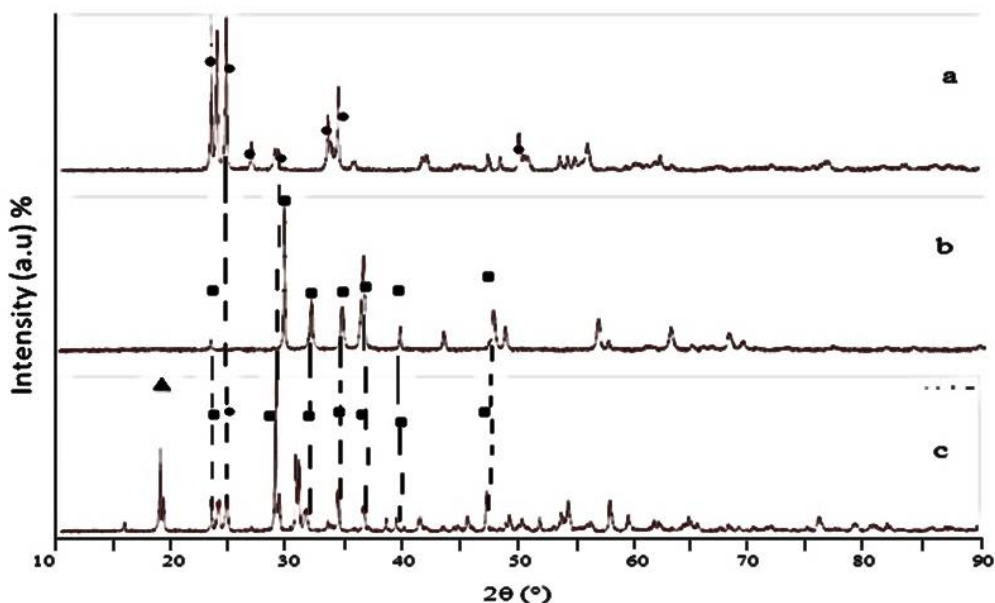


Figure 1. The XRD Result of (a) WO_3 (●), (b) ZnO (■) and (c) ZnO-WO_3 (▲)

(ultrasonic waves at 40kHz) for 3, 5, 7, 9, 13 minutes time variations. After that, it was centrifuged to separate and the filtrate was taken as much as 1mL. The absorbance was measured using a UV-Vis Spectrophotometer. The percentage of degradation is calculated.

Effect of Phenol Concentration

A total of 0.4 grams of ZnO-WO_3 were put into 50mL was added to various concentrations of 10, 20, 30, 40 and 50 ppm phenol solution. It was placed into the sonicator in the optimum contact time that has been decided. It was then separated and taken as much as 1 mL of the filtrate. The absorbance was measured using a UV-Vis Spectrophotometer and the degradation percentage was calculated.

The Effectiveness Test of ZnO-WO_3 Catalyst Reusability and Material Type in Phenol Degradation

The ZnO-WO_3 composite was tested for reusability by separating ZnO-WO_3 from phenol and washing it with distilled water several times. It was then dried for 1 hour at 120°C in the oven before being calcined for 2 hours at 800°C . Furthermore, ZnO-WO_3 was reused for phenol degradation.

Variations in material types were carried out to determine the performance of the material by comparing ZnO , WO_3 and ZnO-WO_3 using the optimum conditions obtained previously against.

Data Analysis

The data was obtained by measuring absorbance in a UV-Vis Spectrophotometer based on ZnO-WO_3 changes in contact time, concentration, and weight in degrading Phenol in order to compute the degradation percentage by the formula below where are the c_0 is initial concentration and c_e is final concentration:

$$\% \text{ Degradation} = \frac{c_0 - c_e}{c_0} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Catalyst Characteristics

XRD was used to determine if the structure of ZnO and WO_3 was changing or whether a new ZnO-WO_3 composited diffraction peak had appeared. In figure 1 (a), the diffraction pattern at $2\theta = 29.42^\circ, 34.41^\circ, 35.95^\circ, 36.22^\circ, 39.43^\circ, 47.18^\circ, 48.52^\circ,$ and 57.42° was indicating that the material is WO_3 refer to JCPDS No. 43-1035, where the WO_3 has a monoclinic structure. Furthermore, based on the research of Shakya et al. (2017) there are some similarities in the diffraction pattern which indicates the material is WO_3 . The diffraction pattern peak at $2\theta = 23.60^\circ, 26.60^\circ, 28.92^\circ, 33.58^\circ, 34.15^\circ, 50.32^\circ,$ and 55.88° is shown in figure 1 (b), which is based on the standard data JCPDS No. 36-1451 the compound was ZnO with the hexagonal structure. This data was similar with Yu et al. (2011) there are some similarities in diffraction patterns which indicate the material is

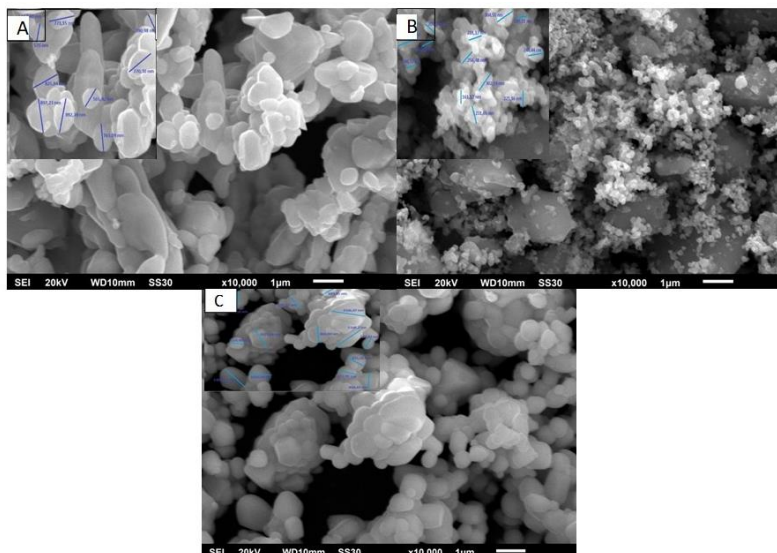


Figure 2. SEM image of (a) WO_3 , (b) ZnO , and (c) ZnO-WO_3

ZnO . Figure 1(c) is after WO_3 and ZnO were composited, the XRD data shows a new compound diffraction pattern ZnWO_4 at $2\theta = 18, 62$. This new ZnO-WO_3 diffraction peak is compared to the standard data JCPDS No. 73-544 explaining ZnO-WO_3 having monoclinic structure. The ZnO-WO_3 composite synthesized by solid method shows a constant ZnO and WO_3 diffraction peak, however it has a lower intensity than before it was composited. The diffraction of WO_3 at $2\theta = 23.12^\circ, 24.37^\circ, 28.92^\circ, 33.26^\circ, 34.16^\circ, 50.69^\circ, 55.88^\circ$. The ZnO diffraction at $2\theta = 23.82^\circ, 29.42^\circ, 31.74^\circ, 34.41^\circ, 36.22^\circ, 39.43^\circ, 48.52^\circ, 57.42^\circ$.

In addition, SEM examination was performed to determine the ZnO , WO_3 , and ZnO-WO_3 morphological forms. SEM data result by 10,000 times magnification at Figure 2 shows that Figure 2 (a) the form of WO_3 is like grains with an elongated and widened shape. Measurement by using ImageJ software shows the smallest particle is 390.98nm, the biggest is 897.23nm and the average size is 707.97nm. The Figure 2 (b) shows the morphology of ZnO which consisted of irregular and randomly distributed small particle. The smallest ZnO particle is 160.33nm, the biggest is 337.10nm, and the average size is 231.42. The smallest particle of ZnO-WO_3 is 577.43nm, the biggest is 1566.07nm, and the average size is 957.62nm. Based on those measurements, it is confirmed that the WO_3 particle is bigger than ZnO particle. Figure 2(c) shows the ZnO-WO_3 composite form, it can be observed that there are 2 kinds particle suspecting that WO_3 particle is bigger than ZnO particle. Both particles are tends to stick

and joined to each other. This is also confirmed at the particle size which becoming bigger when both are composited.

The surface area of WO_3 and ZnO before and after being composited into $\text{WO}_3\text{-ZnO}$ can be seen in Table 1.

Table 1. The result of ZnO , WO_3 and ZnO-WO_3 composited.

Sample	Surface Area (m^2/g)
WO_3	105.15
ZnO	112.52
ZnO-WO_3 composite	180.75

The data shows that the ZnO-WO_3 surface area becoming larger than pure WO_3 . This occurs as a result of the inclusion of ZnO after both have been composited, as ZnO has a larger surface area than WO_3 .

Phenol Sonocatalytic Test Using ZnO-WO_3

Effect of Catalyst Weight

Catalyst weight variation is conducted to know the optimum weight needed by ZnO-WO_3 in degrading phenol. Figure 3 depicts the relation of catalyst weight toward the degradation percentage.

Based on Figure 3, 0.1g catalyst resulted in 60% phenol degradation. A little quantity of catalyst is insufficient to degrade. Then, 0.2g catalyst got 80% and it got increased at 0.3g to 83% and tends to be similar at 0.4g as many 90.1%. Based on the data, it shows the optimum weight is

0.4 g of catalyst. The percentage of phenol degradation will rise as the amount of ZnO-WO₃ increases. The surface area of the sonocatalysis process expands, increasing the supply of OH radical. The phenol degradation process becomes more effective as the radical quantity increases, and the phenol degradation percentage rises. Furthermore, it slightly decreases at 0,5g catalyst to 84.64 %. The percentage of degradation experienced a slight decrease due to the addition of excess catalyst mass causing turbidity in the solution so that the ultrasonic waves entering the solution were blocked and the electron excitation on the catalyst surface would decrease (Arfi et al., 2017).

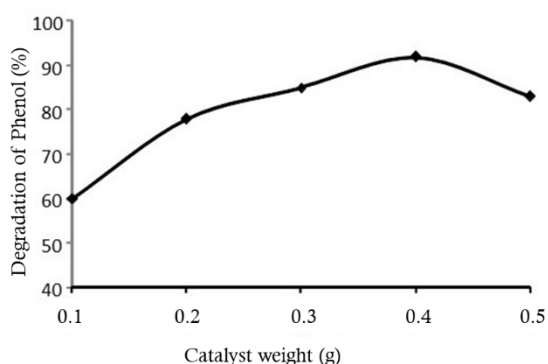


Figure 3. Effect of Catalyst weight.

Effect of reaction duration on Phenol Degradation

Reaction duration was used in this study to determine the optimal contact time required by ZnO-WO₃ to degrade phenol. The contact time was varied 3-13 min, Figure 4 shows the effect of contact time on the percentage of phenol degradation.

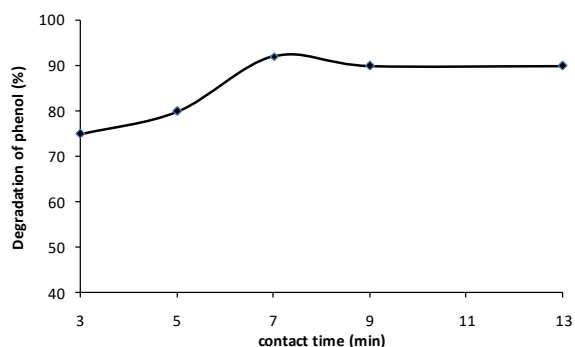


Figure 4. Effect reaction duration.

The percentage of phenol degradation tends to rise from the third minute to the seven-minute reaction duration, as seen in the Figure 4. The percent degradation was 78.2% after three

minutes, and it continued to rise until the seventh minute, when it reached 92.5%. According to Zhou et al. (2015) free electrons (e⁻) and holes (h⁺) are produced sonocatalytically by WO₃ and ZnO catalysts. Following that, electrons in the valence band will be excited into the conduction band. The sonoluminescence mechanism has been used to explain this. Light enters through the recombination of free radicals produced by cavitation bubbles in sonoluminescence. The formation of OH radicals, which can degrade phenol, follows. The more time it takes for ZnO/WO₃ to develop, the more OH radicals it produces. It improves the catalyst's capacity to degrade phenol. The greater the number of OH radicals generated; the more phenol is degraded.

However, the trend did not rise between the 9 and 13 minutes. According to Sheydaei et al. (2019) may be related to the formation of cavities in the solution through the cavitation phenomenon. With increasing time, the continuous mechanical shock of the cavitation bubbles can cause damage to the particle morphology and reduce its catalytic efficiency. In addition, according to Arfi et al. (2017), the contact time being too long in the reaction system causing the adsorption of phenol in surface of catalyst causing agglomeration so that the number of active sites of the catalyst was also reduced in degrading phenol. As a result, the optimal time for degrading 30 ppm phenol is 7 minutes, with a 92.5% degradation rate.

Effect of Phenol Concentration

A concentration of 30 ppm phenol resulted in 91% decomposition, according to the graph above. At a concentration of 40-50 ppm, the percentage tends to drop to 88-78%. The adsorption rate and the degradation rate will be directly proportional as the phenol content decreases. However, at higher concentrations (40-50 ppm), phenol saturation causes the rate of phenol adsorption on the catalyst surface to be not directly proportional to the rate of degradation. According to Moradi et al. (2018), a catalyst's surface being occupied by a greater concentration of pollutants, which prevents the catalyst's surface from having enough active sites, thereby inhibiting the degradation process. Furthermore, that when phenol solution concentration rises, UV photons have a harder time entering the solution and their route lengths shorten. The catalyst's surface is not

photoexcited by the decreased photon absorption, which also slows down photodegradation.

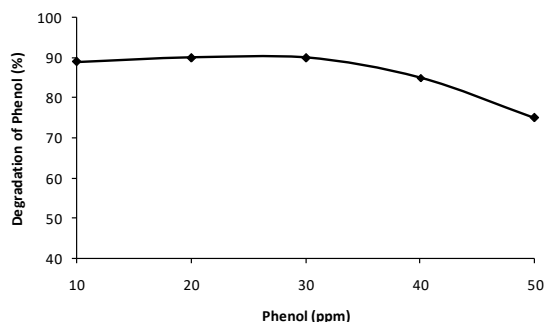


Figure 5. Effect of phenol concentrates.

Reusability of Catalyst

The reuse of ZnO-WO₃ was conducted to see how efficient it was in degrading phenol through a sonocatalytic process. The procedure is carried out by washing the ZnO-WO₃ that was utilized in the preceding sonocatalytic test with distilled water until any remaining phenol dissolves. To eliminate the phenol that was still adhered to the catalyst's surface, the ZnO-WO₃ residue was heated and recalcined. The technique was then repeated under the same ideal conditions as the prior sonocatalytic test.

The percentage of degradation decreases from 92% in the first cycle to 88% in the third repetition, and endure at 85% in five cycles as shown in Figure 6.

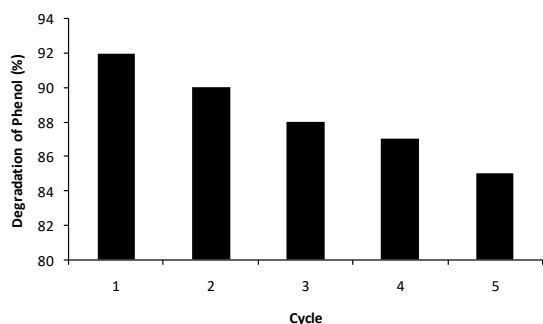


Figure 6. The reusability of Catalyst.

Based on the data gathered, it may be inferred that reusability has decreased by up to five times. It is stated that ZnO-WO₃ has sonocatalytic reusability efficiency in degrading phenol. One of the possible reasons for the decrease in activity, could be due to surface leaching during the catalytic reaction which is associated with loss of active sites. This occurs when the ZnO-WO₃ catalyst gets leached after prolonged usage, resulting in less

radical production OH and its capacity to act as a sonocatalyst are likewise decreasing (Lestari, et al., 2015). The successive heating treatment after each iteration can reduce the surface area of the catalyst resulting in partial aggregation of the catalyst. The intermediate compounds formed during the catalytic process can also be adsorbed on the surface, thereby reducing the overall efficiency of the catalyst. In addition, the loss of catalyst also occurs during the iterative process which results in reduced catalyst reactivity (Adhikari et al., 2015). From the data obtained, it can be concluded that with 3 reuses there is only a slight decrease so that it can be said that ZnO-WO₃ can be reused in sonocatalytically degrading phenol.

Material Type

In this research, various types of materials were conducted to determine the process of degradation phenol using ZnO, WO₃, ZnO-WO₃ (Figure 7). The optimum conditions in the sonocatalytic test were 0.4 grams of catalyst mass, 7 minutes of contact time, and 30 ppm phenol concentration. In figure 7, the usage of WO₃ degraded 80.69%. The ZnO degradation percentage was 51.06%.

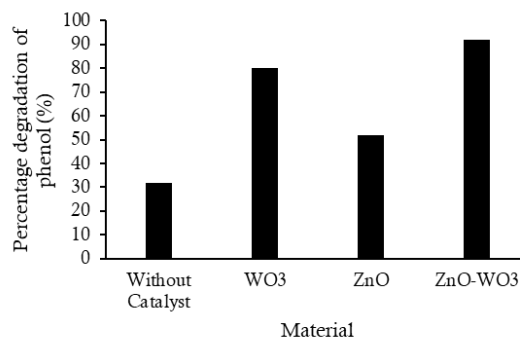


Figure 7. Effect of material on the phenol degradation.

The usage of ZnO-WO₃ degraded 85.93%. Due to charge transfer between the two, WO₃ composited with ZnO showed a greater percentage of phenol degradation, with h⁺ in ZnO being transferred to WO₃ and e⁻ in WO₃ being transferred to ZnO (Zhang, 2010). As a result, sufficient time is available for phenol to be maximally on the surface of the WO₃-ZnO catalyst, resulting in greater sonocatalytic activity than WO and ZnO.

CONCLUSION

The synthesis of ZnO-WO₃ composite has been successfully by solid state reaction. The composite showed the new diffraction peak (ZnWO₄) with monoclinic structure. The morphology of composite from SEM showed the heterogeneous particle size, and the surface area was bigger than before combined. The results of the degradation test on phenol with a concentration of 30 ppm showed that the optimum condition of ZnO-WO₃ was 92.5 %, then at 7 minutes reaction duration. ZnO-WO₃ has been used until five cycles with percent degradation of phenol at 85%.

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REFERENCES

- Adhikari, S., Sarkar, D., Madras, G. 2015. Highly efficient WO₃-ZnO mixed oxides for photocatalysis. *RSC Advances*. 5(16): 11895–11904.
- Arfi, F., Safni, S., Abdullah, Z. 2017. Degradasi Senyawa Paraquat Dalam Pestisida Gramoxone Secara Sonolisis dengan Penambahan ZnO. *Lantanida Journal*. 3(1): 71.
- Azbar, N., Yonar, T., Kestioglu, K. 2004. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere*. 55(1): 35–43.
- Borji, S. H., Nasser, S., Mahvi, A. H., Nabizadeh, R., Javadi, A. H. 2014. Investigation of photocatalytic degradation of phenol by Fe(III)-doped TiO₂ and TiO₂ nanoparticles. *Journal of Environmental Health Science and Engineering*. 12: 101.
- Chung, Y. C., Chen, C. Y. 2009. Degradation of azo dye reactive violet 5 by TiO₂ photocatalysis. *Environmental Chemistry Letters*. 7(4): 347–352.
- Hunge, Y. M., Yadav, A. A., Mathe, V. L. 2018. Ultrasound assisted synthesis of WO₃-ZnO nanocomposites for brilliant blue dye degradation. *Ultrasonics Sonochemistry*. 45: 116–122.
- Kumar, P. S., Paik, P., Raj, A. D., Mangalaraj, D., Nataraj, D., Gedanken, A., Ramakrishna, S. 2012. Biodegradability study and pH influence on growth and orientation of ZnO nanorods via aqueous solution process. *Applied Surface Science*. 258(18), 6765–6771.
- Lestari, Y. D., Wardhani, S., Khunur, M. M. 2015. Degradasi Methylene Blue Menggunakan Fotokatalis TiO₂-N/Zeolit Dengan Sinar Matahari. *Jurnal Ilmu Kimia*. 1(1): 592–589.
- Li, T., Song, L., Zhang, S. 2018. A novel WO₃ sonocatalyst for treatment of rhodamine B under ultrasonic irradiation. *Environmental Science and Pollution Research*. 25(8): 7937–7945.
- Meng, Z. Da, Sarkar, S., Zhu, L., Ullah, K., Ye, S., Oh, W. C. 2014. Sonocatalytic degradation of rhodamine B in the presence of TiO₂ nanoparticles by loading WO₃. *Korean Journal of Materials Research*. 24(1): 6–12.
- Moradi, N., Amin, M. M., Fatehizadeh, A., Ghasemi, Z. (2018). Degradation of UV-filter Benzophenon-3 in aqueous solution using TiO₂ coated on quartz tubes. *Journal of Environmental Health Science and Engineering*. 16(2): 213–228.
- Mozia, S., Tomaszewska, M., Morawski, A. W. 2005. A new photocatalytic membrane reactor (PMR) for removal of azo-dye Acid Red 18 from water. *Applied Catalysis B: Environmental*. 59(1–2): 131–137.
- Rappoport, Z. 2003. The chemistry of phenols. In *PATAI'S Chemistry of Functional Groups*. John Wiley & Sons.
- Sajjad, A. K. L., Sajjad, S., Iqbal, A., Ryma, N. ul A. 2018. ZnO/WO₃ nanostructure as an efficient visible light catalyst. *Ceramics International*. 44(8): 9364–9371.
- Shakya, V., Pandey, N. K., Misra, S. K., Roy, A. 2017. Electrical and optical properties of ZnO-WO₃ nanocomposite and its application as a solid-state humidity sensor. *Bulletin of Materials Science*. 40(2): 253–262.

- Sheydaei, M., Fattahi, M., Ghalamchi, L., Vatanpour, V. 2019. Systematic comparison of sono-synthesized Ce-, La- and Ho-doped ZnO nanoparticles and using the optimum catalyst in a visible light assisted continuous sono-photocatalytic membrane reactor. *Ultrasonics Sonochemistry*. 56(April): 361–371.
- Yu, C., Yang, K., Shu, Q., Yu, J. C., Cao, F., Li, X. 2011. Preparation of WO₃/ZnO composite photocatalyst and its photocatalytic performance. *Cuihua Xuebao/Chinese Journal of Catalysis*. 32(4): 555–565.
- Yunus, N. N., Hamzah, F., So'Aib, M. S., Krishnan, J. 2017. Effect of Catalyst Loading on Photocatalytic Degradation of Phenol by Using N, S Co-doped TiO₂. *IOP Conference Series: Materials Science and Engineering*. 206(1):
- Zhang, D. (2010). Synthesis and characterization of ZnO-doped cupric oxides and evaluation of their photocatalytic performance under visible light. *Transition Metal Chemistry*. 35(6): 689–694.
- Zhou, M., Yang, H., Xian, T., Li, R. S., Zhang, H. M., Wang, X. X. 2015. Sonocatalytic degradation of RhB over LuFeO₃ particles under ultrasonic irradiation. *Journal of Hazardous Materials*. 289: 149–157.