Research Article

Highly-Reusable Photocatalyst from Chromolaena Odorata Leaves

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Abstract: *This research reports the preparation of tin oxide nanoparticles (SnO_2 NPs) via biosynthesis technique using leaves extract of Chromolaena odorata (C. odorata). With this technique, pure SnO_2 NPs was obtained in low-price, repeatable, safe, non-toxic and easy handling compared to the conventional methods, which are hazardous and expensive. The XRD analysis produced a pure tetragonal structure and crystalline nature of SnO_2 NPs. FTIR analysis later supported the purity, proving the Sn-O-Sn bonding at region 604 cm^{-1}. FESEM showed a spherical shape of SnO_2 NPs and the EDX analysis evidenced the presence of Sn and O elements. HRTEM-SAED disclosed the interplanar spacing (d-spacing) of the atomic arrangement as 0.126 nm, while diffraction rings of (110), (101) and (211) planes confirmed its tetragonal structure. Kubelka-Munk equation translated 57% of the reflectance value resulted from UV-DRS to denote a band gap of 3.12 eV. Later, SnO_2 NPs was tested for water remediation process, namely photocatalytic using methylene blue (MB), indicating a degradation rate of about 97% within 70 minutes and most notably its reusability proved to have five consecutive cycles. Having these results, the utilization of C. odorata leaves extract in assisting biosynthesis of SnO_2 NPs was developed and capable for the treatment of dye-polluted water.*

Keywords: Tin (iv) oxide nanoparticles; Chromolaena odorata; photocatalytic.

1. INTRODUCTION

Presently, problematic water pollution has resulted from wastewater discharge whereby it contains an elevated quantity of artificial dyes from textiles industries. The toxicity of synthetic dyes indeed creates major hazards to living organisms, the environment, and the ecological system. The complicated structure and strong formation of synthetic dyes troubled their removal from the dye-polluted water, coupled with the fact that they are known to have low biodegradability and worsen the process. Several procedures to remove the dyes from the wastewater caused subsequent problems, such as the elimination need to be prolonged and implied expensive devices and tools. Besides, the procedures do not eliminate the synthetic dyes in total; in some way, secondary pollution is generated. Thus, the photocatalytic techniques have been emphasized as the inclination for this challenge in which it provides easy handling, safety for users, is environmental-friendly, and, most importantly, is highly effective. Lately, an outstanding performance of the photocatalytic process using metal oxide nanoparticles for removing dyes in effluent has drawn much interest. An n-type semiconductor with a wide band gap of 3.6 eV, namely tin oxide nanoparticles (SnO_2 NPs), has been brought to light as a possible photocatalyst. This material is known to be utilized in lithium-ion batteries, gas sensors, capacitors, electrodes, solar cells and biomedical applications. SnO_2 NPs are befitting to be the photocatalyst based on properties such as highly stable, high surface-to-volume ratio, low resistivity and highly adsorbed. The hazardous and utilization of high energy can be avoided by having the environmentally friendly procedure of biosynthesis process in the preparation of SnO_2 NPs. The plant extract contains several phytochemicals competent to be the reducing and capping agent. The former report explained the biosynthesis process for the production of SnO_2 NPs using *Aspalathus linearis*, *Pruni spinosae flos*, *Calotropis gigantea*, *Pandanus amaryllifolius*, *Cyphomandra betacea*, *Psidium guajava*, *Daphne mucronate*, *Carica papaya*, *Camellia sinensis*, *Citrus aurantifolia* many more. In this report, the production of SnO_2 NPs was biosynthesized from the leaves extract of *Chromolaena odorata* (*C. odorata*), since the leaves are known to contain a flavonoids group that could reduce Sn^{4+} to Sn^0 from precursor salt during the mechanism. The nanostructures were discussed based on the characterization from several instruments such as X-ray diffraction (XRD), Fourier-transform infrared (FTIR), Field emission scanning electron microscopy (FESEM), Energy dispersive X-ray spectroscopy (EDX), High-resolution transmission electron microscopy (HR-TEM), Selected area diffraction (SAED), and UV-Visible Diffuse Reflectance (UV-DRS). The photocatalytic performance of SnO_2 NPs was measured in the degradation percentage of simulated dyes, namely Methylene Blue (Kaur, Prasher, Sharma, 2022; Buniyamin, Eswar, Asli, Abd Halim, Khusaimi, Rusop, 2023; Katheresan, Kansedo, Lau, 2018; Al-Hamdi, Rinner, Sillanpaa, 2017; Matussin, Harunsani, Tan, Mohammad, Cho, Khan, 2020;).

2. METHOD & MATERIAL

The leaves extract of *C. odorata* was mixed with the precursor salt solution, namely a $SnCl4.5H_2O$ for three hours. The jelly solution was centrifuged to remove the supernatant while the precipitate was collected and dried at 50°C overnight. The dried precipitate was ground before being calcined at 700°C for three hours to furnish pure SnO_2 NPs. The characterization procedure was carried out to confirm the nanostructure and the purity of the produced SnO_2 NPs (Buniyamin, Akhir, Asli, Khusaimi, Mahmood, 2021).

3. FINDINGS

The characterization stage utilized FESEM instrument to identify the morphological structure, while EDX analysis determined the percentage of Sn and O elements. Later, the application of the pure SnO_2 NPs was tested using photocatalytic activity to determine the degradation percentage of Methylene Blue dye.

3.1 FESEM and EDX analysis

The calcined powder of SnO_2 NPs was ground intensively using mortar and pestle, and dried to remove the moisture. FESEM appearance of the SnO_2 NPs showing the morphology of spherical shape and uniform distribution in agreement with earlier work. While EDX analysis proved the presence of elemental compositions of O and Sn at 0.5 and 3.5 eV, in which the weight percentages of Sn and O were 59.76% and 40.24% (Gorai, 2018; Buniyamin, Akhir, Nurfazianawatie, Omar, Malek, Rostan, Eswar, Rosman, Abdullah, Asli, Khusaimi, Rusop, 2023)

3.2.2 Photocatalytic activity

About 300 mg of photocatalyst (SnO_2 NPs) was stirred in 100 ml of methylene blue (15 ppm) for 30 min in the dark to allow adsorption-desorption equilibrium before UV irradiation was introduced. Within 10 min intervals, 5 mL of the aliquot was taken and centrifuged. The clear supernatant solution was analyzed using a UV-Vis (Elango & Roopan, 2016).

4. DISCUSSION

Figure 1(a) shows the MB degradation percentage, which has been calculated using Equation 1. C0 and Ct are the concentrations of MB at an initial time and after irradiation. In general, dye-polluted water has a broad pH scale, so in this parameter, the pH variation was made between 3 and 11 by adding a diluted solution of HCl and NaOH. It was found that the degradation efficiency of MB follows the increment of UV irradiation time. The degradation of MB was found to be most effective at pH 7, while the lowest degradation was recorded in alkaline medium. At pH 7, the photocatalytic activity was recorded to be 97% after 70 minutes of UV irradiation. The degradation was found to be the lowest in an alkaline solution in which the photocatalytic activity at pH 3 and 11 was recorded as 90% and 39%, indicating a progression of pH 7 > pH 3 > pH 11. At pH 7, it was presumed zero surface charge resided on SnO2. Having this, the Van Der Waals force helped to avoid the accumulation between particles, easing the dispersal and leading to high degradation. In contrast alkaline medium, the recombination of generated electron-hole pair was probably reinforced. A simplified Langmuir-Hinshelwood (L-H) kinetic model (Equation 2) was used to describe the photocatalytic degradation rate of MB by plotting the graph of -ln (C/C0) versus time at different pH values, representing first-order kinetic. From the result, a linear relationship from the plotting provided the highest reaction rate constant (k) higher at pH 7 as 0.0368 min-1, followed by 0.0300 min-1 and 0.026 min-1 corresponding to acidic and alkaline solution, respectively as shown in Figure 1(b). The reusability of SnO2 NPs photocatalyst has been tested for five consecutive cycles representing by Figure 2, proving its ability to have more than 29% degradation for MB and signified it capability to be workable for photocatalytic process (Yuan & Xu, 2010; Kansal, Singh, Sud, 2007).

$$(C_0 / C_t) / C_0 \times 100 \quad \ldots\ldots (1)$$

$$-\ln (C/C0) = kt \quad \ldots\ldots (2)$$

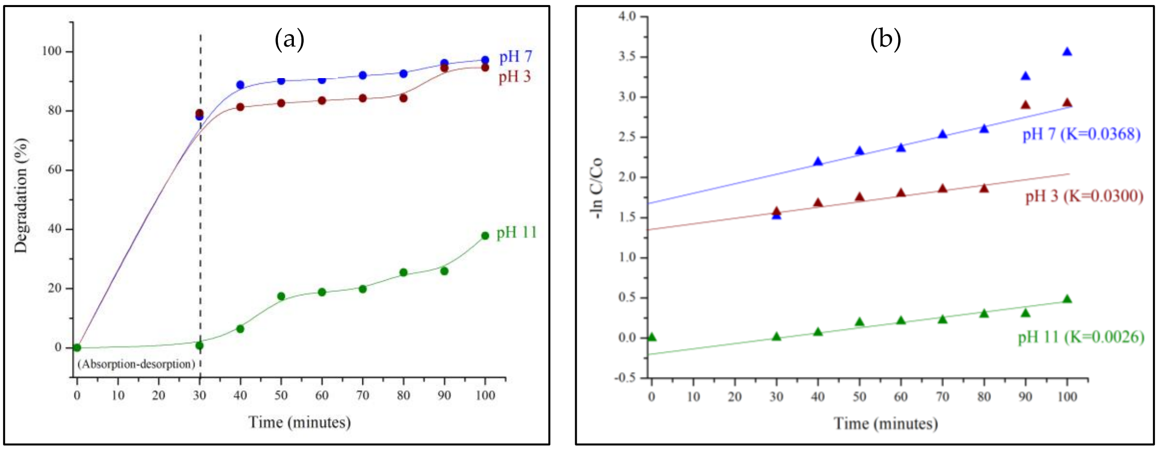

Figure 1. (a) Degradation percentage of Methylene Blue using SnO_2 NPs photocatalyst in different pH values

(b) Reaction rate constant (k) for SnO_2 NPs photocatalyst.

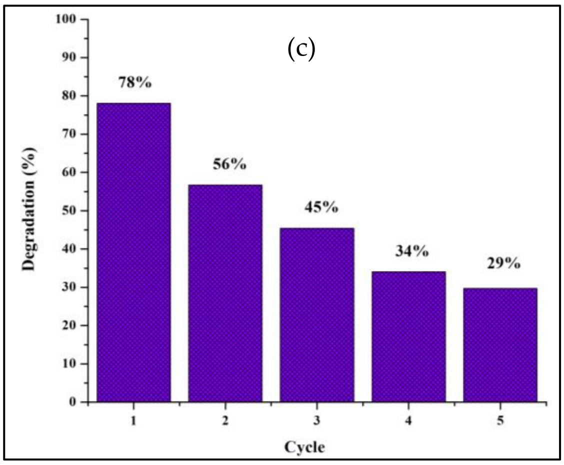

Figure 2. Reusability cycle of SnO_2 NPs photocatalyst.

5. CONCLUSION

This study successfully performed an environmentally friendly biosynthesis procedure using *C. odorata* leaves extract in preparing SnO_2 NPs. Using a photocatalytic process, the purely biosynthesized SnO2 NPs was tested against dye-polluted water. The photocatalytic activity followed first-order kinetics, presenting 97% degradation of Methylene Blue dyes within 70 minutes, proposing a neutral medium at pH 7 to accelerate the photo-excitation. Thus, the biosynthesized SnO_2 NPs propose a positive solution for the treatment of dye-polluted water.

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References

Kaur, M., Prasher, D., Sharma, R. (2022). Recent Developments on II and II Series Transition Elements Doped SnO_2 Nanoparticles and Its Applications for Water Remediation Process. A Review. J. Water Environ. Nanotechnol., 7,194-217. 10.22090/JWENT.2022.02.007

Buniyamin, I., Eswar, K.A., Asli, N.A., Abd Halim, M.F., Khusaimi, Z., Rusop M. (2023). Bio-synthesized Tin Oxide Nanoparticles (SnO_2 NPs) as a Photocatalyst Model. Malaysia Journal of Invention and Innovation, 2, 1-5. https://digit360.com.my/mjii/index.php/home/article/view/31/32

Katheresan, V., Kansedo, J., Lau, S.Y. (2018). Efficiency of Various Recent Wastewater Dye Removal Methods: A Review. J. Environ. Chem. Eng., 6, 4676-4697. https://doi.org/10.1016/j.jece.2018.06.060

Al-Hamdi, A.M., Rinner, U., Sillanpaa, M. (2017). Tin Dioxide as a Photocatalyst for Water Treatment: A Review. Process Saf. Environ. Prot., 107, 190-205. https://doi.org/10.1016/j.psep.2017.01.022

Matussin, S.N., Harunsani, M.H., Tan, A.L., Mohammad, A., Cho, M.H., Khan, M.M. (2020). Photoantioxidant Studies of SnO_2 Nanoparticles Fabricated Using Aqueous Leaf Extract of Tradescantia Spathacea. Solid State Sci., 105, 106279. https://doi.org/10.1016/j.solidstatesciences.2020.106279

Buniyamin, I., Akhir, R.M., Asli, N.A., Khusaimi, Z., Mahmood, M.R. (2021). Biosynthesis of SnO_2 Nanoparticles by Aqueous Leaves Extract of Aquilaria malaccensis (agarwood). IOP Conf. Ser. Mater. Sci. Eng., 1092, 012070. 10.1088/1757-899X/1092/1/012070

Gorai, S. (2018). Bio-based Synthesis and Applications of SnO_2 Nanoparticles-An Overview. J. Mater. Environ. Sci., 9, 2894-2903. https://www.jmaterenvironsci.com/Document/vol9/vol9_N10/317-JMES-3960-Gorai.pdf

Buniyamin, I., Akhir, R.M., Nurfazianawatie, M.Z., Omar, H., Malek, N.S.A, Rostan, N.F., Eswar, K.A., Rosman, N.F., Abdullah, M.A., Asli, N.A., Khusaimi, Z., Rusop M. (2023). Aquilaria malaccensis and Pandanus amaryllifolius mediated synthesis of tin oxide nanoparticles: The effect of the thermal calcination temperature. Materials Today: Proceedings 75, 23-30. https://doi.org/10.1016/j.matpr.2022.09.580

Elango, G., Roopan, S.M. (2016). Efficacy of SnO_2 Nanoparticles Toward Photocatalytic Degradation of Methylene Blue Dye. J. Photochem. Photobiol. B Biol., 155, 34-38. https://doi.org/10.1016/j.jphotobiol.2015.12.010

Yuan, H., Xu, J. (2010). Preparation, Characterization and Photocatalytic Activity of Nanometer SnO_2. Int. J. Chem. Eng. Appl., 1, 1-6. http://ijcea.org/papers/41-C057.pdf

Kansal, S.K., Singh, M., Sud, D. (2007). Studies on Photodegradation of Two Commercial Dyes in Aqueous Phase Using Different Photocatalysts. J. Hazard. Mater., 141, 581-590. 10.1016/j.jhazmat.2006.07.035