Tạp chí phân tích Hóa, Lý và Sinh học - Tập 30, số 03/2024

SYNTHESIS OF CNDs-$CuBi_2O_4$ HETEROGENEOUS CATALYST TO ENHANCE THE DEGRADATION EFFICIENCY OF 2,4-DICHLOROPHENOXYACETIC ACID UNDER VISIBLE LIGHT

Đến tòa soạn 17-07-2024

Nguyen Thi Thanh Huong[1,5], Dang Nguyen Nha Khanh[1,4], Ngo Thi Tuong Vy[1,2], Le Hai Khoa[1,3], Nguyen Ngoc Nghia [2]* Nguyen Thi Kim Phuong[1,2]*
[1] *Graduate University of Science and Technology, VAST, Hanoi, Vietnam*
[2] *Institute of Applied Materials Science, VAST, Ho Chi Minh, Vietnam*
[3] *Institute for Tropical Technology, VAST, Hanoi, Vietnam*
[4] *Institute of Applied Mechanics and Informatics, VAST, Ho Chi Minh, Vietnam*
[5] *Ton Duc Thang University, Ho Chi Minh, Vietnam*
**E-mail: nguyenthikimp@yahoo.ca; nghia10194@gmail.com*

TÓM TẮT

TỔNG HỢP XÚC TÁC DỊ THỂ CNDs-$CuBi_2O_4$ NHẰM NÂNG CAO HIỆU QUẢ PHÂN HỦY 2,4-DICHLOROPHENOXYACETIC AXIT DƯỚI ÁNH SÁNG KHẢ KIẾN

Ôxit đồng bismuth chấm lượng tử cacbon nitrit (CNDs-$CuBi_2O_4$) được tổng hợp thành công bằng phương pháp tái lập cấu trúc. Hơn 90% 2,4-dichlorophenoxyacetic axit (nồng độ ban đầu 30 mg/L) bị quang phân hủy khi sử dụng 1,0 g/L CNDs(1%)-$CuBi_2O_4$ ở pH 4,78 sau 105 phút chiếu ánh sáng khả kiến (với k = 0,0169 phút^{-1}). Không có dấu hiệu bất hoạt chất xúc tác sau bốn chu kỳ tái sử dụng, chứng tỏ độ bền và hiệu quả của CNDs(1%)-$CuBi_2O_4$. Sự cải thiện đáng kể về hiệu suất quang xúc tác của CNDs(1%)-$CuBi_2O_4$ so với CND và $CuBi_2O_4$ là do sự hình thành các khuyết tật tại các bề mặt tiếp xúc dị thể; do đó, sự dịch chuyển của các electron quang sinh tại bề mặt tiếp xúc giữa hai thành phần rất nhanh chóng. Sự phân hủy 2,4-D của CNDs(1%)-$CuBi_2O_4$ khi tiếp xúc với ánh sáng khả kiến được gây ra chủ yếu bởi các gốc superoxide ($O_2^{\bullet-}$) và các lỗ trống quang sinh (h^+).

Từ khóa: *CNDs-$CuBi_2O_4$, 2,4-dichlorophenoxyacetic axit, phân hủy, ánh sáng khả kiến.*

1. INTRODUCTION

The overuse 2,4-dichlorophenoxyacetic acid (2,4-D) in agriculture has led to its residues in the environment due to the relatively long half-life of 2,4-D [1]. The 2,4-D has serious effects on the human endocrine and immune systems. Therefore, 2,4-D removal is an urgent issue that needs to be addressed. Photocatalysis is one of the suitable methods in environmental management because of its high selectivity, low cost, environmental friendliness, and excellent treatment efficiency [2]. As a metal-free semiconductor, graphitic carbon nitride quantum dots (CNDs) are considered promising photocatalysts due to their stability, photochemical low toxicity, and low cost [2]. However, the wide bandgap of 2.6-2.7 eV is still a limitation, to overcome this, CNDs are combined with some other semiconductors such as TiO_2 [3], $BiVO_4$ [4], etc. As a spinel oxide, $CuBi_2O_4$ is considered a promising semiconductor photocatalyst, due to its stability, fairly small bandgap, and good response to visible radiation [5]. The combination of $CuBi_2O_4$ with another semiconductor with a compatible band gap is a feasible strategy to extend the separation time of the electron (e^-)/hole (h^+) to improve the activity of $CuBi_2O_4$ [6]. Due to the compatibility of the band gap between CNDs and $CuBi_2O_4$ as well as the desire to overcome the limitations of pristine CNDs and pristine $CuBi_2O_4$, in this study, CNDs-$CuBi_2O_4$ heterojunction was synthesized by the restructuring method and the photocatalytic activity of the heterojunction was evaluated under visible light. Factors such as solution pH, catalyst dosage, 2,4-D concentration as well as active radicals affecting catalyst activity were also investigated.

2. EXPERIMENT

2.1. Materials

All chemicals were of analytical grade from Sigma Aldrich including urea, sodium citrate, $Bi(NO_3)_3.5H_2O$, $Cu(NO_3)_2.3H_2O$, HNO_3, NaOH, *tert*-butanol, *p*-benzoquinone, Na_2EDTA, 2,4-D.

2.2. Equipment

Rigaku Ultima IV X-ray diffractometer with CuKα anode ($\lambda = 0.1542$ nm) was applied to identify the crystal structure of the material. The chemical structures of the materials were confirmed by Fourier transform infrared (FT-IR) spectra on a Magna-IR 560 Nicolet. The band gap energy (*Eg*) of the materials was found from the ultraviolet-visible diffuse reflectance spectrum (DRS) which was measured on an absorption spectrometer (Jasco V-670). The Scanning Electron Microscope (SEM) of materials was operated on an S-4800 (Hitachi). Transmission Electron Microscope (TEM) of materials were measured using JEOL JEM-2100F.

2.3. Fabrication of photocatalyst

Briefly, 1 mol citrate and 6 mol urea were heated at 180 °C in a Teflon-lined (PTFE) hydrothermal autoclave for 1 hour. The result material was cleaned with ethanol and dialyzed for 24 hours in purified water, then freeze-dried the dialysis solution to gain solid CNDs [7]. A 5% HNO_3 solution containing Cu^{2+} and Bi^{3+} (3:1 molar ratio) was slowly added to a 1 M NaOH solution (pH = 10). The suspended product was sonicated at a power of 100 W for 24 hours at 75 ± 5°C. $CuBi_2O_4$ was gained by rinsing with deionized water until pH 7, followed by drying at 70 °C for 24 hours and heating at 450 °C for 3 hours. Dispersion of solid CNDs (0, 1 or 2%) and $CuBi_2O_4$ in distilled water, operating conditions including ultrasonic power, temperature and time were 75 ± 5 °C, 100 W and 6 hours, respectively. The resulting products were then dried at 70 °C for 24 h and labeled as $CuBi_2O_4$, CNDs(1%)-

$CuBi_2O_4$, and CNDs(2%)-$CuBi_2O_4$.

2.4. Photodegradation experiment

The photocatalyst and 2,4-D solution were magnetically mixed in the dark for 60 min before a 300 W halogen lamp (Osram, Germany) equipped with a UV filter ($\lambda > 420$ nm) was turned on. Samples were collected every 15 min, the catalyst was removed and measured on UV/Vis spectrometer at 220 nm (Lamda XLS+, PerkinElmer, USA). The degradation rate of 2,4-D was achieved using Lagergren's pseudo-first-order model given by: $\ln(C_o/C_t) = kt$. In which, k, C_o and C_t are the degradation rate constant (min^{-1}), 2,4-D concentration (mg/L) at the time before and during visible light irradiation, respectively. The effect of CNDs in catalyst on degradation of 2,4-D (30 mg/L) were carried out using 1.0 g/L of each catalyst at pH 4.2. The effect of pH on the degradation of 30 mg/L 2,4-D was carried out by varying the pH from 2.0 to 7.0 using 1.0 g/L CNDs(1%)-$CuBi_2O_4$. The effect of catalyst dosage was evaluated by varying the amount of CNDs(1%)-$CuBi_2O_4$ from 0.5 to 1.5 g/L, while maintaining 2,4-D concentration of 30 mg/L and pH 4.78. The effect of 2,4-D concentration was performed by varying initial 2,4-D concentration from 30 to 40 mg/L using 1.0 g/L CNDs(1%)-$CuBi_2O_4$ at pH 4.78. The recyclability experiment was performed 5 consecutive cycles with 1.0 g/L of CNDs(1%)-$CuBi_2O_4$, pH 4.78 and 2,4-D of 30 mg/L. The CNDs(1%)-$CuBi_2O_4$ was recycled by heating for 90 minutes at 100°C. The role of active radicals in the degradation of 30 mg/L 2,4-D using 1.0 g/L of CNDs(1%)-$CuBi_2O_4$ at pH 4.78 was investigated by adding 2 mM *tert*-butanol, 2 mM *p*-benzoquinone and 1 mM Na_2EDTA to scavenge hydroxyl radicals ($OH^\bullet$), superoxide radicals ($O_2^{\bullet-}$) and the hole in the valence band (h^+_{VB}), respectively, before visible light irradiation.

3. RESULTS AND DISCUSSION

3.1. Physicochemical properties

The weak peak at 13.1°(100) found in The XRD pattern of CNDs represents in-plane repeating tri-s-triazine units (Figure 1a). The strong peak at 27.7°(002) indicates interlayer stacking of conjugated aromatic systems (PDF No. 87-1526) [8, 9]. For $CuBi_2O_4$, the main peaks located at 2θ values of 27.76° (211), 30.05° (220), 32.64° (102) and 38.78° (212) indicating tetragonal crystal of copper bismuth oxide (PDF No. 42-0334). A diffraction peak at 35.4 (-111) indicated CuO crystallizes in a monoclinic state (PDF No. 80–0076). The diffraction peaks of CNDs(1%)-$CuBi_2O_4$ sample was similar to those of $CuBi_2O_4$.

Considering the FTIR spectrum of $CuBi_2O_4$ (Figure 1b), peaks below 1000 cm^{-1} indicated the interactions between metal ions with oxygen [10]. A very typical peak for the triazine ring was found in the FTIR spectrum of CNDs. The peaks at about 1625-1670 cm^{-1} were assigned to O–H bending of water and the stretching vibration of C=O [3]. Peaks found at about 1078-1451 cm^{-1} were believed to be involved to C-N and C_3N_3 deformation [3]. The FTIR spectrum of CNDs(1%)-$CuBi_2O_4$ varies significantly compared to those of CNDs and $CuBi_2O_4$. The change includes lowering of intensity and disappearance of many characteristic peaks. The new and sharp peak at about 1380 cm^{-1} was believed to be formed from the peaks 1272-1451 cm^{-1}, implying the tight binding of the surface functional groups of CNDs to the metal ions in $CuBi_2O_4$.

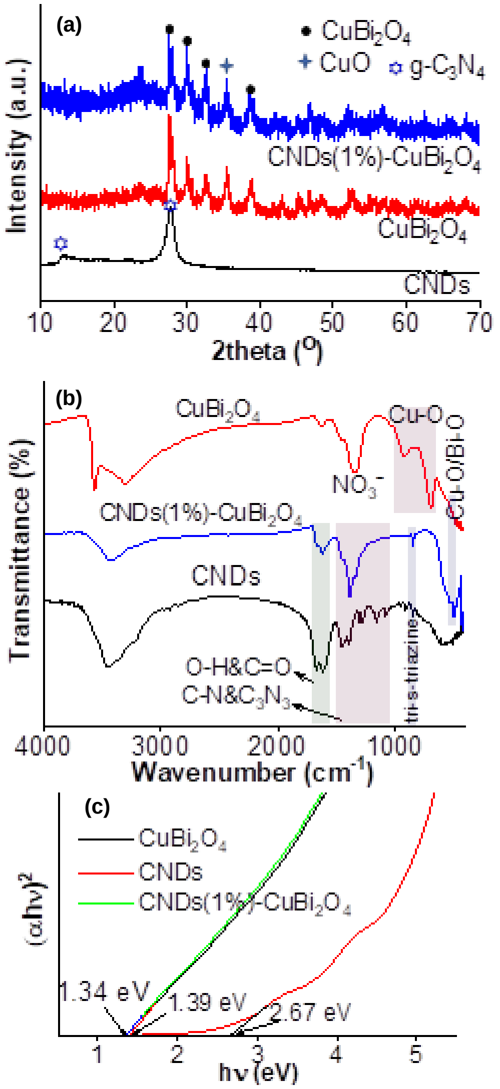

Figure 1. (a) XRD pattern, (b) FT-IR spectrum and (c) band gap energy of materials

The *Eg* was found to be 1.39 eV for $CuBi_2O_4$, 2.67 eV for CNDs and 1.34 eV for CNDs(1%)-$CuBi_2O_4$ (Figure 1c). The *Eg* of CNDs(1%)-$CuBi_2O_4$ was obviously narrower than that of $CuBi_2O_4$. The *Eg* narrowing of CNDs(1%)-$CuBi_2O_4$ confirmed that an intimate chemical bond was formed between the functional groups (−COOH, −OH, C–OC, $-NH_2$ and −CO –NH–) of CNDs [11] with Cu^{2+}, Bi^{3+} of $CuBi_2O_4$. This result confirms that CNDs(1%)-$CuBi_2O_4$ is more easily excited by visible light, leading to enhanced photocatalytic activity under visible light.

The SEM image in Figure 2 shows that $CuBi_2O_4$ is a crystalline rod, with diverse sizes and chaotic distribution. By crystal structure recovery method, $CuBi_2O_4$ was successfully combined with CNDs to create CNDs(1%)-$CuBi_2O_4$ crystal flakes. The CNDs(1%)-$CuBi_2O_4$ TEM image shows the homogeneity between CNDs and $CuBi_2O_4$. The observed lattice fringes are 0.323 nm for $CuBi_2O_4$ and 0.321 nm for CNDs.

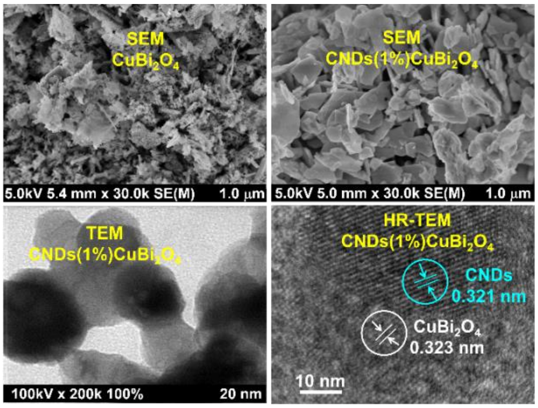

Figure 2. SEM, TEM and HR-TEM of materials

3.2. Photocatalytic properties

The photolysis experiment confirmed that 2,4-D is relatively stable under visible light (Figure 3). About 20.2% and 60.1% of 2,4-D were degraded by CNDs and $CuBi_2O_4$ in visible light for 105 min, respectively. By introducing an appropriate amount of CNDs into $CuBi_2O_4$, the photocatalytic activity was improved. The activity of the CNDs(1%)-$CuBi_2O_4$ was significantly high, ~89.2% of 2,4-D was degraded by CNDs(1%)-$CuBi_2O_4$ at pH 4.2. However, the amount of CNDs in the catalyst was more than 1%, low degradation of the 2,4-D was detected. Only 65.6% of 2,4-D was degraded by CNDs(2%)-$CuBi_2O_4$. The excellent activity of the CNDs(1%)-$CuBi_2O_4$ catalyst is due to a sufficient percentage of CNDs, which prolonged separation of photogenerated e^{-}/h^{+} pairs [12]. However, the decreased activity of the catalyst with further increase in CNDs may be due to the decrease in effective surface area of the catalyst as its active sites are occupied by CNDs [12]. Experimental kinetic data for 2,4-D degradation by CNDs-$CuBi_2O_4$ were modeled by the Lagergren's pseudo first-order model. Remarkably, the 2,4-D degradation rate constant (k) of the CNDs-$CuBi_2O_4$ catalyst were much higher than that of individual components. The CNDs(1%)-$CuBi_2O_4$ had superior activity, with k = 0.0156 min^{-1}, and the degradation efficiency was about 11.14, 2.33 and 2.11 times higher than those of the CNDs (k = 0.0014 min^{-1}), $CuBi_2O_4$ (k = 0.0067 min^{-1}) and CNDs(2%)-$CuBi_2O_4$ (k = 0.0074 min^{-1}), respectively.

Since CNDs(1%)-$CuBi_2O_4$ gives the best catalytic activity, it will be used for further research.

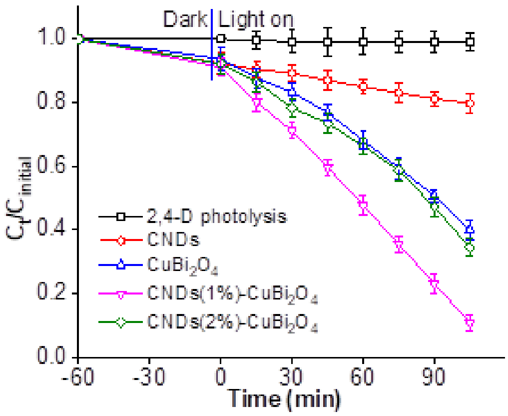

Figure 3. Photodegradation of 30 mg/L 2,4-D at pH 4.2 using 1.0 g/L catalysts in visible light for 105 min

3.3. Effect of pH, CNDs(1%)-$CuBi_2O_4$ dosage, 2,4-D concentration and reusability

The surface charge of a photocatalyst is largely regulated by the pH of the solution. Therefore, pH is an important parameter that determines the efficiency of pollutant degradation. Notably, 2,4-D concentrations dropped dramatically at pH 4.78 in visible light for 105 min. About 90.9% of 2,4-D was degraded (with k = 0.0169 min^{-1}) by CNDs(1%)-$CuBi_2O_4$ at pH 4.78 (Figure 4a), whereas the degradation of 2,4-D achieved ~60.5% (k = 0.0069 min^{-1}), 89.2 % (k = 0.0156 min^{-1}) and 69.4% (k = 0.0085 min^{-1}) for pH of 2.0, 4.2 and 7.0, respectively. The decrease in 2,4-D degradation efficiency at pH lower or higher than 4.78 can be understood as follows. The catalytic activity was controlled by the point of zero charge (pH_{PZC}), while the protonation of the carboxyl groups was controlled by the pKa of 2,4-D. The pH_{PZC} of CND(1%)-$CuBi_2O_4$ was found to be ~7.0 (Figure 4a inset). When solution pH <pH_{PZC}, the surface charge of

CNDs(1%)-$CuBi_2O_4$ is positive. However, at solution pH = 2.0 < pKa of 2,4-D (2.74), the ability to protonate 2,4-D molecules is limited, resulting in less decomposition of 2,4-D molecules. For comparison, at solution pH = 7.0 (≈pH_{PZC}), the surface charge of CND(1%)-$CuBi_2O_4$ is neutral. The electrostatic attraction that exists between the surface of CND(1%)-$CuBi_2O_4$ and the 2,4-D anion in solution is negligible, so the degradation of 2,4-D is less. At pH 4.78, the better 2,4-D degradation is due to the fully protonated carboxyl groups, which are favorable for 2,4-D anions to reach positively charged CNDs(1%)-$CuBi_2O_4$, leading to significant 2,4-D degradation.

The CNDs(1%)-$CuBi_2O_4$ of 1.0 g/L provides optimal 2,4-D decomposition efficiency (Figure 4b), ~90.9% of 2,4-D was degraded in visible light for 105 min, while the degradation of 2,4-D achieved ~64.1% (k = 0.0082 min^{-1}) and 71.3% (k = 0.0101 min^{-1}) for 0.5 and 1.5 g/L catalyst, respectively. Catalyst dosage higher or lower than 1.0 g/L did not give the best 2,4-D degradation which was due to the reasonable ratio between the amount of CNDs(1%)-$CuBi_2O_4$, the 2,4-D concentration and the number of photons on CNDs(1%)-$CuBi_2O_4$, which led to the best 2,4-D degradation rate. A very low dosage of CNDs(1%)-$CuBi_2O_4$ resulted in insufficient generation of oxidizing radicals (•OH, and $O_2^{\bullet-}$) to decompose 2,4-D. Meanwhile, excessive dosage of CNDs(1%)-$CuBi_2O_4$ would increase turbidity, making it impossible for light to reach the active site of the catalyst, leading to a decrease in the formation of photogenerated e^-/h^+ pairs followed by a decrease in the formation of •OH, and $O_2^{\bullet-}$.

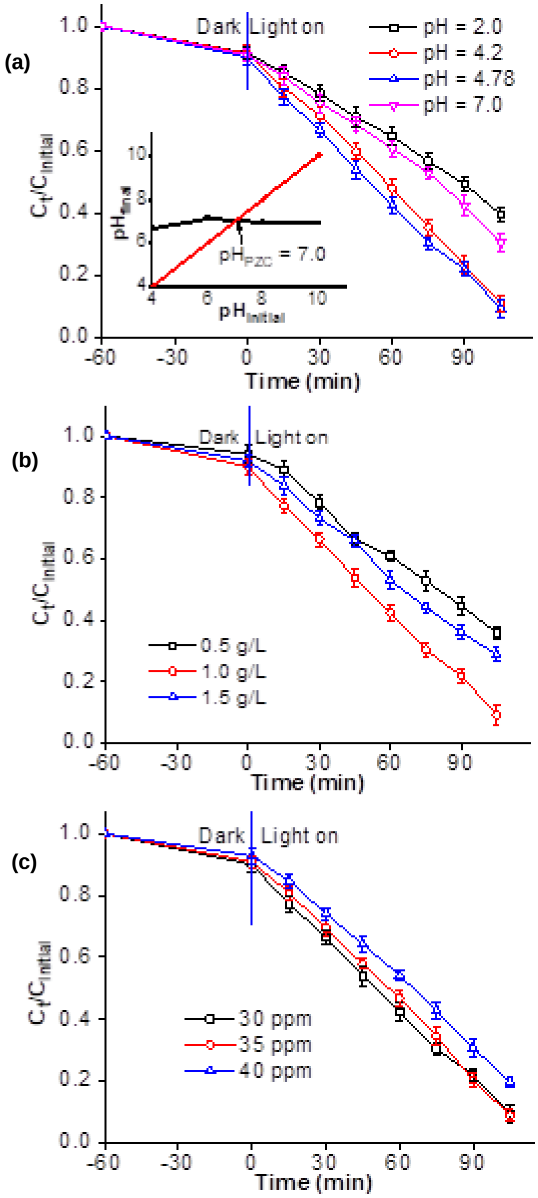

Figure 4. Photodegradation of 2,4-D (a) Effect of the pH solution (inset: pH_{PZC} of CNDs(1%)-$CuBi_2O_4$ using pH drift method); (b) Effect of CNDs(1%)-$CuBi_2O_4$ dosage (2,4-D of 30 mg/L at pH 4.78) and (c) Effect of 2,4-D concentration (CNDs(1%)-$CuBi_2O_4$ of 1.0 g/L at pH 4.78)

The degradation rate of 2,4-D achieved 0.0169, 0.0167 and 0.0120 min^{-1} for initial 2,4-D concentration 30, 35 and 40 mg/L, respectively. High 2,4-D concentration leads to low degradation efficiency (Figure 4c) which can be explained as follows: Because the amount of CNDs(1%)-$CuBi_2O_4$ and the light intensity were constant, the number of reactive radicals produced such as e^-/h^+ pairs, •OH, and $O_2^{\bullet-}$ were also constant while the initial concentration of 2,4-D increased. Therefore, the low 2,4-D degradation for high 2,4-D concentrations is due to the insufficient number of reactive radicals to attack 2,4-D.

The activity of CNDs(1%)-$CuBi_2O_4$ is more favorable than previous catalytic systems. More than 83% of 2,4-D (100 mg/L) was removed by 0.5 g/L TiO_2@$MgFe_2O_4/H_2O_2$ at pH 2 in visible light for 240 min [13]. About 90% of 2,4-D (30 mg/L) was removed by 1.0 g/L 2.0rGO/$ZnBi_2O_4$ at pH 2.45 in visible light for 120 min [14].

Along with catalytic activity, catalyst stability and recyclability are equally important for practical applications. The reusability results indicated that CNDs(1%)-$CuBi_2O_4$ exhibited significant photo-stabilization after 105 min, and the 2,4-D decomposition efficiency reached 90.9 ± 3.0% for the 1st use, 87.9 ± 1.8% for the 2nd reuse, 86.8 ± 2.4% for the 3rd reuse, 85.5 ± 2.5% for the 4th reuse and 84.4 ± 1.9% for the 5th reuse.

3.4. Experiments to capture active radicals

It is known that $OH^\bullet$, $O_2^{\bullet-}$ and h^+_{VB} are strong active radicals, which mainly act in photocatalysis to decompose pollutants. Figure 5 shows that when 2.0 mM *tert*-butanol was added as an $OH^\bullet$ scavenger to the photocatalytic experiment, about 63.6% of 2,4-D was degraded by CNDs(1%)-$CuBi_2O_4$. The rate of degradation was found to be ~ 0.0077 min^{-1}, thus the $OH^\bullet$ radical did not play a major role in the degradation of 2,4-D by CNDs(1%)-$CuBi_2O_4$.

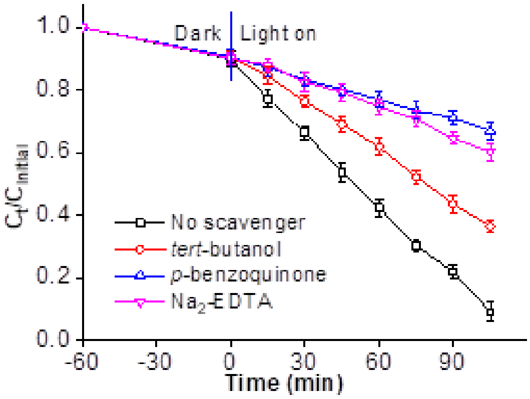

Figure 5. Effect of different scavengers on the degradation of 30 mg/L 2,4-D using 1.0 g/L CNDs(1%)-$CuBi_2O_4$ at pH 4.78 in visible light for 105 min

By adding 2.0 mM *p*-benzoquinone as an $O_2^{\bullet-}$ scavenger to the photocatalytic experiment, the degradation efficiency of 2,4-D by CNDs(1%)-$CuBi_2O_4$ was significantly reduced. Without the presence of oxidizing agent $O_2^{\bullet-}$, ~ 33.0% of 2,4-D was degraded under visible light with degradation rate of 0.0028 min^{-1}. When adding to the degradation reaction 1.0 mM Na_2EDTA as the h^+_{VB} scavenger, the degradation efficiency of 2,4-D by CNDs(1%)-$CuBi_2O_4$ was dramatically reduced. About 39.7% of 2,4-D was degraded with degradation rate of 0.0035 min^{-1}. These findings demonstrate that $O_2^{\bullet-}$ and h^+_{VB} are the powerful agents for the degradation of 2,4-D by CNDs(1%)-$CuBi_2O_4$, while the $OH^\bullet$ radical is not a strong agent.

4. CONCLUSION

The CNDs-$CuBi_2O_4$ photocatalyst was successfully synthesized and showed much better photocatalytic performance than the individual components. The best sample is CNDs(1%)-$CuBi_2O_4$, which achieved a degradation efficiency of 90.9% of 2,4-D (k = 0.0169 min^{-1}) in visible light for 105 min. All active species ($O_2^{\bullet-}$, $OH^{\bullet}$ and h^+_{VB}) got involved in 2,4-D removal, in which $O_2^{\bullet-}$ and h^+_{VB} play the major role. CNDs(1%)-$CuBi_2O_4$ has great potential for practical applications because of its relatively good stability in at least five consecutive experiments.

Acknowledgment: This work is supported by Vietnam Academy of Science and Technology (VAST) under grant number THTETN.08/23-24.

REFERENCES

1. F. Amiri, M. Dehghani, Z. Amiri, S. Yousefinejad, A. Azhdarpoor, (2021). Photocatalytic degradation of 2,4-dichlorophenoxyacetic acid from aqueous solutions by Ag3PO4/TiO2 nanoparticles under visible light: kinetic and thermodynamic studies. *Water Science Technology*, **83(12)**, 3110-3122.
2. A.Y. Goren, Y.K. Recepoglu, V. Vatanpour, Y. Yoon, A. Khataee, (2023). Insights into engineered graphitic carbon nitride quantum dots for hazardous contaminants degradation in wastewater. *Environmental Research*, **223,** 115408.
3. P. Kumar, U.K. Thakur, K. Alam, P. Kar, R. Kisslinger, S. Zeng, S. Patel, K. Shankar, (2018). Arrays of TiO2 nanorods embedded with fluorine doped carbon nitride quantum dots (CNFQDs) for visible light driven water splitting. *Carbon*, **137,** 174-187.
4. X. Lin, C. Liu, J. Wang, S. Yang, J. Shi, Y. Hong, (2019). Graphitic carbon nitride quantum dots and nitrogen-doped carbon quantum dots co-decorated with BiVO4 microspheres: A ternary heterostructure photocatalyst for water purification. *Separation and Purification Technology*, **226,** 117-127.
5. Z. Zhang, B. Zhu, X. Guan, (2022). Operational Spectroelectrochemical Investigation on the Interfacial Charge Dynamics of Copper Bismuth Oxide Based Photocathode. *Journal of Physical Chemistry Letters,* **13(10)**, 2356-2364.
6. X. Chen, C. Yu, R. Zhu, N. Li, J. Chen, S. Li, W. Xia, S. Xu, H. Wang, X. Chen, (2019). Ag3PO4 Deposited on CuBi2O4 to Construct Z-Scheme Photocatalyst with Excellent Visible-Light Catalytic Performance Toward the Degradation of Diclofenac Sodium. *Nanomaterials*, **9,** 959.
7. J. Zhou, Y. Yang, C.-y. Zhang, (2013). A low-temperature solid-phase method to synthesize highly fluorescent carbon nitride dots with tunable emission. *Chemical Communications*, **49(77)**, 8605-8607.
8. Z. Zhao, W. Zhang, X. Shen, T. Muhmood, M. Xia, W. Lei, F. Wang, M.A. Khan, (2018). Preparation of g-C3N4/TiO2/BiVO4 composite and its application in photocatalytic degradation of pollutant from TATB production under visible light irradiation. *Journal of Photochemistry and Photobiology A: Chemistry*, **358,** 246-255.
9. M.A. Khan, S. Mutahir, F. Wang, W. Lei, M. Xia, S. Zhu, (2019). Facile one-step economical methodology of metal free g-C3N4 synthesis with remarkable photocatalytic performance under visible

light to degrade trans-resveratrol. *Journal of Hazardous Materials*, **367,** 293-303.

10. C. Parvathiraja, S. Shailajha, (2021). Bioproduction of CuO and Ag/CuO heterogeneous photocatalysis-photocatalytic dye degradation and biological activities. *Applied Nanoscience,* **11(4)**, 1411-1425.
11. M.M. Xavier, N.N. Adarsh, P.R. Nair, S. Mathew, (2021). Carbon Nitride Quantum Dot-Embedded Poly(vinyl alcohol) Transparent Thin Films for Greenish-Yellow Light-Emitting Diodes. *ACS Omega*, **6(35)**, 22840-22847.
12. R. Noroozi, M. Gholami, V. Oskoei, M. Hesami Arani, S.A. Mousavifard, B. Nguyen Le, M. Fattahi, (2023). Fabrication of new composite NCuTiO2/CQD for photocatalytic degradation of ciprofloxacin and pharmaceutical wastewater treatment: degradation pathway, toxicity assessment. *Scientific Reports*, **13(1)**, 16287.
13. Bui The Huy, D.-s. Jung, Nguyen Thi Kim Phuong, Y.-I. Lee, (2017). Enhanced photodegradation of 2,4-dichlorophenoxyacetic acid using a novel TiO2@MgFe2O4 core@shell structure. *Chemosphere*, **184,** 849-856.
14. Nguyen Thi Mai Tho, Dang Nguyen Nha Khanh, Nguyen Quoc Thang, Y.-I. Lee, Nguyen Thi Kim Phuong, (2020). Novel reduced graphene oxide/ZnBi2O4 hybrid photocatalyst for visible light degradation of 2,4-dichlorophenoxyacetic acid. *Environmental Science and Pollution Research*, **27(10)**, 11127-11137.