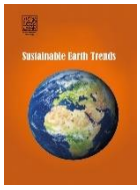
Shahid Beheshti University

Sustainable Earth Trends

Journal homepage: http://sustainearth.sbu.ac.ir



Synthesis of G-C_3N_4/Mxene composite for enhanced photocatalytic degradation of eosin Y dye in aqueous solutions under visible light

Mehran Bijari[a], Afsaneh Shahbazi[*a], Vahid Vatanpour[b], Habibollah Younesi[c]

[a] Department of Environmental Technologies, Environmental Sciences Research Institute, Shahid Beheshti University, 1983969411, Tehran, Iran
[b] Department of Applied Chemistry, Faculty of Chemistry, Kharazmi University, 15719-14911 Tehran, Iran
[c] Department of Environmental Science, Faculty of Natural Resources, Tarbiat Modares University, 46414-356, Noor, Iran

ABSTRACT

In this study, MXene nanosheets were utilized as a co-catalyst to modify the graphitic carbon nitride photocatalyst and synthesize the g-C_3N_4/MXene composite. Eosin Y dye was employed as a model organic pollutant to evaluate the photocatalytic degradation performance. Eosin Y, an anionic dye, poses significant environmental and health risks due to its resistance to biodegradation, as well as its toxicity and carcinogenicity. To synthesize this composite, graphitic carbon nitride was initially produced using a simple thermal polymerization method. Subsequently, it was protonated and assembled with MXene nanosheets through a self-assembly process. The MXene nanosheets were synthesized using a Mild method. Characterization and confirmation of the successful synthesis of the g-C_3N_4/MXene composite were conducted through X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy-dispersive X-ray spectroscopy (EDS) analyses. The results of the Eosin Y degradation experiments indicated that the composite with a 7% weight ratio of MXene nanosheets exhibited the highest photocatalytic performance among the various weight ratios tested. The incorporation of MXene nanosheets more than doubled the photocatalytic degradation efficiency of graphitic carbon nitride. The MCN7 sample was able to remove 98% of 25 mg/L Eosin Y dye from an aqueous solution within 120 minutes, using a photocatalyst dosage of 0.4 g/L. The findings of this study demonstrate that the integration of MXene nanosheets with graphitic carbon nitride significantly enhances the photocatalytic performance of graphitic carbon nitride in the degradation of organic pollutants.

ARTICLE INFO

Keywords:
Eosin Y
g-C_3N_4/MXene
MXene
Photocatalytic degradation
Visible light

Article history:
Received: 15 Apr 2024
Accepted: 18 Jun 2024

*Corresponding author
E-mail address:
a_shahbazi@sbu.ac.ir
(A. Shahbazi)

Citation:
Bigari, M. et al., (2024). Synthesis of g-c3n4/mxene composite for enhanced photocatalytic degradation of eosin y dye in aqueous solutions under visible light, *Sustainable Earth Trends:* 4(4), (1-9).

DOI: 10.48308/set.2024.236700.1063

1. Introduction

Despite the vast amount of water on Earth, potable water resources are extremely limited and unevenly distributed. Only 3% of this immense water supply is suitable for drinking. Furthermore, since a significant portion of this 3% is trapped in inaccessible glaciers, it can be concluded that less than 1% of the Earth's water is readily available for human consumption (Skuse et al., 2021). Moreover, the global population and demand for drinking water are continuously increasing. This situation is exacerbated by the fact that these limited water resources are often subjected to various forms of pollution (Kamari et al., 2024). One of the most significant contributors to water pollution, both in Iran and worldwide, is the industries involved in the production and application of organic and synthetic dyes, such as the paint and textile industries (Mahmood et al., 2021).

Organic dyes represent a significant class of environmental pollutants that enter aquatic ecosystems through industrial effluents, posing a severe threat to environmental health. Annually, approximately 700,000 tons of various organic dyes and pigments are produced worldwide, with an estimated 10-15% of these colorants ending up in industrial wastewater (Barka et al., 2011; Haleem et al., 2024). Some of these dyes are toxic

and carcinogenic, making their removal from industrial effluents a significant environmental challenge. Furthermore, due to their complex aromatic structures, these dyes are often resistant to biodegradation and exhibit high environmental persistence. As a result, conventional biological methods are ineffective in eliminating these dyes (Yan et al., 2024). According to the Iranian Standard and Industrial Research Institute Standard No. 1053, the maximum permissible color for drinking water is established at 15 Platinum-Cobalt Units (TCU) (ISIRI, 2010). It is important to note that the human eye can detect concentrations of color in water as low as 1 mg/L. Consequently, organic dyes can create significant aesthetic issues in aquatic ecosystems. Given these factors, it is imperative to remove organic dyes from industrial effluents before they are discharged into aquatic environments (Bijari et al., 2018). Photocatalytic processes for the degradation of dyes, driven by visible and ultraviolet light, have garnered significant attention for their effectiveness in removing pollutants from wastewater. These environmentally friendly methods can effectively degrade a wide range of dyes and organic contaminants (Iqbal et al., 2024). Common photocatalysts employed in this field include TiO_2, ZrO_2, Ga_2O_3, Ta_2O_5, ZnO, CeO_2, CdS, ZnS, MoO_3, SnO_2, Fe_2O_3, and WO_3 (Ahmed et al., 2019). In general, semiconductors are chosen as photocatalysts because of their unique electronic structures (Taghiloo and Larimi, 2023). However, to effectively absorb light and enhance photocatalytic efficiency in the visible light region, it is crucial to develop photocatalysts that maximize light absorption within the visible spectrum, such as graphitic carbon nitride (g-C_3N_4).

Graphitic carbon nitride, which has a structure similar to that of graphite, is composed of carbon and nitrogen atoms. Due to its remarkable properties, including high chemical and thermal stability, pollutant adsorption capacity, antibacterial characteristics, and visible-light photocatalytic activity, it has attracted considerable attention across various fields, particularly in wastewater treatment (Shoran et al., 2024). The photocatalytic performance of g-C_3N_4 under visible light, attributed to its band gap of 2.7 eV, renders it an ideal candidate for harnessing sunlight, of which 43% comprises visible light. In contrast, conventional photocatalysts such as TiO_2 are solely active in the UV spectrum, which constitutes only 4% of sunlight (Shahbazi et al., 2024). The photocatalytic performance of g-C_3N_4 under visible light, which is attributed to its band gap of 2.7 eV, makes it an ideal candidate for harnessing sunlight, of which 43% consists of visible light. In contrast, conventional photocatalysts such as TiO_2 are only active in the UV spectrum, which accounts for merely 4% of sunlight (Azimi et al., 2018). To enhance the photocatalytic performance of g-C_3N_4, various bandgap engineering strategies have been employed, including dimensional tuning, surface sensitization, and heterojunction construction (Zhang et al., 2023). Among all methods, the creation of composites is particularly significant due to its straightforward procedure (Chand and Mondal, 2023).

The novelty of this research lies in the use of MXene nanosheets to modify and enhance the photocatalytic performance of graphitic carbon nitride. MXene is a recently discovered two-dimensional nanomaterial that has attracted significant attention from researchers in this field in recent years. In this study, graphitic carbon nitride was modified with MXene nanosheets, and its enhanced photocatalytic performance was investigated for the removal of the dye Eosin Y from aqueous solutions. The main application of eosin Y is in biological staining techniques (Eftekharazam et al., 2024). Eosin Y is an anionic dye that poses risks to human health and other animals, leading to various health issues, including skin disorders, liver and kidney dysfunction, and cancer. Its use in food products is strictly prohibited (Alminderej et al., 2023; Bibi et al., 2024).

2. Material and Methods

All of the chemicals were analytical grade, so there was no further purification necessary. Dicyandiamide powder was purchased from Merck as the precursor for the synthesis of graphitic carbon nitride. Titanium aluminum carbide (Ti_3AlC_2) MAX phase powder was purchased from RedoxKala Co, Iran. Eosin Y dye, with a molecular weight of 691.9 g/mol and a linear molecular structure of $C_{20}H_6Br_4Na_2O_5$, was purchased from Sigma [1]. The molecular structure of Eosin Y dye is shown in Fig. 1.

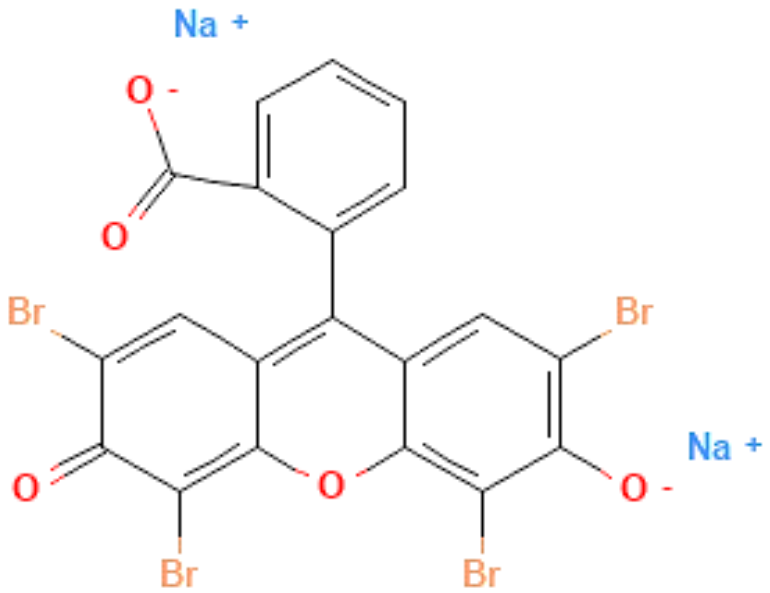


Fig. 1. Molecular structure of Eosin Y dye

2.1. Synthesis of MXene nanosheets

For the purpose of this investigation, the MILD method was modified to create the single-layer MXene nanosheets. After adding 0.8 g of LiF to 10 mL of 9 M HCl, the mixture was stirred for five minutes. Next, the above etchant was gradually mixed with 0.5 g of Ti_3AlC_2 powder over a 5-minute period. The mixture was then left to stir for 48 hours at 40°C. The sediment was subsequently collected using a centrifuge operating at 3500 rpm, and it underwent a series of washings with deionized water until its pH reached 5. After ten iterations of this cycle, 100 milliliters of colloidal solution were made. The unexfoliated residue was extracted from the above solution by centrifuging it for an hour at 3500 rpm. After that, the supernatant solution was ultrasonically treated for 30 minutes at 5°C with Ar gas to produce single-layers with smaller dimensions. A freeze dryer was used to dry the colloidal solution, which had a concentration of 1 point 8 mg/mL. To avoid oxidation, the powder that was produced by expelling Ar gas was kept cold.

2.2. Synthesis of graphite carbon nitride (g-C_3N_4)

Graphitic carbon nitride (g-C_3N_4) was synthesized via thermal pyrolysis of dicyandiamide in a tube furnace at 550 °C for 3 hours, using a heating rate of 5 °C/min. After cooling the furnace, the resulting light-yellow masses were ground into a powder. To synthesize graphitic carbon nitride nanosheets, 1 g of bulk graphitic carbon nitride nanomaterial was initially dissolved in 100 mL of 1 M hydrochloric acid and subjected to ultrasonic treatment for 1 hours. Subsequently, it was stirred on a magnetic stirrer for 12 hours. This process was carried out to exfoliate the bulk carbon nitride and protonate the sheets, thereby facilitating better attachment of functional groups with opposite charges on the surfaces of graphitic carbon nitride and MXene. The carbon nitride powder was then washed with deionized water and dried in a vacuum oven at 70 °C for 12 hours.

2.3. Synthesis of g-C_3N_4/Mxene composite

The g-C_3N_4 /MXene composites were synthesized via a self-assembly method. To this end, graphitic carbon nitride nanosheet powder was mixed with a specific weight ratio of MXene (0.5%, 1%, 3%, 5%, 7%, and 9%) in 50 mL of deionized water, followed by 1 hour of ultrasonication and subsequent magnetic stirring for 24 hours. The resulting precipitate was then separated by centrifugation and dried in a vacuum oven for 12 hours. The obtained powders were named MCN0.5 to MCN9. A schematic illustration of the MXene/g-C_3N_4 composite synthesis is shown in Fig. 2.

2.4. Photocatalytic Performance Evaluation

To evaluate the photocatalytic performance of the synthesized g-C_3N_4/MXene composites,

their photocatalytic activity was assessed under identical conditions, including a dye volume of 50 mL, a concentration of 25 mg/L, a solution pH of 4, a photocatalyst dosage of 25 mg, and a 50 W LED lamp as the light source. This experiment was conducted to confirm the successful synthesis of the composites and to determine the optimal synthesis ratio. To calculate the removal percentage of eosin Y dye, the spectrum of Eosin Y (400-700 nm) was analyzed using a Hach DR6000 spectrophotometer to identify the wavelength of maximum absorbance. The removal efficiency of Eosin Y dye was determined at the maximum absorption wavelength of 518 nm, according to Equation 1. In this context, Ci represents the initial concentration of the dye in mg/L, and Cf denotes the final concentration of the dye in mg/L at a specified time point.

$$\frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

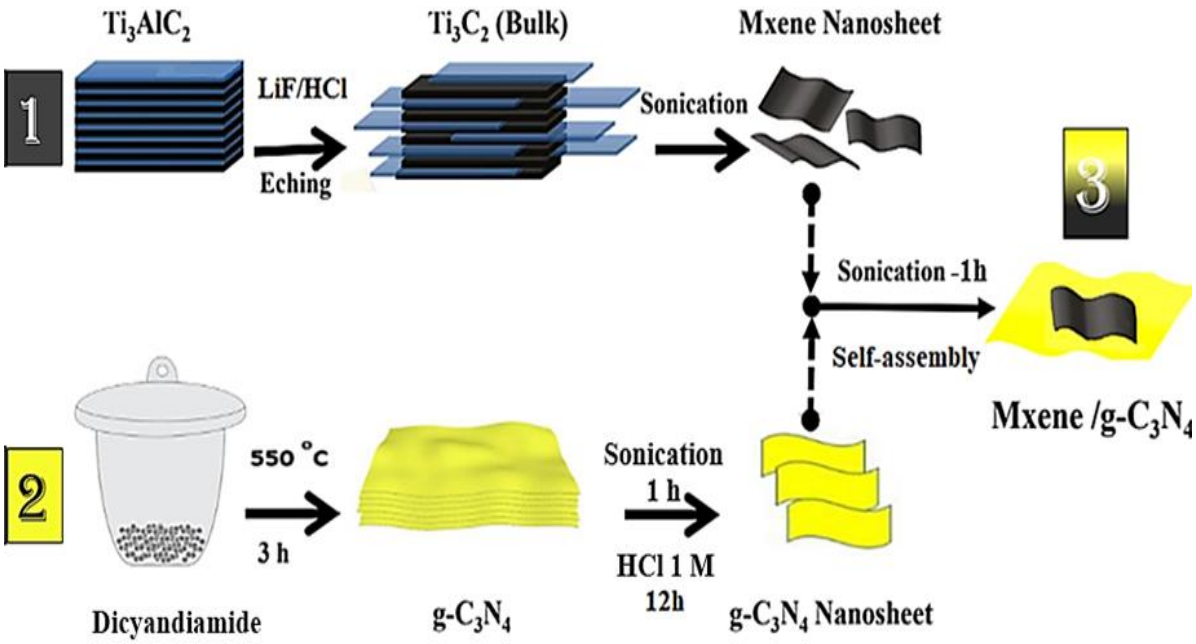


Fig. 2. Schematic synthesis of g-C3N4/MXene composite

3. Results and discussion

3.1. Characteristics of nanomaterials

X-ray diffraction (XRD) analysis is a widely used technique for identifying the compounds and phases present in materials, falling under the category of spectroscopic analyses. The XRD results presented in Fig.3 demonstrate the successful synthesis of graphitic carbon nitride and MXene. Graphitic carbon nitride exhibits two prominent peaks at 27° and 13°, corresponding to the (002) and (100) planes, respectively. Furthermore, the synthesis of MXene nanosheets is clearly confirmed by the absence of the strong peak at 39° corresponding to the Ti_3AlC_2 MAX phase, which is attributed to the chemical etching process that removes the Al layer from the Ti3AlC2 MAX phase structure. Finally, the XRD pattern of the synthesized MXene/g-C_3N_4 composite confirms its successful formation, as evidenced by the presence of peaks associated with graphitic carbon nitride at 27° and a strong peak corresponding to MXene nanosheets at 9° (Wang and Wang, 2022; Xu et al., 2023).

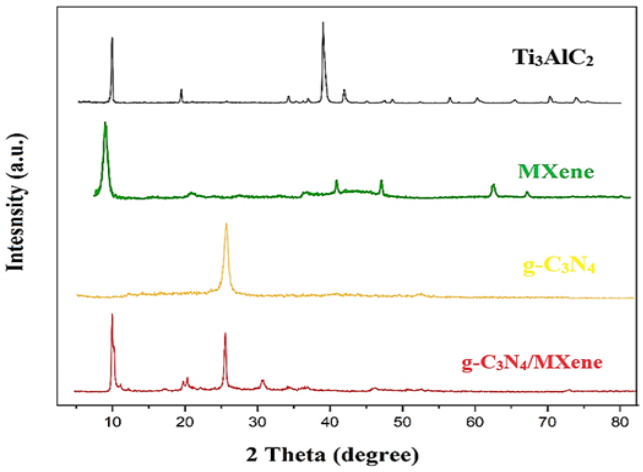


Fig. 3. X-ray diffraction spectrum of synthesized nanomaterials

Field Emission Scanning Electron Microscopy (FE-SEM) is an electron-based imaging technique used to study the surface morphology of samples at high resolution. In this technique, electrons emitted from an electron source are directed towards the sample. Upon interaction with the sample's surface, the morphology is captured by a detector system. The FE-SEM image of the synthesized nanomaterials in this study is presented in Fig. 4. Fig. 4a presents the surface morphology of the Ti_3AlC_2 MAX phase, revealing the expected dense layers. Through chemical etching, exfoliation of Ti_3AlC_2 occurred, resulting in the synthesis of MXene nanosheets (Fig. 4c) via the removal of aluminum from the structure. Additionally, Fig. 4b illustrates dense agglomerates of graphitic carbon nitride. Fig. 4d corresponds to the MXene/g-C_3N_4 composite. The presence of both sheet-like and bulk structures, attributed to graphitic carbon nitride and MXene, respectively, in Fig. 4d confirms the successful synthesis of the g-C_3N_4/MXene composite.

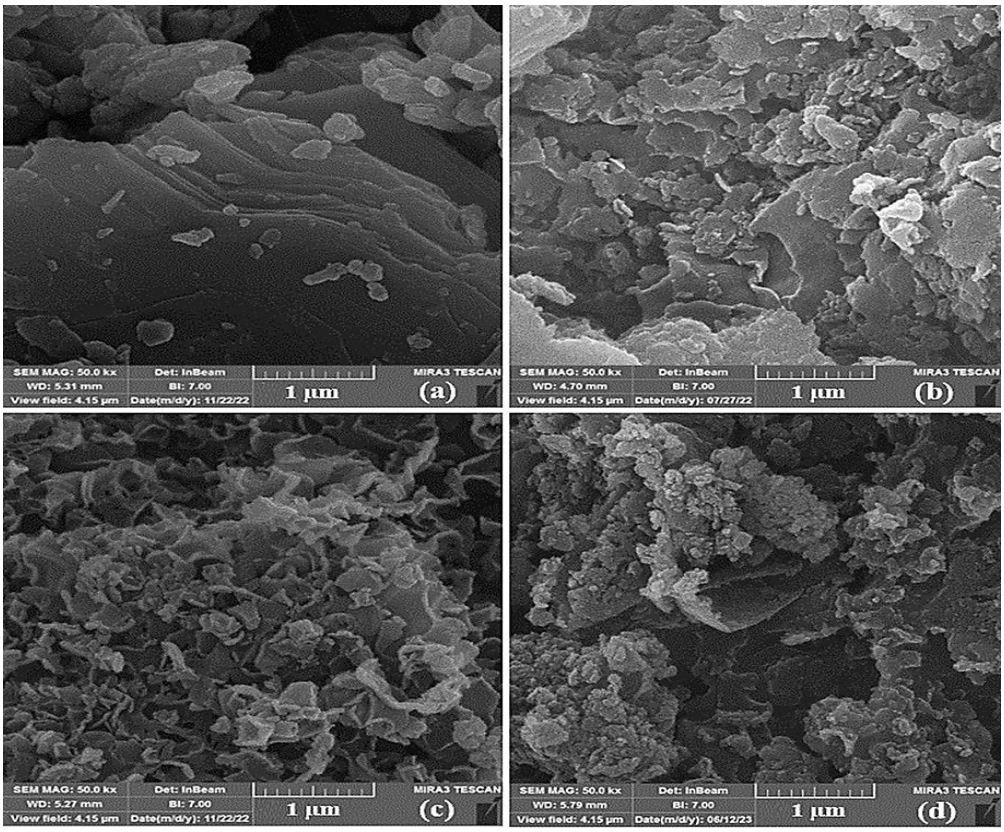


Fig. 4. FE-SEM analysis of synthesized nanomaterials including; a: Max phase Ti_3AlC_2, b: Graphitic carbon nitride (g-C_3N_4), c: MXene, d: g-C_3N_4/MXene composite

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique commonly attached to scanning electron microscopes (SEMs) for elemental analysis of solid samples. By measuring the energy of X-rays emitted from the sample, EDS can identify the types of elements present and determine their relative atomic or weight percentages. Fig. 5 presents the EDX spectrum and elemental mapping of the g-C_3N_4/MXene composite. The presence of titanium, carbon, and nitrogen elements within the g-C_3N_4/MXene composite structure is confirmed by the observed peaks in the EDX spectrum.

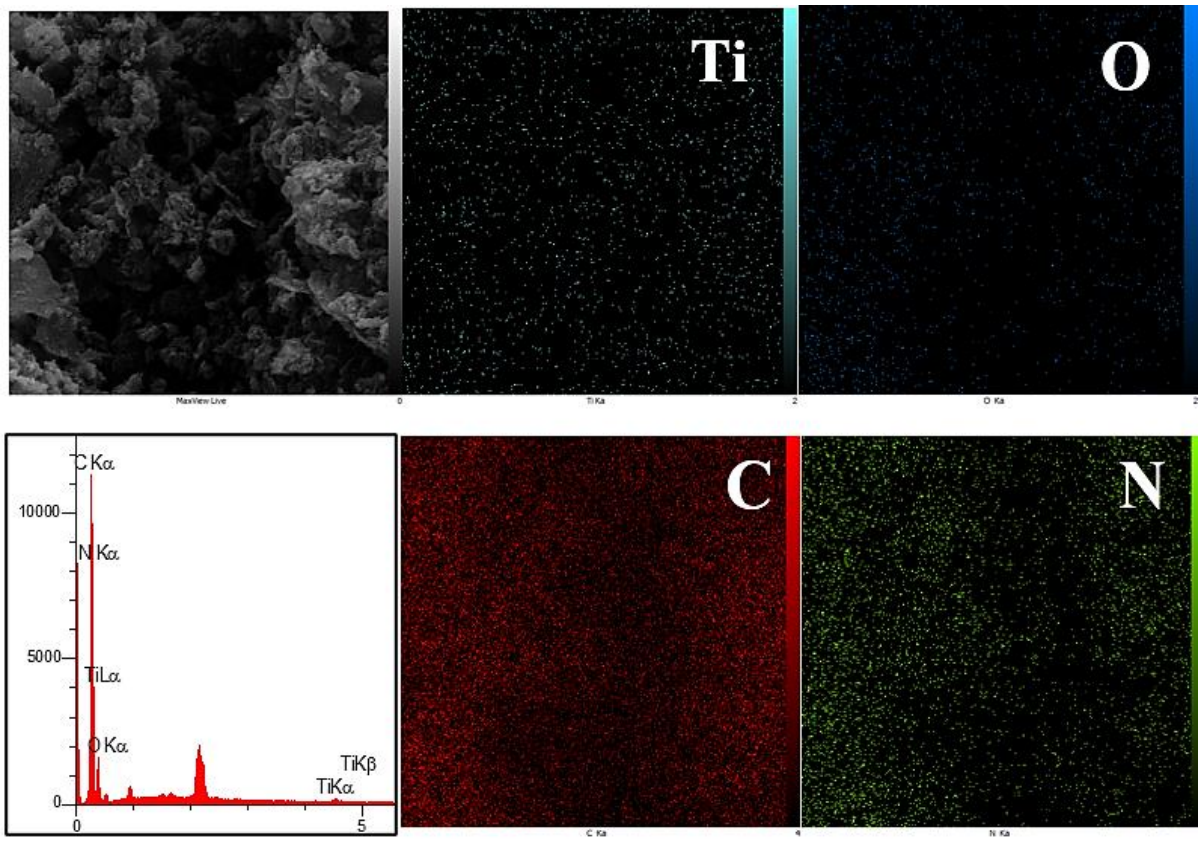


Fig 5. X-ray energy diffraction (EDX) analysis of g-C_3N_4/Mxene composite

3.2. Photodegradation performance of Eosin Y dye

The photocatalytic performance of g-C_3N_4/MXene composites were evaluated to determine the optimal ratio of graphitic carbon nitride and MXene for the synthesis of g-C_3N_4/MXene composites. To this end, the photocatalytic performance of composites synthesized with various weight percentages (0.5%, 1%, 3%, 5%, 7%, and 9% by weight) was investigated under identical conditions, including a dye volume of 50 mL, a dye concentration of 25 mg/L, a solution pH of 4, a photocatalyst dosage of 25 mg, and a 50 W LED lamp as the light source. Fig. 6 presents a comparison of the photocatalytic degradation of Eosin Y dye by the synthesized composites with different weight percentages. As shown in the figure, the composite synthesized with a 7 wt% MXene loading exhibited the highest photocatalytic activity (72%) among the synthesized photocatalysts. Moreover, according to Fig. 6, the photocatalytic performance of the g-C_3N_4/MXene composite with a 7 wt% loading (MCN 7) was approximately two times higher than that of the pristine graphitic carbon nitride (CN) photocatalyst.

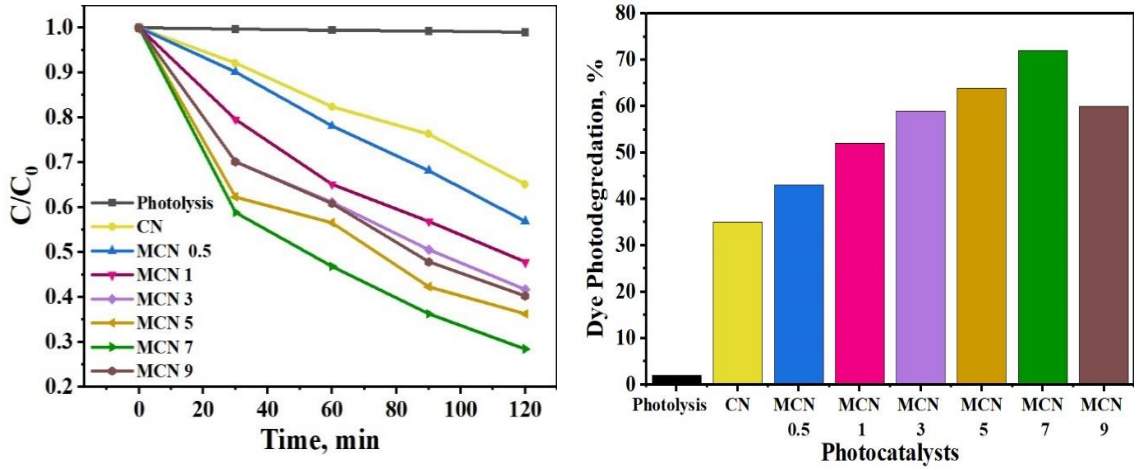


Fig. 6. Results of photocatalytic performance of synthesized composites with different weight percentages

3.3. The effect of different parameters on the degradation of Eosin Y dye

To investigate the parameters affecting the degradation of Eosin Y dye by g-C_3N_4/MXene composite, various parameters such as pH, photocatalyst dosage, dye solution concentration, and temperature were examined. In these experiments, the MCN 7 sample, identified as the optimal photocatalyst in this study, was employed. Fig.7a presents the results of the Eosin Y degradation experiments at various pH levels. As shown in the figure, the degradation of Eosin Y by the MCN 7 sample exhibits an inverse relationship with increasing pH. In this study, the highest degradation was observed at pH 2, while the lowest degradation of Eosin Y was reported at pH 10. The enhanced degradation of Eosin Y in acidic conditions can be attributed to the alteration of the surface charge of the synthesized photocatalyst. Consequently, by decreasing the pH in acidic environments, the photocatalysts can be protonated, acting as acids and reacting with basic groups in Eosin Y. Therefore, the photodegradation of Eosin Y by the MCN 7 sample is more efficient at acidic pH levels. For subsequent experiments, a pH of 4 was chosen as the optimal condition (Azimi et al., 2018). Fig .7b presents the results of the experiment investigating the effect of photocatalyst dosage. Various amounts of g-C_3N_4/MXene were employed as shown in Fig. 7b. The results indicated a direct correlation between the color removal efficiency and the photocatalyst dosage. The enhancement in color removal efficiency with increasing photocatalyst dosage can be attributed to the increased number of active sites for light absorption as a result of the increased photocatalyst dosage. Considering the acceptable removal efficiency of 98% for a dosage of 0.4 g/L, this value was selected as the optimal dosage for subsequent parameters. Fig . 7c presents the results of Eosin Y degradation at various concentrations. The results indicated that the degradation rate of Eosin Y by the MCN 7 sample was significantly influenced by the dye solution concentration. Consequently, the degradation rate of Eosin Y decreased with increasing dye concentration. This can be attributed to the adsorption of a large number of dye molecules onto the photocatalyst surface, rendering the active sites for light absorption inactive and causing what is known as photocatalyst poisoning. Additionally, at high dye concentrations, the photocatalyst has access to lower-quality light. In this study, a dye concentration of 25 ppm was selected as the optimal concentration, as the photocatalytic performance of the synthesized sample decreased at higher concentrations (Hasanah et al., 2024). Fig.7d shows that the rate of color removal is directly proportional to the reaction temperature. Results indicated a 22% increase in color removal when the temperature was increased from 15 to above 45 °C. The increased temperature enhances the intermolecular thermodynamic driving forces, which in turn can accelerate the generation of free radicals and thus enhance the reactions between free radicals and pollutants (Meng et al., 2018).

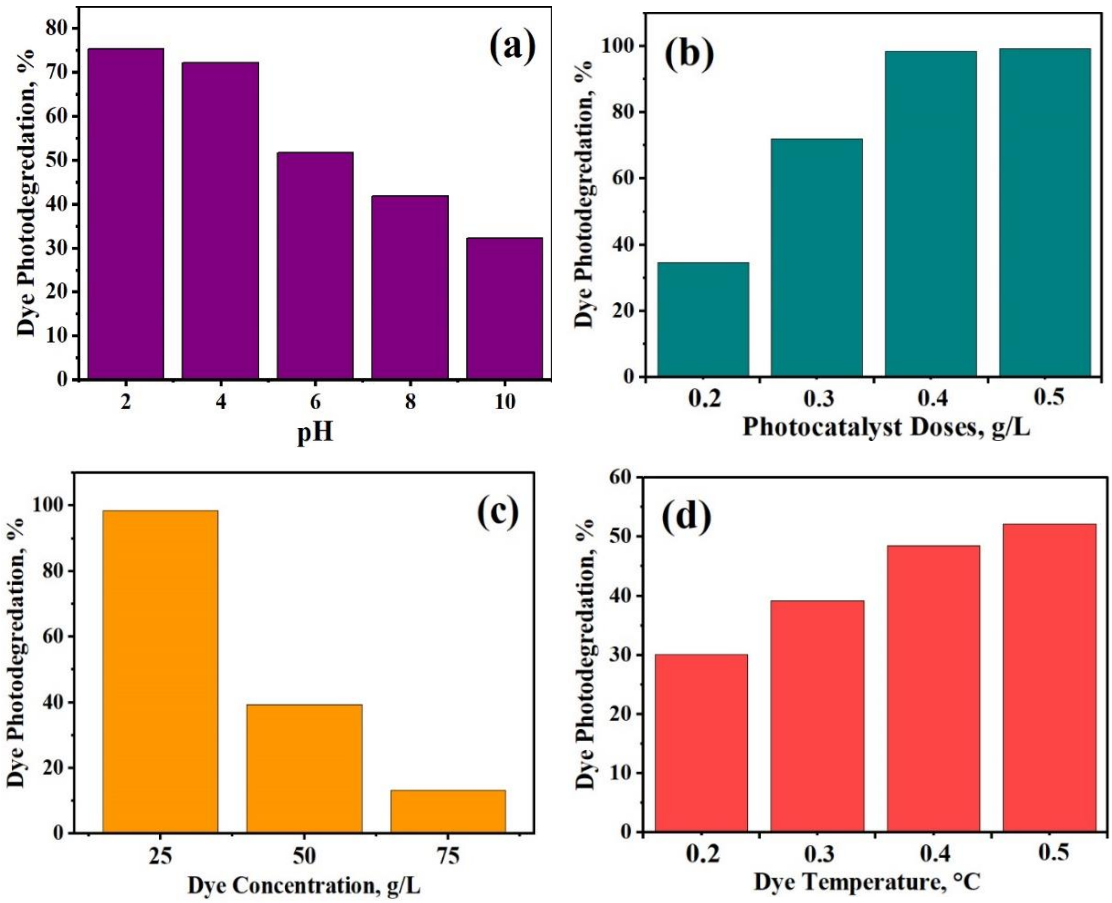


Fig. 7. Effect of a: various pH levels, b: photocatalyst dosages, c: dye concentrations, and d: dye temperatures on the photocatalytic degradation of Eosin Y dye

4. Conclusion

In this study, MXene nanosheets were employed as a co-catalyst to modify graphitic carbon nitride photocatalyst. The results demonstrated that the coupling of MXene nanosheets with graphitic carbon nitride significantly enhanced the photocatalytic performance of graphitic carbon nitride for the degradation of eosin Y dye. The optimal weight ratio of MXene nanosheets to graphitic carbon nitride was determined to be 7%. The findings of this research indicated that MXene nanosheets effectively improved the photocatalytic performance of graphitic carbon nitride in the removal of organic dyes from the environment.

Acknowledgments

The authors acknowledge the laboratory support they received from Shahid Beheshti and Tarbiat Modares Universities.

References

Ahmed, K.E., Kuo, D.-H., Zeleke, M.A., Zelekew, O.A. & Abay, A.K., 2019. Synthesis of Sn-WO3/g-C_3N_4 composites with surface activated oxygen for visible light degradation of dyes. *Journal of Photochemistry and Photobiology A: Chemistry*, 369, 133-141.

Alminderej, F.M. et al., 2023. Sustainable and Green Synthesis of Carbon Nanofibers from Date Palm Residues and Their Adsorption Efficiency for Eosin Dye. *Sustainability*, 15, 10451.

Azimi, E.B., Badiei, A., Sadr, M.H. & Amiri, A., 2018. A template-free method to synthesize porous G-C_3N_4 with efficient visible light photodegradation of organic pollutants in water. *Advanced Powder Technology*, 29, 2785-2791.

Barka, N., Abdennouri, M. & Makhfouk, M.E., 2011. Removal of Methylene Blue and Eriochrome Black T from aqueous solutions by biosorption on Scolymus hispanicus L.: Kinetics, equilibrium and thermodynamics. *Journal of the Taiwan Institute of Chemical Engineers*, 42, 320-326.

Bibi, S. et al., 2024. Synthesis of Cit-Fe3O4@TiO_2 Photocatalyst for the Degradation of Eosin-Y and Methylene Blue Dye. *Ceramics International*.

Bijari, M., Younesi, H. & Bahramifar, N., 2018. Optimization of activated carbon production by using K_2CO_3 at different temperatures for the

removal of Reactive Black 5 dye from aqueous solutions.

Chand, S. & Mondal, A., 2023. g-C_3N_4/ZrO2 composite material: A pre-eminent visible light-mediated photocatalyst for rhodamine B degradation in the presence of natural sunlight. *Ceramics International*, 49, 5419-5430.

Shahbazi, A., Dusti, S., Mahmoodi, B. & Bijari, M., 2024. Investigating the effect of various precursors in the synthesis and improvement of the photocatalytic performance of graphite carbon nitride in the degradation of Rhodamine B dye under visible light. *Journal of Color Science and Technology*.

Eftekharazam, P., Khalaji, A.D., Mokhtari, A. & Karimian, H., 2024. Synthesis, Characterization and Adsorption of Eosin Y Using New Chitosan Schiff Base Functionalized Malic Acid/Fe2O3 Composite. *Journal of Polymers and the Environment*, 1-10.

Haleem, A. et al., 2024. In-Depth Photocatalytic Degradation Mechanism of the Extensively Used Dyes Malachite Green, Methylene Blue, Congo Red, and Rhodamine B via Covalent Organic Framework-Based Photocatalysts. *Water*, 16, 1588.

Hasanah, A.U., Ikbal, M.S. & Tahir, D., 2024. Advances in Rare Earth-Doped ZnO Photocatalysts: Enhancing Photogenerated Electron-Hole Pairs for Radical Atom Generation. ChemBioEng Reviews.

Iqbal, M.A. et al., 2024. Advanced Photocatalysis as a Viable and Sustainable Wastewater Treatment Process: A Comprehensive Review. *Environmental Research*, 118947.

ISIRI, 2010. Drinking Water: Physical and Chemical Specifications (ISIRI No. 1053). Institute of Standards and Industrial Research of Iran (ISIRI) Tehran, Iran.

Kamari, S., Shahbazi, A. & Ghorbani, F., 2024. Adsorption optimization and modeling of Hg2+ ions from aqueous solutions using response surface methodology by SNPs–CS bionanocomposite produced from rice husk agro–industrial waste as a novel environmentally–friendly bionanoadsorbent. *Chemosphere*, 351, 141279.

Mahmood, A., Bilal, B., Naeem, Z. & Iram, S., 2021. Physical, chemical, and biological remediation techniques for textile effluents in context with developed and developing countries. *Rhizobiont in bioremediation of hazardous waste*, 409-441.

Meng, F. et al., 2018. Temperature dependent photocatalysis of g-C_3N_4, TiO2 and ZnO: Differences in photoactive mechanism. *Journal of Colloid and Interface Science*, 532, 321-330.

Shoran, S., Dahiya, S. & Sharma, A., 2024. Modification Strategies of Applications g-C_3N_4 for in Potential Photocatalysis. *Bioremediation for Sustainable Environmental Cleanup*, 292.

Skuse, C., Gallego-Schmid, A., Azapagic, A. & Gorgojo, P., 2021. Can emerging membrane-based desalination technologies replace reverse osmosis? *Desalination*, 500, 114844.

Taghiloo, A. & Larimi, A., 2023. A Review on Photocatalytic Conversion of CO2 Over Modified TiO2 Photocatalysts. *Iranian Chemical Engineering Journal*, 22, 121-134.

Wang, J. & Wang, S., 2022. A critical review on graphitic carbon nitride (g-C_3N_4)-based materials: Preparation, modification and environmental application. *Coordination Chemistry Reviews*, 453, 214338.

Xu, L., Chen, Y., Su, W., Cui, J. & Wei, S., 2023. Synergistic adsorption of U (VI) from seawater by MXene and amidoxime mixed matrix membrane with high efficiency. *Separation and Purification Technology*, 309, 123024.

Yan, B. et al., 2024. Research progress in the degradation of printing and dyeing wastewater using chitosan based composite photocatalytic materials. *International Journal of Biological Macromolecules*, 130082.

Zhang, X. et al., 2023. Graphite carbon nitride photocatalytic materials: A roadmap to modification for current and future water purification. *Journal of Environmental Chemical Engineering*, 110869.