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Degradation of Emamectin Benzoate by Chemical Catalytic Reaction of Graphitic Carbon Nitride Based Nanoparticle

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Abstract: In recent years, metal–organic frameworks (MOFs), a new class of porous crystalline materials, have attracted great attention as a promising candidate for environmental remediation and catalytic applications. In this study, g-C_3N_4@ZIF-8 containing graphitic carbon nitride (g-C_3N_4) was synthesized to be used as a catalyst for the catalytic degradation of Emamectin benzoate pesticide with $NaBH_4$. The synthesized g-C_3N_4@ZIF-8 were characterized by Fourier Transform Infrared Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy, Electron Dispersive X-ray and point of zero charge pH analysis. The degradation experiments of the synthetic pesticide were carried out in the presence of sodium borohydride ($NaBH_4$) used as reducing agent and the degradation times of the pesticide were monitored in UV-Vis Spectrophotometer (UV-Vis). The catalytic activity of the prepared composite has been tested in aqueous medium at room temperature across a broad spectrum. Degradation experiments were conducted at room temperature in the presence of $NaBH_4$, and the impact of various parameters such as pH, catalyst quantity, emamectin benzoate concentration, and $NaBH_4$ amount has been thoroughly investigated in detail. g-C_3N_4@ZIF-8 nanocomposite showed superior NaBH4-induced chemical catalytic activity in degrading the toxic pollutant emamectin benzoate pesticide in a very short time. Kinetic parameters (k) for the degradation reactions were calculated and upon exposure to g-C_3N_4@ZIF-8 nanoparticles, effective degradation of emamectin benzoate occurred in approximately 60 min. In the reduction reaction of emamectin benzoate pesticide with g-C_3N_4@ZIF-8, 70% degradation occurred within 60 min. This study provides insight into understanding nanoscale metal-organic frameworks (MOFs) in the removal of pesticides from wastewater.

Keywords: Catalysis, Graphitic carbon nitride, Degradation, Emamectin benzoate

Introduction

In recent years, the number of pesticides used in the environment and their production amount have increased significantly. The persistence and toxicity of pesticides have been considered as a problem for many years and the subject of various treatment methods for the removal of pesticides from wastewater will continue to be an area of research (Sajjadi et al., 2019). Despite their adverse effects on human health and the environment,

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pesticides are widely used chemicals in the agricultural industry (Nam et al., 2021). The use of pesticides plays an important role to ensure good crop yields, but it is known that if used for a long time and in large quantities, they constantly accumulate in crops, soil and water, posing a great threat to the environment and human life safety (Liu et al., 2023). Emamectin benzoate (EMB), derived from the avermectin family, is very stable and undergoes almost no degradation in the dark and remains stable in soil (Burkhard et al., 2015). Emamectin benzoate is a novel macrocyclic lactone insecticide derived from the avermectin family with a substitution of an epi-methylamino (-$NHCH_3$) group for a hydroxyl (-OH) group at the 4″-position on the disaccharide and is produced as a benzoate salt. In darkness, there is almost no degradation and emamectin is stable in soils (Zhu et al., 2011). Although it is widely used and poses a threat to the environment, there are very few studies investigating the removal of EMB (Zhou et al., 2016).

MOFs are a new category of porous materials that exhibit the high porosity, large surface area, and structural diversity required for catalysis. Compared to many types of MOFs, zeolitic imidazolate frameworks (ZIFs) are low cost and therefore stand out for wastewater treatment over other types of MOFs. here are many types of MOFs, but especially zinc-based ZIFs such as ZIF-8, which consists of Zn ions and 2-Methylimidazole, have recently attracted great attention in the field of catalysis due to their simple synthesis, high stability, and good adsorption performance with high surface area (Weng et al., 2023). The production of new composites with ZIF-8 combined with different supports has attracted great interest due to their promising properties and applications (Sarkarzadeh et al., 2023).

Graphitic carbon nitride, g-C_3N_4, can be synthesized in one step from various common carbon (C) and nitrogen (N) rich precursors such as urea, melamine, dicyanamide, etc. Adjusting the electronic structure of g- C_3N_4 can improve the mass transfer by improving the surface area of the catalyst and increase the number of active sites on the catalyst surface (Roy et al., 2021).

The catalyst was used for the emamectin benzoate reduction reaction in the presence of $NaBH_4$ as reducing agent at ambient conditions. The catalytic activity of the synthesized composite was tested in aqueous media at room temperature over a broad spectrum. Moreover, as the ZIF-8 structure and the g-C_3N_4 framework are highly tunable to incorporate many functionalities, this process has great scope to modify the catalytic potential of the composite catalyst. Overall, this study reveals the synthesized g-C_3N_4@ZIF-8 composite as an effective and promising candidate for the reduction of the pesticide emamectin benzoate under ambient conditions. In this study, the g-C_3N_4@ZIF-8 composite was successfully utilized for the reduction of emamectin benzoate using $NaBH_4$.

Experimental

Materials and Method

Melamine ($C_3H_6N_6$), emamectin benzoate, zinc nitrate tetrahydrate ($Zn(NO_3)_2 \cdot 4H_2O$) and 2-methylimidazole, sodium borohydride ($NaBH_4$), NaCl, HCl and NaOH were purchased from Sigma-Aldrich and used in the synthesis and catalysis stages. Experimental solutions were prepared using deionized water. Schimadzu UV-1700 model UV-visible spectrophotometer was used to determine the concentration of emamectin benzoate remaining without degradation in the removal experiments.

Synthesis and Application

Synthesis of g-C3N4 and g-C_3N_4@ZIF-8

In the synthesis of g-C_3N_4, 5 g of melamine powder was heated at 550 ˚C for 4 hours in a capped alumina crucible at a heating rate of 10 ◦C/min. A yellow g-C_3N_4 powder was obtained as a product. For g-C_3N_4@ZIF-8 synthesis, it was first obtained by the ZIF-8. Then a mixture of ZIF-8, a certain amount of melamine and ethanol was stirred in a magnetic stirrer for 20 minutes until a homogeneous distribution was reached. The mixture was heated at 70 °C to evaporate the ethanol. The resulting homogeneous mixture was placed in a 15 mL crucible for calcination and gradually heated (at a heating rate of 50 °C for 5 min) and kept at this temperature for 3.30 h after reaching 520 °C. The resulting product (g-C_3N_4@ZIF-8) was powdered and stored indoors(Zhao et al., 2020).

Emamectin Benzoate Removal

EMB solution (1,000 mg/L) was prepared by dissolving the calculated amount of pesticide in water and stored in the dark at 4 °C. During the working stages of EMB, 25 mg/L concentrations were prepared by appropriately diluting this solution. The working standard solution was prepared by diluting the calibration curve (0.05–25 mg/L) with water. All solutions were prepared fresh before use(Tariq et al., 2014). For the pesticide degradation experiments, 2 mL of the EMB solution prepared at the desired concentration and pH was taken and a certain amount g-C_3N_4@ZIF-8 was added, and then the required amount of 0.01 M $NaBH_4$ solution was added. The concentration of emamectin benzoate in the solution was determined by measuring the absorbance values of the resulting solution with a UV-Visible spectrophotometer at a wavelength of 240 nm. The ratio of the concentrations (C_t) obtained at the end of the contact period to the initial concentration (C_o) and k is the rate constant (mgL^{-1}min^{-1}) was calculated and the ln(C_t/C_o)-time graph was drawn(Asadi et al., 2022).

$$\frac{dCt}{dt} = -kCo \Rightarrow \ln\left(\frac{Ct}{Co}\right) = -kt$$

The effects of parameters such as contact time, pH, $NaBH_4$ concentration and catalyst amount on EMB removal were investigated and the optimum values of these parameters were found through removal experiments. The pH of the solution of both human drugs and animal and plant drugs plays a vital role in chemical catalytic decomposition reactions. In this study, the EMB solution was analyzed for both acidic and alkaline pH by adding appropriate amount of NaOH and HCl solution. The experiment was repeated for the sample keeping the pH of the EMB solution 3–10. The degradation efficiency of the catalyst was estimated using the formula:

$$Degaradation\ efficiency\ \% = \frac{\text{Ct}-\text{Co}}{Co}\text{x100}$$

C_0 is the EMB concentration before degradation and Ct is the EMB concentration after degradation at time t.

Results and Discussion

To investigate their catalytic activity, g-C_3N_4@ZIF-8 particles were used in the degradation of EMB in the presence of sodium borohydride. The progress of the catalytic degradation of EMB was monitored only by the decrease in optical density at the absorbance wavelength (240 nm). The effects of factors such as catalyst amount, pH, $NaBH_4$ concentration, contact time on EMB removal were investigated. The optimum values of these parameters used to provide the highest removal were found. The degradation efficiency of the pesticide was analyzed every 10 minutes over time. In order to examine the effect of other parameters, the parameter value for optimum removal was determined and experiments were carried out to examine the effect of another parameter using this optimum value. Also, experiments were conducted to see their efficiencies alone, without adding $NaBH_4$ solution to the mixture, and without adding g-C_3N_4@ZIF-8 to the mixture for the catalyst-free degradation process. $NaBH_4$ and g-C_3N_4@ZIF-8 were added to the mixture for the catalytic degradation process. As seen in Fig. 1b from the graph of ln*(C_t/C_o)-time*, a linear relationship was observed for the catalyst. The first-order rate constant, *k*, was determined from the slope of the line. The rate constant value was found to be 0.0104 min^{-1} for the synthesized composite.

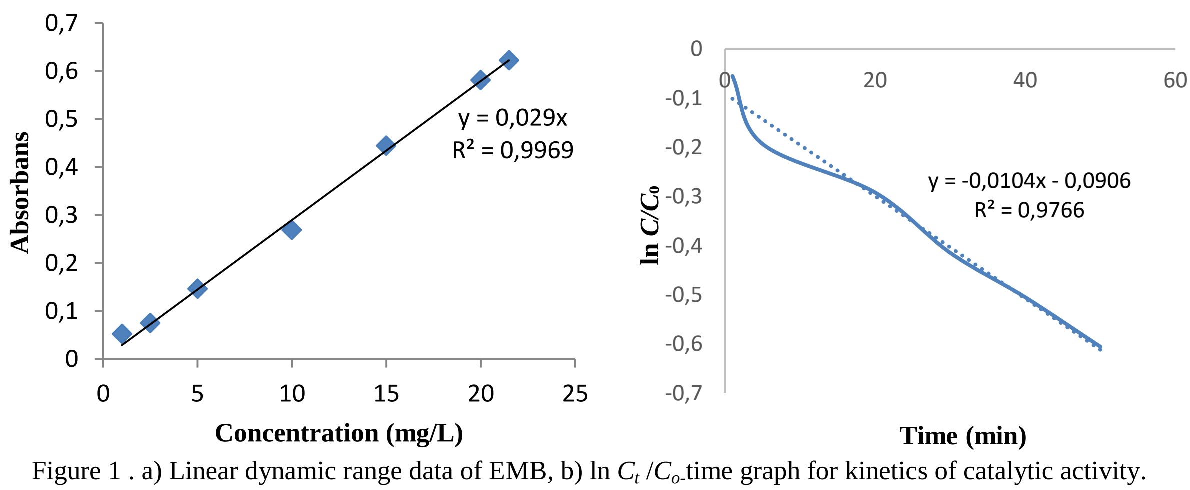

Figure 1 . a) Linear dynamic range data of EMB, b) ln C_t/C_o-time graph for kinetics of catalytic activity.

Effect of pH, $NaBH_4$ Concentration and g-C_3N_4@ZIF-8 Dosage

In any catalytic reaction, the surface of the catalysis can become positively charged or negatively charged depending on the solution pH relative to the zero charge point of the catalysis in question. This difference in surface charge may affect the degradation efficiency of reactive oxygen species. The effect of varying the initial solution pH (pH 3-10) was investigated(Edebali, 2023). In order to determine the effect of pH on EMB removal, catalytic degradation processes were applied to EMB solutions with pHs of 3, 6.5, 7.5, 10. The results obtained are presented graphically in Fig. 2. pH_{pzc} of the g-C_3N_4@ZIF-8 was found to be 7.45. That is, g-C_3N_4@ZIF-8 surface is positively charged at pH below pH_{pzc} and negatively charged at pH greater than 7.45. EMB molecules should be positively charged at pH=3, pH=6.5, neutral at pH=7.5, and negatively charged at pH=10. Pesticide removal rate in acidic and basic environments pH=7(Tariq et al., 2014). It was found to be lower compared to 5 and the minimum time required for the degradation of EMB pesticide was obtained at this pH =7.5. This situation can be explained by the surface charge of the nanoparticle, that is, its pH_{pzc} value, and the forms of the EMB pesticide at different pH values.

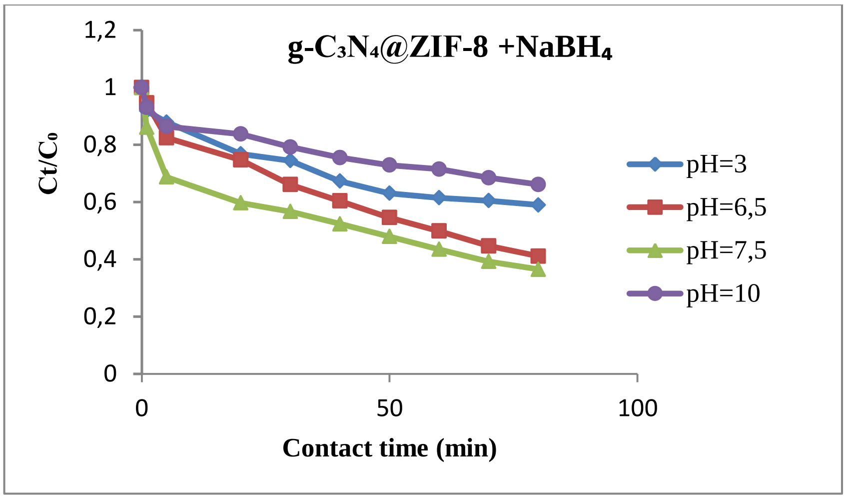

Figure 2. Effect of pH on EMB removal via catalytic degradation (Process parameters: $NaBH_4$ concentration 0.5 mM, g-C_3N_4@ZIF-8 dosage 1 g/L, EMB initial concentration 25 ppm)

In order to examine the effect of $NaBH_4$ concentration on EMB removal, both catalytic and non-catalytic degradation experiments were carried out and the results are presented graphically in Fig. 3. In order to examine the effect of g-C_3N_4@ZIF-8 dosage on the degradation of EMB, the results of degradation experiments using different dosages of EMB are presented in Fig. 4. The amount of particles used was chosen between 0.0 -1.5 g/L. It can be seen that the removal efficiencies obtained at separate dosages of the results are very close together. As a result of this study, a divided dosage of 2 mg was determined as the optimum dosage, in which optimum removal could be achieved, but maximum removal could not be achieved, in order to cut off excess material and examine other leaks in more detail.

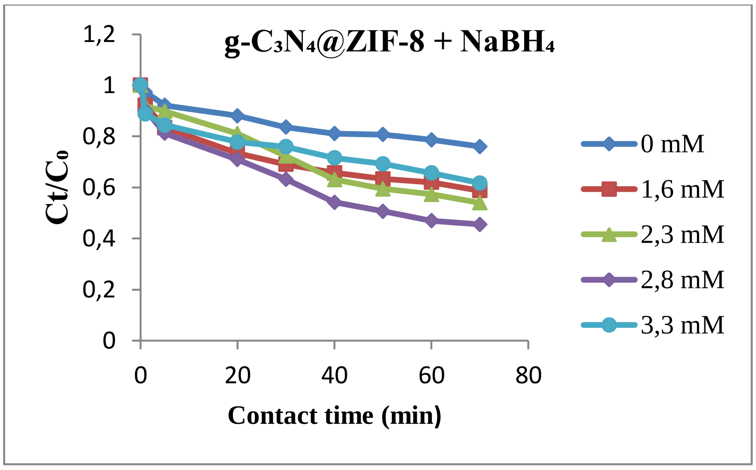

Figure 3. Effect of $NaBH_4$ concentration on EMB degradation (Process character: pH 6.5, g-C_3N_4@ZIF-8 dosage 2 mg, EMB starting point 25 ppm)

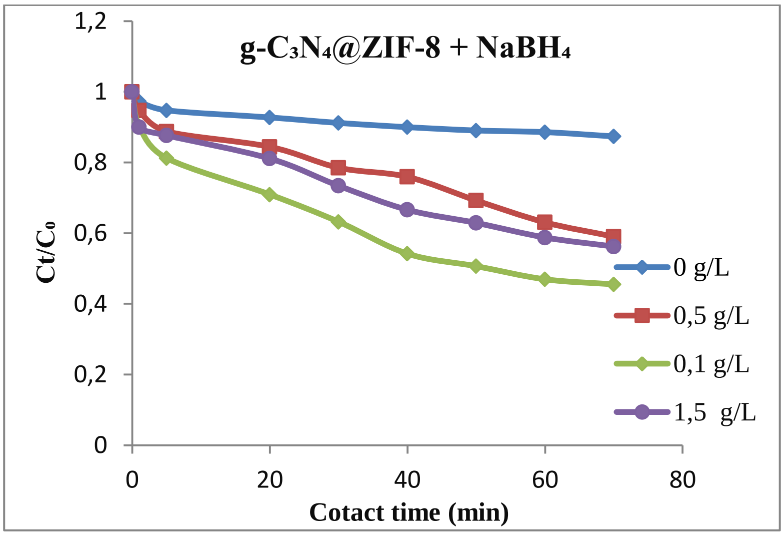

Figure 4. Effect of $g-C_3N_4$@ZIF-8 dosage on EMB degradation (Process character: pH 6.5, 800 µL $NaBH_4$, EMB starting point 25 ppm)

UV-vis Spectrum Analysis

Degradation experiments of EMB pesticide were carried out at room temperature in the presence of $NaBH_4$ as reductant using ZIF-8 and $g-C_3N_4$@ZIF-8 nanoparticles. In order to demonstrate the catalytic activity of EMB, experiments were carried out separately with both ZIF-8 and $g-C_3N_4$@ZIF-8 nanoparticles. Catalytic reductions of EMB were visualized by recording time-resolved UV-Vis absorption spectra at wavelengths in the range of 200-700 nm using UV-Vis. The spectra observed for the degradation of EMB in the presence of $NaBH_4$ are shown in Fig. 5-6. The characteristic absorption peak of EMB was observed at 240 nm (Mo et al., 2021). Fig. 7 shows the catalytic reduction of EMB with ZIF-8 in UV-Vis. When the reduction reaction of EMB with ZIF-8 is initiated, the peak intensity at 240 nm decreases depending on time. It has been observed that the catalytic activity of ZIF-8 under optimum conditions is very low Fig. 7. However, in the reduction reaction carried out with the $g-C_3N_4$@ZIF-8 nanoparticle under optimum conditions, 62% degradation occurred within 60 minutes. It was observed that the addition of $g-C_3N_4$ increased the catalytic activity of the particle in the degradation of EMB.

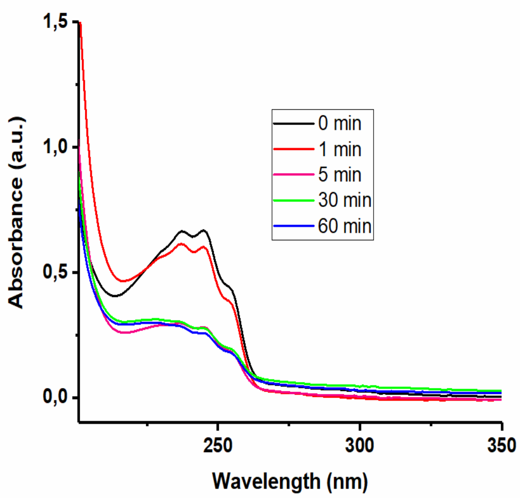

Figure 5. UV–vis absorption spectra of the degradation of EMB by $g-C_3N_4$@ZIF-8s in the presence of $NaBH_4$ (Process character: pH 6.5, 800 µL $NaBH_4$, $g-C_3N_4$@ZIF-8 dosage 2 mg, EMB starting point 25 ppm, **pH= 6,38**).

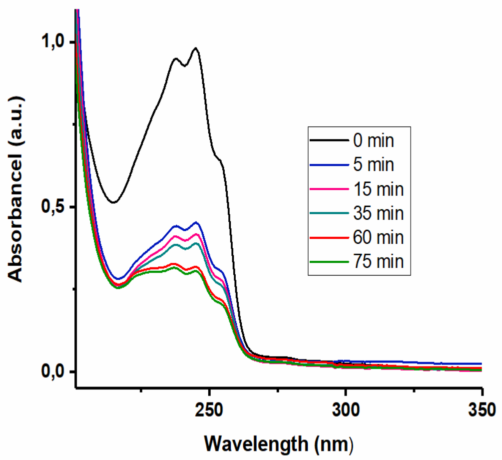

Figure 6. UV–vis absorption spectra of the degradation of EMB by $g-C_3N_4$@ZIF-8s in the presence of $NaBH_4$ (Process character: pH 6.5, 800 µL $NaBH_4$, $g-C_3N_4$@ZIF-8 dosage 2 mg, EMB starting point 25 ppm, **pH= 7,58**).

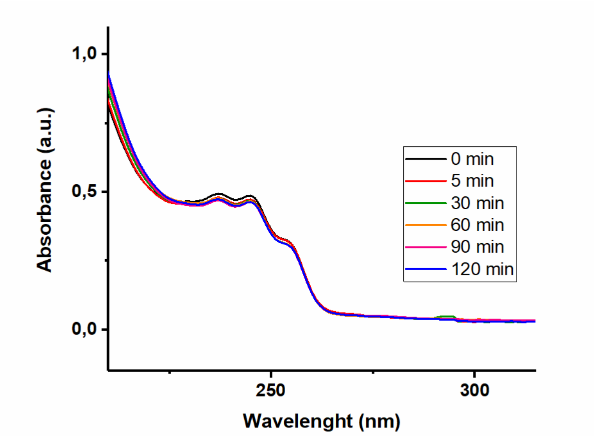

Figure 7. UV–vis absorption spectra of the degradation of EMB by ZIF-8s in the presence of $NaBH_4$ (Process character: 800 µL $NaBH_4$, EMB starting point 25 ppm, **pH 6.5**).

Fig. 6 shows the catalytic activity of EMB by g-C_3N_4@ZIF-8s in the presence of $NaBH_4$ in about one hour with UV–vis absorption spectra. As shown in Fig. 6, it can be clearly seen that the characteristic peak of EMB at 240 nm gradually decreases with the extension of time and remains almost unchanged after 70 min. Unfortunately, the spectrum of EMB did not completely disappear in the study, indicating that EMB molecules were not fully mineralized and a certain amount of intermediates were formed in solution. The EMB removal efficiency of g-C_3N_4@ZIF-8s was determined as 62%. This indicates that only a fraction of EMB molecules are mineralized by g-C_3N_4@ZIF-8. The effective removal of EMB molecules demonstrated that g-C_3N_4@ZIF-8s have great application potential in wastewater treatment.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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