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Visible-light-driven photocatalytic degradation of toxic insecticide thiamethoxam using Ni-doped PbS nanoparticles under visible light irradiation

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The widespread use of the toxic insecticide Thiamethoxam (TMX) poses significant risks to environmental and human health, necessitating effective remediation methods. This study reports the successful synthesis of novel Nickel-doped Lead Sulfide (Ni-PbS) nanoparticles via a straightforward co-precipitation approach for the visible-light-driven photocatalytic degradation of TMX. Structural analysis confirmed that the Ni-PbS nanoparticles crystallize in a face-centred cubic structure. Morphological examination revealed a flower-like architecture composed of nanosheets. Optical studies showed a narrowed band gap of 2.2 eV, confirming visible-light responsiveness. X-ray photoelectron spectroscopy (XPS) further verified the presence of Pb²⁺, S²⁻, and the successful incorporation of Ni²⁺ into the PbS lattice. The Ni-PbS catalyst demonstrated significantly enhanced photocatalytic activity, achieving 78.93% TMX degradation within 210 min with a rate constant of 0.02225 min⁻¹. Optimal performance was observed at pH 3 and a catalyst loading of 0.5 g/L. The catalyst also exhibited excellent stability and reusability over five consecutive cycles. Scavenger studies revealed that valence band holes (h⁺) and hydroxyl radicals (•OH) were the dominant reactive species driving the degradation. Overall, this work highlights Ni-PbS as a robust and efficient photocatalyst for the remediation of water contaminated with neonicotinoid insecticides.

KEYWORDS

PBS, Ni doping, photocatalysis, visible light, insecticide

1 Introduction

In the contemporary world, the rapid increase in human population has led to excessive use of pesticides and insecticides in agriculture to protect crops and improve yields. Although these chemicals improve agricultural yield, their persistence in the environment poses serious risks to aquatic ecosystems and human health (Díez et al., 2019). These chemicals are non-biodegradable and

recalcitrant, limiting the effectiveness of conventional removal methods and causing long-term accumulation in soil and groundwater (Singh et al., 2024).

Among these, TMX, a neonicotinoid insecticide derived from natural toxins, has attracted particular concern. Initially considered relatively safe for crop protection (Žabar et al., 2012), later studies revealed significant risks. TMX induces chronic toxicity in aquatic insects, with Chaoborids larvae showing high sensitivity, leading to ecological imbalance in freshwater systems (Finneg et al., 2017). It has also been implicated in pollinator mortality, with bee populations (*Apis mellifera*) experiencing high losses when exposed to TMX alone or in combination with fungicides such as tetraconazole (Li et al., 2023). Such mixtures have been shown to increase toxicity synergistically, raising concern over combined pesticide exposures (Finneg et al., 2017). Beyond ecological impacts, chronic human exposure has been linked to developmental and neurological effects. Toxicokinetic studies in rats suggested that TMX can accumulate in lung tissues at concentrations associated with developmental toxicity (Ayare and Gogate; Yi et al., 2023). A review by Qamar et al. further highlighted potential health risks, including skin and eye irritation, asthma, nervous system disorders, and hormonal imbalances leading to reproductive issues (Qamar et al., 2023).

Widespread detection of TMX in surface waters further underscores its environmental significance, with concentrations reported up to 4,315 ng/L globally (Mohamed et al.). In India, TMX is widely applied to crops such as *Capsicum annuum* L., *Vigna unguiculata*, and *Mangifera indica* (Bhattacharjee and Dikshit, 2016). Residue analysis revealed detectable amounts in food products and runoff waters: for example, ~0.13 mg/kg of TMX on cowpea 5 days after spraying (Reddy and Paul, 2021), and ~0.08–0.13 mg/kg on mango even after 20 days (Bhattacharjee and Dikshit, 2016). Runoff into waterbodies reached levels ranging from 199 ng/L to 13,264 ng/L (Sahoo and Patra, 2023), with peak concentrations during cropping seasons. Laboratory studies further confirmed the persistence of TMX in Indian soils, with half-lives ranging from 46.3 to 301 days depending on moisture, indicating its high environmental stability (Banerjee et al., 2008).

Several treatment strategies have been developed for TMX contaminated water. Adsorption using activated carbon, magnetic nanocomposites, and modified adsorbents has shown effectiveness, but performance is limited by saturation and regeneration requirements (de et al., 2022; Baskar et al., 2022). Advanced oxidation processes (AOPs), including Fenton reaction, ozonation, and electrochemical oxidation, have been successfully applied, though their high cost and energy demand limit large-scale implementation (García-Segura, 2022). Biological methods using bacterial strains such as *Pseudomonas aeruginosa* and *P. putida* offer environmentally friendly alternatives but exhibit slower degradation rates and require specific reaction conditions (Rani and Shanker, 2018; Singh and Basu, 2020). In contrast, photocatalytic oxidation provides an efficient and sustainable solution, utilizing light energy to mineralize pesticides into harmless products without producing secondary pollutants (Singh and Basu, 2020; Nayak et al., 2024). Semiconductors such as TiO_2 , ZnO, and g- C_3N_4 have been widely studied as photocatalysts due to their stability, reusability, and ability to achieve complete degradation (Kourkouvelis et al., 2021; Azim et al., 2018).

To enhance visible-light utilization, strategies such as bandgap engineering, morphology control, and heterojunction construction have been employed (Singh et al., 2020; Ahmad, 2025). Metal sulfides, especially PbS, are attractive candidates because of their narrow bandgap (bulk ~0.41 eV) and strong absorption in the visible region. Nano structuring and doping can further tune its bandgap up to ~2.0 eV, improving solar light harvesting (Bayram et al., 2025; Nam et al., 2014). Several PbS-based photocatalysts have already shown activity for degrading organic contaminants. For instance, Ni–PbS synthesized via chemical routes achieved significant degradation of methyl orange (89%) and methylene blue (75%) under visible light (et al., 2018; et al., 2016), while PbS–clinoptilolite nanocomposites reached 76% degradation of ciprofloxacin (et al., 2024). Other heterojunction systems, such as $\text{WO}_3/\text{g-C}_3\text{N}_4$, have also demonstrated high efficiency in pollutant removal (Singh et al., 2019).

In this report, Ni–PbS nanostructures offer a promising yet unexplored strategy for TMX remediation. Ni^{2+} incorporation not only reduces PbS particle size and tunes the bandgap but also enhances charge separation and reactive oxygen species generation (Horoz et al., 2018). Moreover, the co-precipitation synthesis route provides a simple and scalable approach to prepare such doped sulfide nanoparticles. Previous studies have reported the advantages of Ni doping and PbS-based nanostructures for enhanced photocatalysis. For instance, Ni-modified g- C_3N_4 photocatalysts exhibited improved charge separation and visible-light activity (She et al., 2019), while PbS nanostructures have been explored for their tunable optical properties and photocatalytic behaviour (Parveen et al., 2018). However, these studies did not address the degradation of TMX, nor did they investigate Ni doping in PbS specifically for environmental remediation.

The novelty and importance of this study can be summarized as follows: Ni–PbS nanoparticles were synthesized through a simple co-precipitation method and, for the first time, applied for TMX degradation under visible light. Ni doping effectively tuned the band gap of PbS and enhanced charge separation, resulting in significantly improved photocatalytic activity and stability compared to pristine PbS. This work therefore establishes Ni–PbS as a green, cost-effective, and sustainable strategy for the removal of TMX from contaminated water.

In contrast, the present work introduces Ni–PbS nanoparticles synthesized via a simple co-precipitation route and applies them, for the first time, to the visible-light-driven degradation of TMX. This dual novelty targeting a highly persistent neonicotinoid pollutant and demonstrating band-gap tuning through Ni incorporation differentiates our study from previous reports and highlights its environmental relevance.

2 Experimental

2.1 Materials

Nickel Sulphate Extra pure hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) ($\geq 99.86\%$) and Sodium Sulphide hydrate flak ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$) ($\geq 60.0\%$) and sodium hydroxide (NaOH) was purchased from Loba Chemic Pvt. Ltd. Lead acetate trihydrate ($(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$)

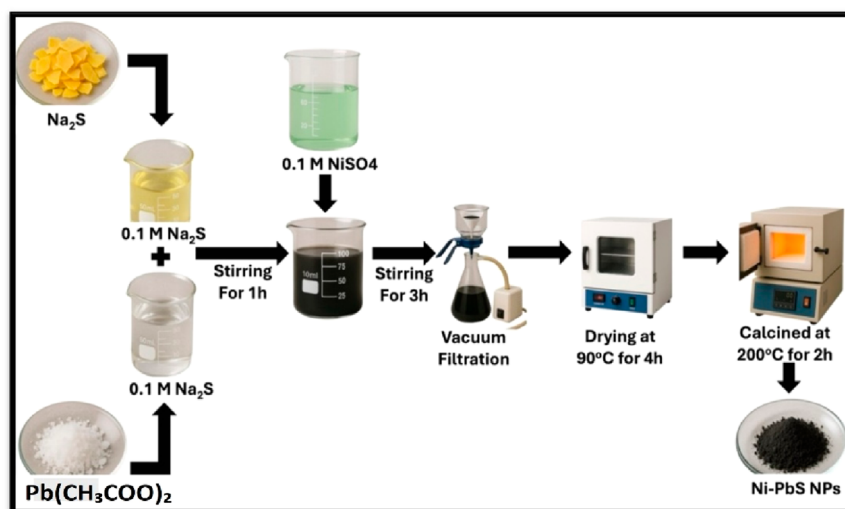


FIGURE 1
Schematic representation for the synthesis of Ni-PbS nanoparticles.

(≥99.96%) was purchased from Qualikems fine Chem Pvt. Ltd. All the chemicals were used as received without further purification.

2.2 Synthesis of Ni doped PbS

Ni doped PbS catalyst was synthesized by using chemical synthesis route. Initially, 0.1 M lead acetate dissolved in 25 mL water and in other beaker, 0.1 M sodium sulfide was dissolved in 25 mL water. Both the solution was sonicated for 15 min and then mixed both solutions and further stirred for 1 h. Subsequently, a 0.2 M solution of NaOH in 10 mL of water was prepared and added to the mixture. The resulted solution was stirred for 3 h

at room temperature. In parallel, a separate solution of 0.1 M NiSO_4 was prepared in 50 mL of water and stirring the mixture for 30 min. This NiSO_4 solution was then carefully mixed with the previously prepared mixture and stirred for an additional 3 h to facilitate the formation of Ni-PbS. After 3 h reaction period, the resulting solution underwent filtration to isolate the Ni-PbS product. The product was then washed thoroughly with distilled water and dried in a hot air oven for 3–4 h. Finally, the crystals of Ni-PbS were collected and subjected to calcination at 200 °C for 2 h. For the synthesis of PbS, the above process was repeated without the addition of NiSO_4 . Figure 1 shows the schematic diagram for the synthesis of Ni-PbS.

2.3 Characterization techniques

The synthesised particles were analysed by X-ray powder diffraction (XRD) patterns recorded by Bruker D8 Advance. The surface morphology was examined by scanning electron microscopy (SEM) images using FE-SEM: JEOL JSM-7610F plus. The adsorbents BET surface area was measured by a BET surface area analyser using Bel, Japan, Inc., Microtec BELSORP MINI-II. The elemental composition of the synthesized nanomaterials was analysed through Energy-Dispersive X-ray System (EDS) carried out in an OXFORD EDS LN2. X-ray Photoelectron Spectroscopy (XPS) for the samples was investigated by Nexsa G2; Surface Analysis System (Thermo Scientific). The diffuse reflectance spectroscopy (DRS) of the samples were recorded using a Jasco V-750 spectrophotometer.

2.4 Photocatalytic degradation

The photocatalytic experiments for the degradation of TMX were done in visible light (CFL lamp, 70W, 125W/m). The stock

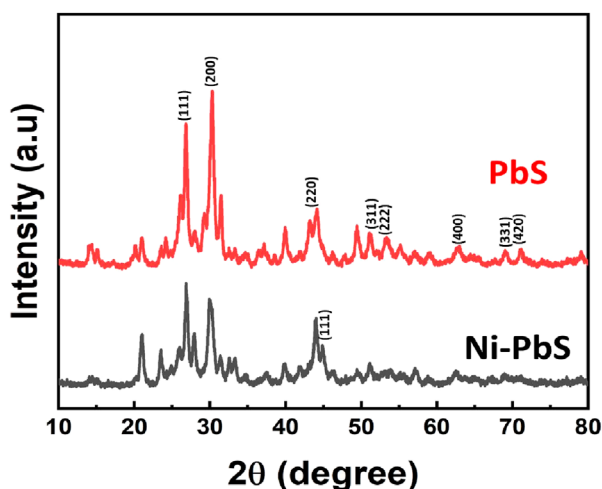


FIGURE 2
XRD patterns of pure PbS and Ni-PbS nanoparticles.

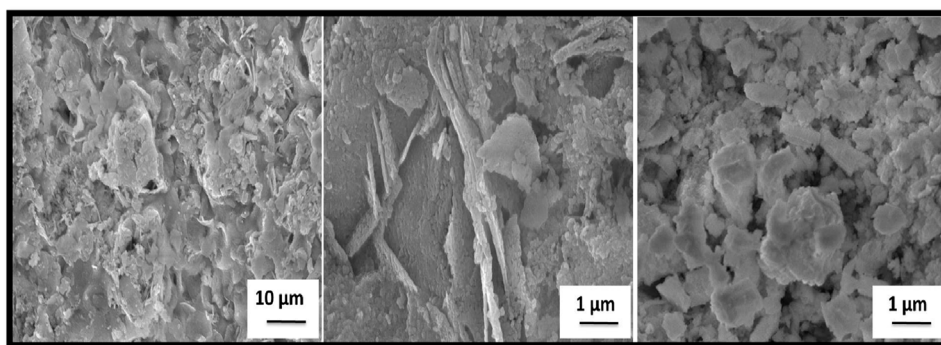


FIGURE 3
FE-SEM images of Ni-PbS nanoparticles.

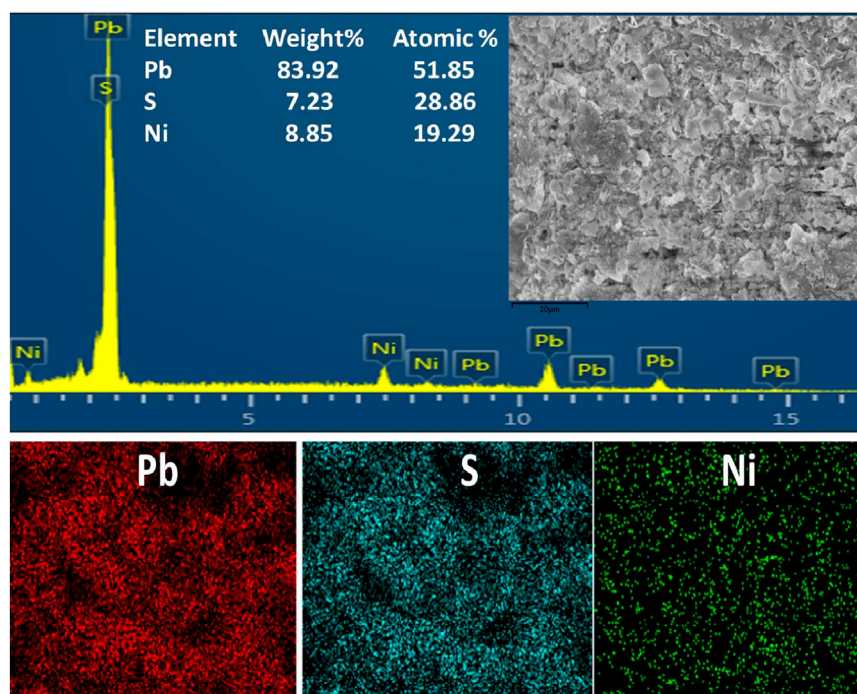


FIGURE 4
EDX spectrum and mapping for Ni-PbS nanoparticles confirming the presence of Pb, S, and Ni elements.

solution of 5 ppm TMX was prepared in a 1 L water solution. For each experiment, 10 mL of solution was taken with the desired amount of sample and stirred under the light for a fixed treatment time. The absorbance of the treated solution was examined using a UV-visible spectrophotometer at $\lambda_{\max} = 250$ nm. The degradation efficiency was calculated by the following Equation 1:

$$\text{Degradation \%} = \left\{ \frac{(C_0 - C)}{C_0} \right\} \times 100 \quad (1)$$

Where C_0 and C are the initial and final concentrations of the solution.

3 Results and discussion

3.1 Characterization results

The XRD patterns of the as-synthesised PbS nanoparticles (Figure 2) exhibit broad diffraction peaks typical of nanocrystalline materials, which can be indexed to the face-centred cubic (fcc) phase of PbS. The main peaks appear at 2θ values of $\sim 24.9^\circ$, 26.9° , 30.5° , 40.0° , 45.9° , 50.2° , 62.7° , 71.7° , and 79.2° , corresponding to the (111), (200), (220), (311), (222), (400), (331), and (420) planes, respectively (Salavati-Niasari et al., 2008), in good agreement with standard JCPDS data, confirming the formation of phase-pure PbS.

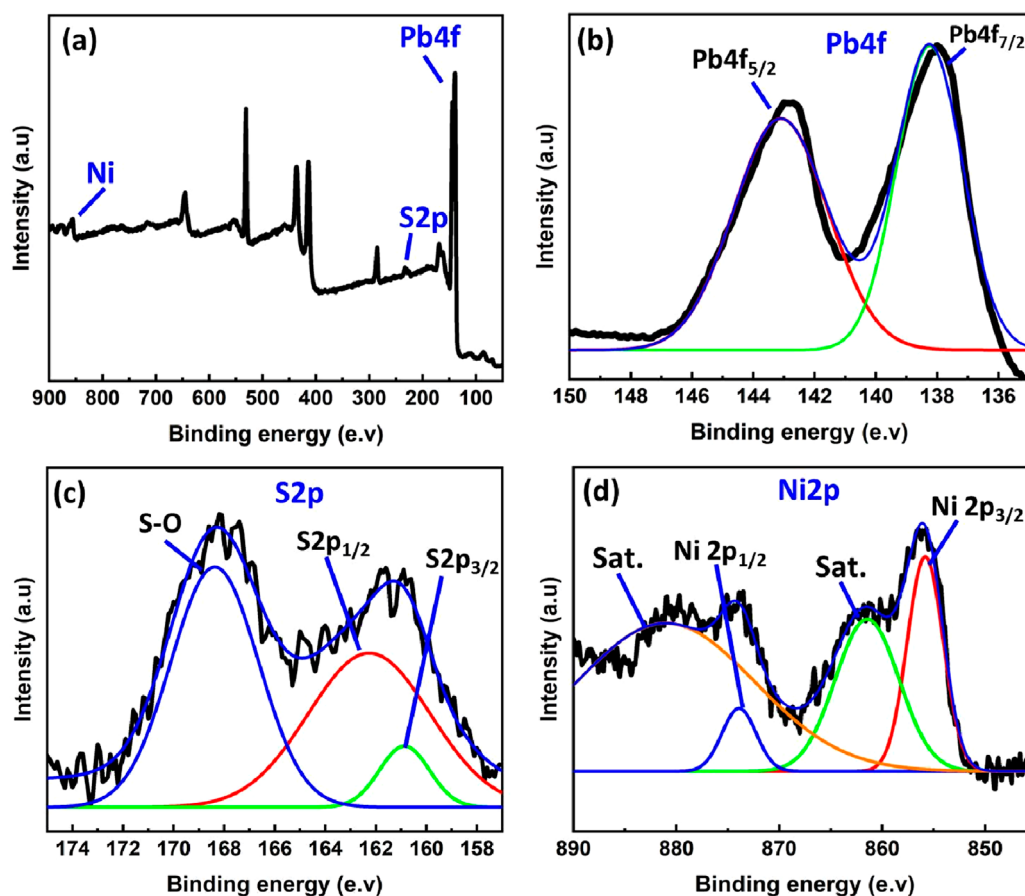


FIGURE 5

(a) Full XPS spectrum for Ni-PbS and deconvoluted XPS spectrum for (b) Pb 4f, (c) S2p and (d) Ni2p.

The broadness of these peaks reflects the small crystallite size, which enhances surface-to-volume ratio and benefits photocatalysis. For Ni-PbS, the diffraction pattern retains the fcc structure but shows subtle modifications: an additional signal near the (111) plane and slight peak shifts, without any secondary phases related to Ni or NiO (Ubale, 2012; Mohammed et al., 2018), indicating successful Ni incorporation into the PbS lattice rather than forming separate phases. A notable change is the shift in preferential orientation from the (200) plane in pristine PbS to the (111) plane in Ni-PbS, along with variations in relative peak intensities. These changes, together with shifts toward higher 2θ values, arise from lattice contraction due to substitution of larger Pb^{2+} ions (~ 1.19 Å) with smaller Ni^{2+} ions (~ 0.69 Å). This contraction modifies interplanar spacing, crystallite growth, and electronic structure while preserving the overall fcc framework (Ahmad and Niaz). Such structural tuning by Ni doping is directly linked to enhanced charge separation and improved photocatalytic activity.

FE-SEM was employed to investigate the microstructural features of the samples, with particular attention to morphology. Figure 3a presents the SEM micrographs of Ni-PbS, which reveal an uneven distribution of particles with varying sizes and shapes. In Figure 3b, taken at the same magnification but from a different region, another dominant morphology

is observed. The structure is primarily composed of thin, flat nanoflakes or nanosheets (Kuppan et al., 2014), which tend to agglomerate into larger three-dimensional clusters resembling “flower-like” or “rosette-like” architectures. Such hierarchical self-assembly, frequently reported for wet chemical synthesis methods, generates a material with a significantly enhanced effective surface area (Kumar et al., 2016). This high surface area facilitates greater adsorption of TMX molecules and provides more active sites for photocatalytic reactions. Furthermore, the interconnected flake-like network promotes light harvesting and efficient charge transport, thereby reducing electron-hole recombination. Although this morphology is commonly observed in PbS-based nanostructures, the distinctive aspect of the present work lies in the synergistic role of Ni incorporation. Nickel doping introduces lattice distortions and modifies the electronic structure of PbS, thereby complementing the surface-driven effects of the nanoflake morphology and leading to enhanced visible-light photocatalytic degradation performance.

Figure 4 illustrates the EDX and mapping of Ni-PbS, which demonstrates the presence of lead, sulphur, and nickel elements in the sample. The weight percentages for Pb, S, and Ni are 83.92%, 7.23%, and 8.85%, respectively. Moreover, all the elements have homogeneous distribution throughout the catalyst surface.

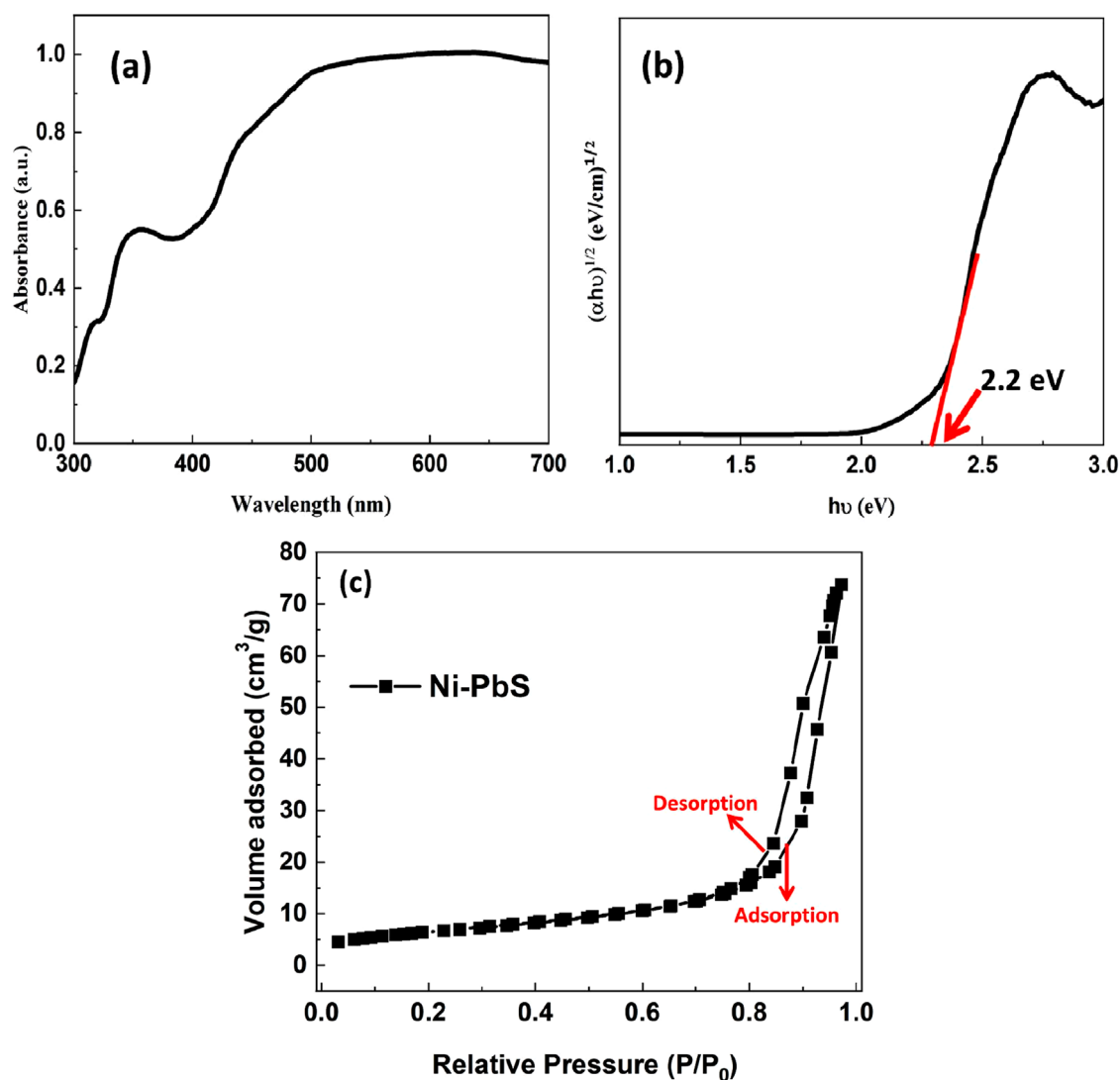


FIGURE 6
UV-Vis absorption spectra of PbS and Ni-PbS nanoparticles (a) and Tauc plot (b) of Ni-PbS and (c) N₂ sorption isotherms for Ni-PbS.

Figure 5a displays the whole XPS survey spectrum of Ni-PbS, highlighting the distinctive peaks of Pb4f, S2p, Ni2p, and O1s. The S2p peak is clearly seen in the proper binding energy range (158–174 eV) after the apparent mismatch in the survey scan has been fixed. The Ni-doped PbS sample's elemental valence states and chemical makeup were thoroughly examined. Pb²⁺ in PbS is characterised by two distinct peaks at ~138.0 eV (Pb 4f_{7/2}) and ~142.9 eV (Pb 4f_{5/2}) in the high-resolution Pb 4f spectrum (Figure 5b). Deconvoluting the S2p spectrum (Figure 5c) revealed two primary components: a broader pattern at ~168.5 eV assigned to surface-oxidized sulphate (S–O) species, and a doublet at ~161.0 eV corresponding to S²⁻ in PbS (Saraidarov et al., 2007). A Ni 2p_{3/2} peak at ~855.5 eV with a corresponding shake-up satellite is visible in the Ni2p region (Figure 5d), indicating the Ni²⁺ oxidation state and the successful incorporation of Ni into the PbS lattice (Ohno, 2007).

The optical properties of the Ni-doped PbS (Ni-PbS) sample were investigated using UV-Vis Diffuse Reflectance Spectroscopy

(DRS). The absorbance spectrum, shown in Figure 6a, reveals that the material exhibits strong and broad optical absorption across the entire visible light region (400–700 nm), which is characteristic of a narrow band gap semiconductor. To determine the optical band gap (E_g) from this data, the Tauc relation was employed. Figure 6b shows the Tauc plot, where $(\alpha h\nu)^{1/2}$ is plotted against the photon energy ($h\nu$). The use of the exponent 1/2 indicates that the optical transition in the Ni-PbS material is an indirect allowed transition. By extrapolating the linear portion of the curve to the energy axis (where $(\alpha h\nu)^{1/2} = 0$), the optical band gap of the sample is determined. As indicated on the plot, the band gap (E_g) for the Ni-PbS nanoparticles was found to be 2.2 eV. This value is significantly larger than that of bulk PbS (~0.41 eV), a phenomenon known as a “blue shift,” which is attributed to the quantum confinement effect in the nanoparticles and the influence of Ni doping on the electronic structure of PbS (Maharaz et al., 2018).

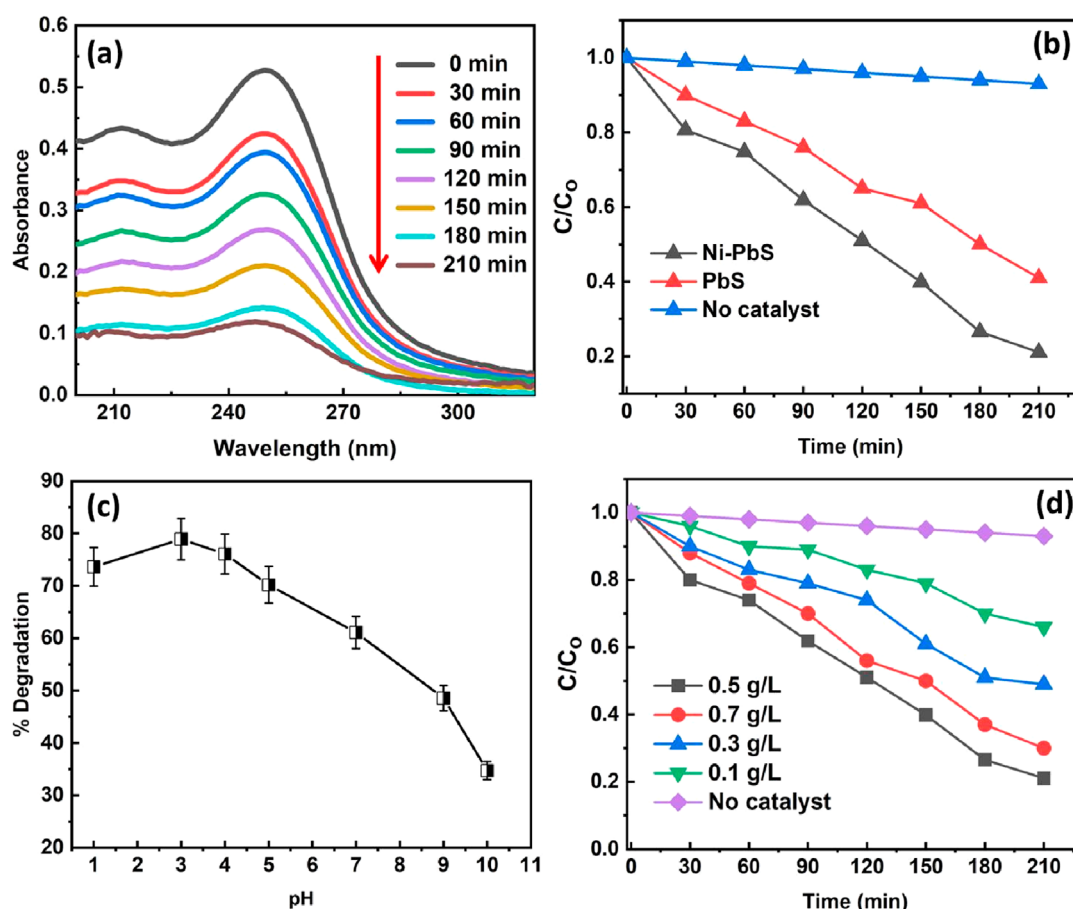


FIGURE 7 (a) UV-visible spectrum, (b) degradation rate using different samples (c) effect of pH and (d) catalyst amount on the photodegradation of TMX (experimental conditions: catalyst loading-0.5 g/L, pH 3, Temperature- Room temp).

The mesoporous structure of the material is confirmed by the nitrogen adsorption-desorption isotherm of Ni-PbS nanoparticles, as shown in Figure 6C. The isotherm displays a typical type IV curve with a discernible H3 hysteresis loop in the relative pressure range of 0.8–1.0. This clearly signifies the mesoporous nature of the material. The significant increase in adsorption volume at higher relative pressures is caused by capillary condensation inside mesopores. A significant number of active sites for catalytic processes are provided by Ni-PbS, which has an estimated BET surface area of 23.3 m²/g. The parallel adsorption and desorption branches further demonstrate the existence of slit-like pores, which are commonly associated with nanoparticle agglomerates. Such surface area is advantageous for photocatalytic applications as it enhances light absorption. It also permits easy diffusion of reactants and enables effective charge separation. These factors collectively improve the degradation process.

3.2 Photocatalytic activity

Figure 7A shows the UV-Visible spectrum for the TMX removal using Ni-PbS at different time intervals. This figure displays the time-dependent UV-Vis absorption spectra of the TMX solution during

the photocatalytic process using the Ni-PbS catalyst. The spectra, recorded at intervals from 0 to 210 min, show a characteristic absorption peak for TMX at approximately 254 nm. As the reaction progresses under light irradiation, the intensity of this peak systematically decreases. This reduction in absorbance is a direct indication of the diminishing concentration of TMX in the solution, signifying that its molecular structure, particularly the chromophore responsible for UV absorption, is being broken down. The consistent decrease over time provides clear qualitative evidence of the successful and continuous degradation of the pesticide by the Ni-PbS photocatalyst. The absorbance peaks decrease with the treatment time of the TM solution under visible light, which shows the effective degradation of TMX using Ni-PbS.

The photocatalytic efficiency of Ni-doped PbS against pure PbS and a control experiment with no catalyst (photolysis) is illustrated in Figure 7b. The plot of normalised concentration (C/C_0) versus time shows that in the absence of a catalyst, TMX undergoes negligible degradation, indicating its stability against direct photolysis. While pure PbS shows moderate photocatalytic activity, achieving approximately 58.63% degradation ($C/C_0 \approx 0.4$) after 210 min, the Ni-PbS sample demonstrates significantly superior performance, degrading about 78.93% of the TMX ($C/C_0 \approx 0.2$) in the same period. The improved performance is likely

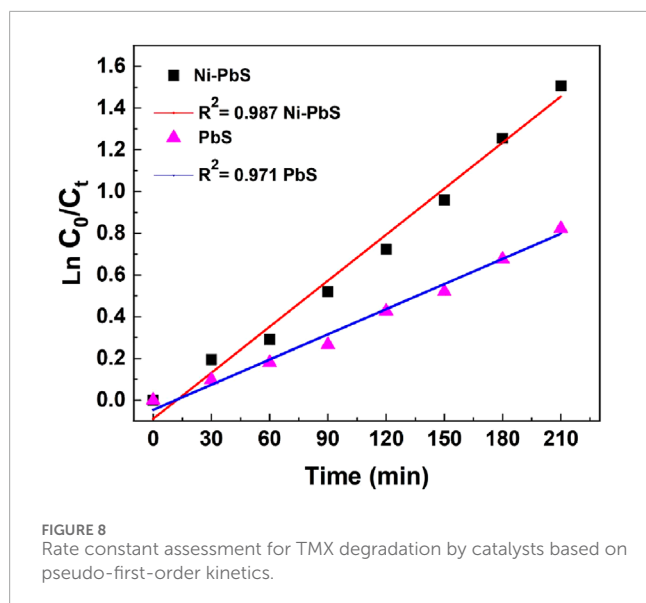


TABLE 1 Rate constants of various catalysts for TMX degradation.

Sample	Rate constant (k, min ⁻¹)
PbS	0.01261
Ni-PbS	0.02225

due to nickel helping to separate charges more effectively, reducing recombination and boosting photocatalytic activity (Cui et al., 2024; Yao and Zhou, 2024). This improved charge separation leads to a higher quantum yield and, consequently, a more efficient degradation process (M'Bra et al., 2019).

Figure 7c illustrates the profound impact of the initial solution pH on the photocatalytic degradation efficiency of TMX. The plot reveals that the process is highly pH-dependent, with optimal performance occurring in acidic conditions. The degradation percentage is low at pH 1, increases dramatically to a maximum of nearly 78.93% at an optimal pH of 3, and then steadily declines as the solution becomes less acidic and more alkaline. The low performance at pH 1 could be due to excessive protonation, which may suppress radical formation or reduce TMX adsorption. This behaviour is governed by the surface charge of the photocatalyst and the speciation of the pollutant. At the optimal pH, the electrostatic interaction between the catalyst surface and the TMX molecules is most favourable, maximising adsorption onto the catalyst's active sites. Deviations from this optimal pH likely led to repulsive forces or changes in the catalyst's surface chemistry, hindering the reaction rate (Krishnan et al., 2021).

The effect of the catalyst amount from 0.1 to 0.7 g/L on the photodegradation of TMX can be seen in Figure 7d. The highest degradation% (78.93%) was obtained by using a 0.5 g/L catalyst amount. However, the degradation decreases by increasing the catalyst amount to 0.7 g/L. This may be due to the agglomeration of catalyst particles by increasing the catalyst amount. It provides a limited surface area and fewer active sites during

the photodegradation reaction, which decreases the photocatalytic degradation (Mohagheghian et al., 2015).

The pseudo-first-order kinetic model, represented as $\ln(C_0/C_t)$ vs. time in Figure 8, was used to analyse the photocatalytic degradation kinetics of TMX over catalysts. The degradation process follows first-order kinetics, as confirmed by the linear fitting of the experimental data, which had strong correlation with regression coefficients (R^2) of 0.987 for Ni-PbS and 0.971 for PbS. Ni doping effectively improves the charge separation and lowers recombination. It also produces more reactive species, as evidenced by the steeper slope seen for Ni-PbS. This indicates a larger rate constant compared to PbS. Ni-PbS shows the highest rate constant of 0.02225 min^{-1} , whereas undoped PbS exhibits 0.01261 min^{-1} (Table 1). The higher photocatalytic efficiency of Ni-PbS over undoped PbS is further supported by this enhanced kinetic performance.

The rate constant associated with each individual catalyst may be computed through the employment of the following equation:

$$\ln(C/C_0) = -kt$$

Here C_0 and C are the concentrations of the TMX at $t = 0$ and at a selected time (t , min).

Figure 9a illustrates the stability and reusability of the Ni-PbS photocatalyst over five consecutive degradation cycles. The results demonstrate excellent operational stability, which is a critical factor for the practical and economic viability of a photocatalyst. In the first cycle, the catalyst exhibited its highest efficiency, achieving approximately 79% degradation of the target pollutant. In subsequent cycles, there is a very slight and gradual decrease in performance, with the degradation efficiency dropping to approximately 71% by the fifth cycle. This minor loss of activity (less than 10% over five runs) can be attributed to factors such as the inevitable loss of a small amount of catalyst mass during the recovery and washing process between cycles, or minor surface deactivation (Ajibade et al., 2021). Overall, the ability of the catalyst to maintain high efficiency over repeated uses confirms that Ni-PbS is a robust and highly reusable material, promising for sustainable water treatment applications.

Figure 9b presents the results of scavenger experiments designed to identify the primary reactive oxygen species (ROS) responsible for the degradation of TMX. The dominant degradation mechanism can be elucidated by introducing specific chemical scavengers that selectively quench different ROS. The control experiment with no scavenger shows the maximum degradation of 78.93%. Introducing Benzoquinone (BQ), a scavenger for superoxide radicals ($O_2^{\bullet-}$), causes a moderate drop in efficiency to ~65%. A more significant decrease to ~59% is observed with Isopropyl Alcohol (IPA), a well-known scavenger of hydroxyl radicals ($\bullet OH$). The most drastic inhibition occurs with the addition of Methanol, which reduces the degradation to ~42%. Methanol is an efficient scavenger of photogenerated valence band holes (h^+) (Mureithi et al., 2022). These results suggest that while multiple species are involved, the degradation of TMX is primarily driven by direct oxidation via valence band holes (h^+), followed by attack from hydroxyl radicals ($\bullet OH$). Superoxide radicals ($O_2^{\bullet-}$) also play a role, but to a lesser extent. Therefore, it can be concluded that the valence band holes (h^+) are the most dominant reactive species responsible for TMX degradation under visible light irradiation.

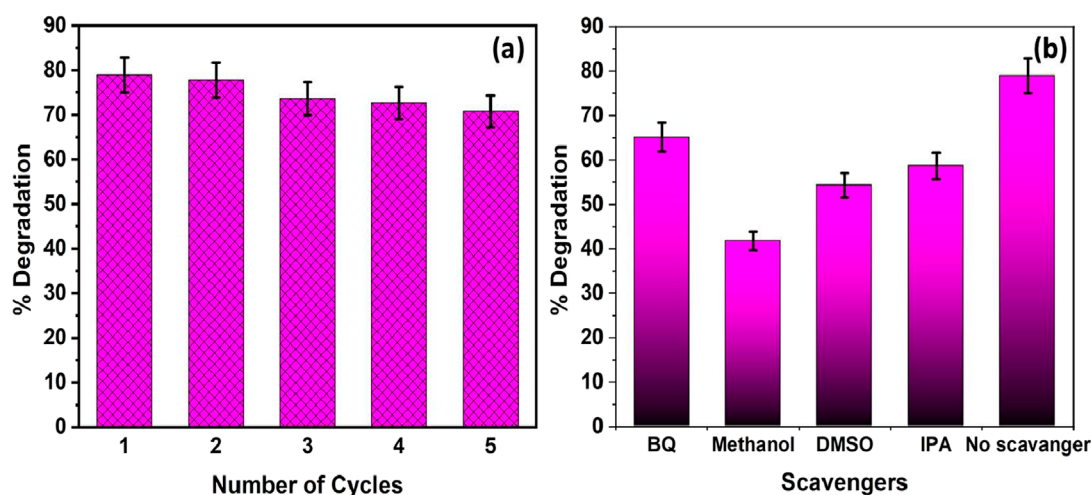


FIGURE 9 (a) Reusability studies for five consecutive cycles and (b) effect of scavengers on the TM degradation efficiency using Ni-PbS catalyst (experimental conditions: catalyst loading-0.5 g/L, pH 3, Temperature- Room temp).

TABLE 2 Comparison table for the degradation studies of the present work with the literature.

Catalyst	Pollutant	Light source	% Degradation	Ref.
Ni-PbS	MB	Ultraviolet	75	Liu et al. (2016)
PbS-NCP	CPX	Ultraviolet	76	Gharbalifard et al. (2024)
PbS	RhB	Ultraviolet	50.58	Oluwalana and Ajibade (2021)
Ni-MoO ₃	MB	Ultraviolet -Visible	77	Rajiv Chandar et al. (2021)
Ni-WO ₃	Tetracycline	Visible	76	Phuong et al. (2023)
S doped Ag ₃ PO ₄	TM	Visible	39.94	Lee et al. (2020)
CuO	TM	Visible	48.65	Jansanthea et al. (2021)
PbS/Ni ₂ P	MB	Ultraviolet	75	Liu et al. (2016)
Bi-PbS	MB	Visible	70.92	Jeya et al. (2023)
Cu-Sr-PbS	MB	Ultraviolet	74.02	Jeya et al. (2023)
Ni-PbS	TM	Visible light	78.93	Present Study

Table 2 shows the comparison of the catalytic activity of synthesized Ni-PbS with other reported catalysts for the removal of pollutants in aqueous solution. It has been seen that very few studies contain the degradation of colourless pollutants using catalysts. In the present study, Ni-PbS shows the maximum degradation of 78.93% in visible light for colourless pollutant, i.e., TMX.

A mechanism for TMX degradation across Ni-PbS ($E_g \approx 2.22$ eV) is proposed in Figure 10. When exposed to visible light, Ni-PbS produces e^- (CB) and h^+ (VB). While holes oxidise adsorbed H_2O/OH^- to create hydroxyl radicals ($\bullet OH$) or directly oxidise adsorbed TMX, photogenerated electrons go to the surface and reduce O_2 to make superoxide radicals ($O_2^{\bullet -}$). The gradual cleavage of TMX into intermediates and ultimate mineralisation is facilitated

by both direct hole oxidation and radical species. Crucially, XRD and XPS data show that Ni is incorporated into the PbS lattice as Ni^{2+} . This incorporation probably adds defect/charge-transfer sites that help trap electrons and transfer electrons across the interface to O_2 , which inhibits bulk e^-/h^+ recombination and increases the production of ROS. Benzoquinone produces moderate inhibition, indicating $O_2^{\bullet -}$ is involved but less critical; IPA ($\bullet OH$ scavenger) produces significant inhibition, indicating a major role for $\bullet OH$; and methanol (hole scavenger) produces the greatest inhibition, confirming h^+ -driven oxidation is dominant, according to scavenger experiments. Ni-induced charge separation and increased surface ROS flux work together to explain how Ni-PbS performs better photocatalytic than undoped PbS.

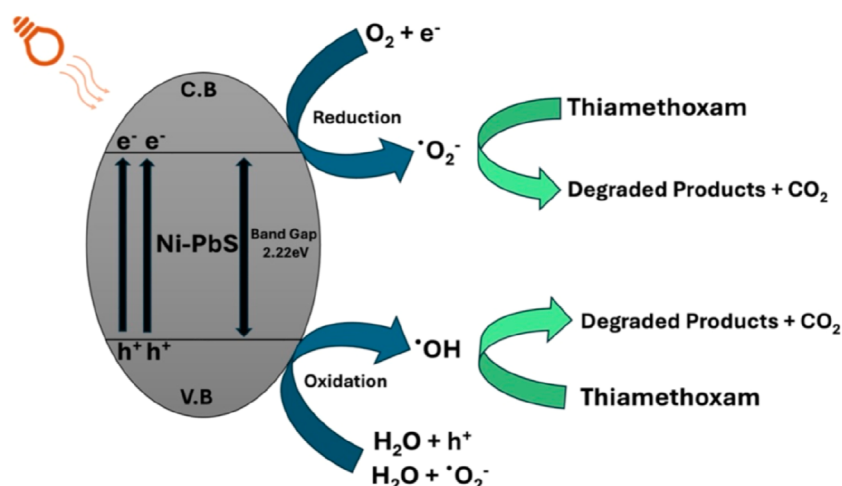


FIGURE 10
Plausible Mechanism for the degradation of TMX using Ni-PbS.

4 Conclusion

Cost-effective chemical method was used to produce innovative and efficient Ni-PbS nanoparticles. Multiple methods, including XRD, EDX, SEM, and XPS, were employed to characterise the materials. PbS production and Ni²⁺ inclusion into the crystal lattice were verified by XRD. The elemental makeup and chemical states of Pb, Ni, S, and O were examined using XPS. Under visible light, the maximum degradation efficiency of 78.93% for TMX was attained in 210 min at pH 3. Additionally, the catalyst demonstrated exceptional reusability after five cycles of deterioration. All things considered, combining Ni and PbS in a photocatalyst system shows a lot of promise for treating insecticide contamination in water and providing an efficient and long-lasting way to clean up the environment.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

RF: Investigation, Methodology, Writing – original draft. MS: Investigation, Methodology, Writing – original draft. JS: Investigation, Supervision, Validation, Writing – review and editing. AM: Supervision, Writing – review and editing, Conceptualization, Funding acquisition, Resources.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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