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# Photocatalytic removal of imidacloprid containing frequently applied insecticide in agriculture industry using $\text{Co}_3\text{O}_4$ modified $\text{MoO}_3$ composites

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Water pollution caused by the frequent utilization of pesticides in the agriculture industry is one of the major environmental concerns that require proper attention. In this context, the photocatalytic removal of pesticides from contaminated water in the presence of metallic oxide photocatalysts is quite in approach. In the present study, Orthorhombic  $\text{MoO}_3$  has been modified with varying amount of cobalt oxide through wet impregnation for the removal of imidacloprid and imidacloprid-containing commercially available insecticide. The solid-state absorption response and band gap evaluation of synthesized composites revealed a significant extension of absorption cross-section and absorption edge in the visible region of the light spectrum than pristine  $\text{MoO}_3$ . The indirect band gap energy varied from  $\sim 2.88$  eV ( $\text{MoO}_3$ ) to  $\sim 2.15$  eV (10%  $\text{Co}_3\text{O}_4$ - $\text{MoO}_3$ ). The role of  $\text{Co}_3\text{O}_4$  in minimizing the photo-excitons' recombination in  $\text{MoO}_3$  was studied using photoluminescence spectroscopy. The orthorhombic shape of  $\text{MoO}_3$  was confirmed through X-ray diffraction analysis and scanning electron microscopy. Moreover, the presence of distinct absorption edges and diffraction peaks corresponding to  $\text{Co}_3\text{O}_4$  and  $\text{MoO}_3$  in absorption spectra and XRD patterns, respectively verified the composite nature of 10%  $\text{Co}_3\text{O}_4$ - $\text{MoO}_3$ . The photocatalytic study under natural sunlight irradiation showed higher photocatalytic removal ( $\sim 98\%$ ) of imidacloprid with relatively higher rate by 10%  $\text{Co}_3\text{O}_4$ - $\text{MoO}_3$  composite among all contestants. Furthermore, the photocatalytic removal ( $\sim 93\%$ ) of commercially applied insecticide, i.e., Greeda was also explored.

## KEYWORDS

insecticide, imidacloprid, greeda,  $\text{MoO}_3$  composites, photocatalysis

## Introduction

With the arrival of the Green Revolution in the 20<sup>th</sup> century, farmers started to use pesticides, insecticides, and herbicides to get higher yields. These chemicals are frequently applied by farmers not only in crops and farms but also in backyard gardens to prevent the agriculture field from the pest attack. The use of pesticides and insecticides at various stages has significantly increased food production and made food storage safer (Foster et al., 1991; Mateo-Sagasta et al., 2017). However, the excessive use of these toxins causes many adverse effects such as pollution of brooks, rivers, marshy areas, lakes, and also valleys, as these toxic manufactured chemicals run off into the nearby water streams which ultimately leads to the scarcity of clean water (Kaur et al., 2019). It is reported that the world is utilizing approximately 2.5 million tons of pesticides on an annual basis wherein very small quantities reach the target while the rest disperse through air, soil, and water which consequently leads to pollution (Hodgson and Levi, 1996).

Many concerns are shown by researchers nowadays because of the permanent existence of pesticides and insecticides in water and food as they also have inauspicious effects on human health and the equilibrium of the ecosystem (Carvalho, 2017; de Souza et al., 2020). Human health is badly affected by these toxins in the drinking water. These toxins have critical effects on mortals such as carcinogenesis, neurotoxicity effects on reproduction, and cell development effects, commonly in the early stages of life (Villaverde et al., 2017; Liang et al., 2019). Their effects are equally harmful to human beings, animals, and marine life. The situation is much critical in countries where water resources are limited, and lives are restricted to utilize contaminated water for various purposes. Therefore, it is an acute need to come up with an efficient and cost-effective technology for the removal of these toxins from contaminated water (Ahmed et al., 2011; Khan et al., 2015a).

Several water decontamination techniques have been utilized to remove the pollutants from the contaminated water such as adsorption, filtration, chemical oxidation, and biological treatments. In addition, many studies are available for the utilization of advanced oxidation methodologies such as photocatalytic process, heterogeneous catalytic oxidation with H<sub>2</sub>O<sub>2</sub>, Fenton/photo-Fenton oxidation, ozonation, and UV/H<sub>2</sub>O<sub>2</sub> treatment for water purification (Swaminathan et al., 2013; Cardoso et al., 2021). Among these, heterogeneous photocatalysis for the complete removal and mineralization of organic toxins is becoming advantageous over others due to its reusability, recovery of photocatalysts, suitability, and sustainability (Qamar et al., 2017; Alhogbi et al., 2020; Aslam et al., 2022). Moreover, it is considered as a green process because natural sunlight can be used to initiate a photocatalytic process while generating reactive oxygen species (ROS) which ultimately leads to the conversion of pollutants into benign species (Zangeneh et al., 2015; Charanpahari et al., 2019).

The progress of photocatalysis is significantly based on the choice of a photocatalyst. In this context, metal oxides and metal oxide-based photocatalysts are being studied extensively for the removal of toxins due to their tunable morphological, structural, optical and photocatalytic properties (Mathiarasu et al., 2021; Hannachi et al., 2022a; Maqbool et al., 2022). Recently, ternary composite of MoO<sub>3</sub> with CuO, MoO<sub>3</sub>/ZnO heterostructures, CuO/

MoO<sub>3</sub> heterojunction, ZnO co-doped with Ce and Yb and MoO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> have been used as photocatalysts wherein a synergic effect of the components in a composite was considered responsible for the enhanced photocatalytic removal of organic dyes (Xue et al., 2019; Ramesh and Shivanna, 2021; Hannachi et al., 2022b; Hussain et al., 2022). In addition, many investigations related to the photocatalytic activities of TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Cu<sub>2</sub>O, NiO, etc., have also been reported (Khan et al., 2015b; Mathiarasu et al., 2021; Velemplini et al., 2021; Hannachi et al., 2022a; Maqbool et al., 2022). However, the quest to investigate the potential contestant for the effective removal of toxic pollutants from the wastewater has not over yet and researchers are also paying attention to study the photocatalytic removal of pesticides and insecticides from the aqueous system in the illumination of light.

For the above-mentioned purpose, Molybdenum trioxide (MoO<sub>3</sub>), an n-type semiconductor, can be an interesting candidate because of having wide band gap energy, ionic conductivity as a result of oxygen vacancies, layered structure, tunable optoelectronic properties and photocatalytic activity (Ijeh et al., 2020; Ali and Ahmad, 2022). Due to its enthralling electrical and optical properties, it is being used in various applications such as gas sensing, LED, smart windows, supercapacitors, batteries, energy storage, DSSCs, optical switch coatings and photocatalysis (Al-Muntaser et al., 2022; Noby et al., 2022; Selvakumar and Palanivel, 2022). However, its wide application in photocatalytic removal of organic toxins is limited due to its large band gap (~3.1 eV), smaller visible-light absorption cross-section and lower photo-excitons separation (Zheng et al., 2021).

In the above contexts, this study has been designed to address the two issues; Firstly, orthorhombic MoO<sub>3</sub> has been modified with Co<sub>3</sub>O<sub>4</sub> through the wet-impregnation method to come up with a photocatalyst having larger light absorption spectrum, lower band gap energy and greater charge separation and transferability. Secondly, the successful removal of 15 ppm imidacloprid and imidacloprid containing commercially applied insecticide (Greda) in the agriculture field under the exposure of natural sunlight. The reason for the utilization of Co<sub>3</sub>O<sub>4</sub> to modify n-type MoO<sub>3</sub> is due to its light absorption capacity, narrow band

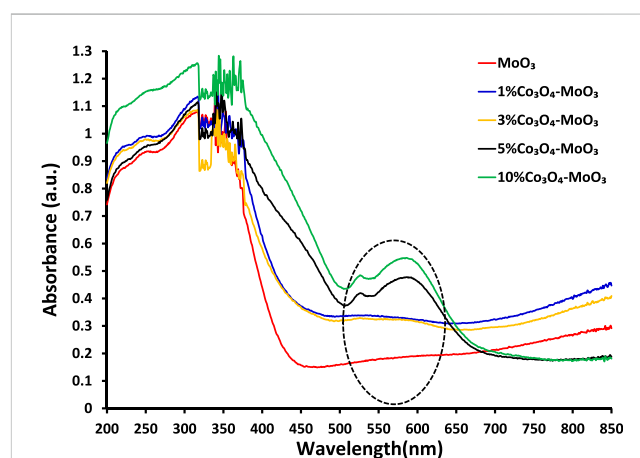
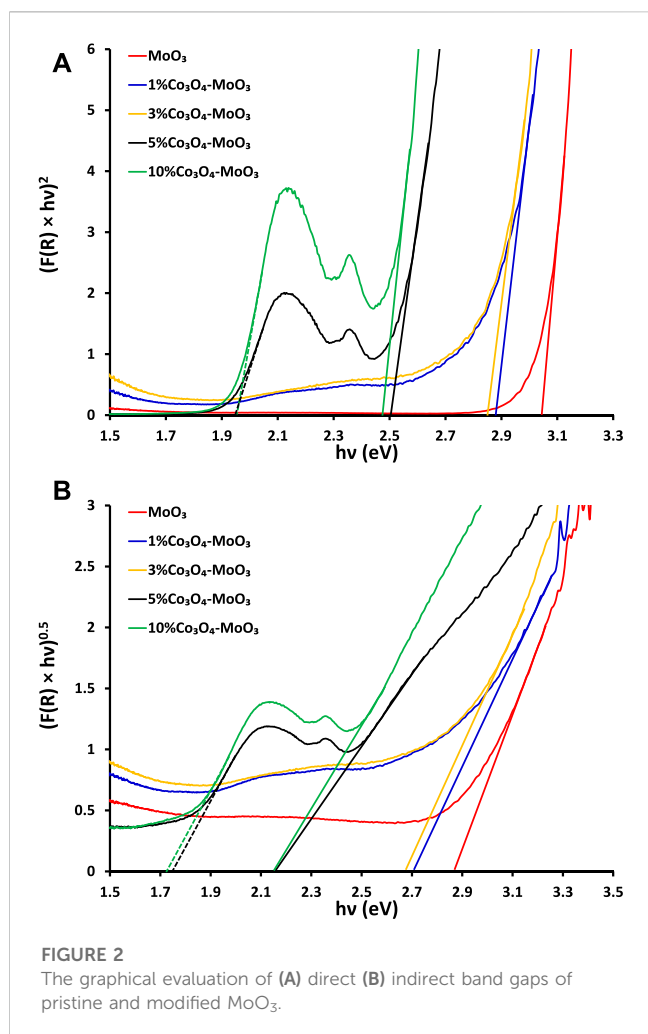


FIGURE 1  
The comparison of solid-state absorption spectra of pristine and modified MoO<sub>3</sub>.



gap, good charge transportability and p-type semiconducting nature (Cao et al., 2022; Wang et al., 2023). Moreover, the successful contribution of Co<sub>3</sub>O<sub>4</sub> in enhancing the photocatalytic activity of CeO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> while generating photo-excitons' separation is well established (Ranjith et al., 2019; Niu et al., 2022; Reena et al., 2022). Previously, rare studies are available

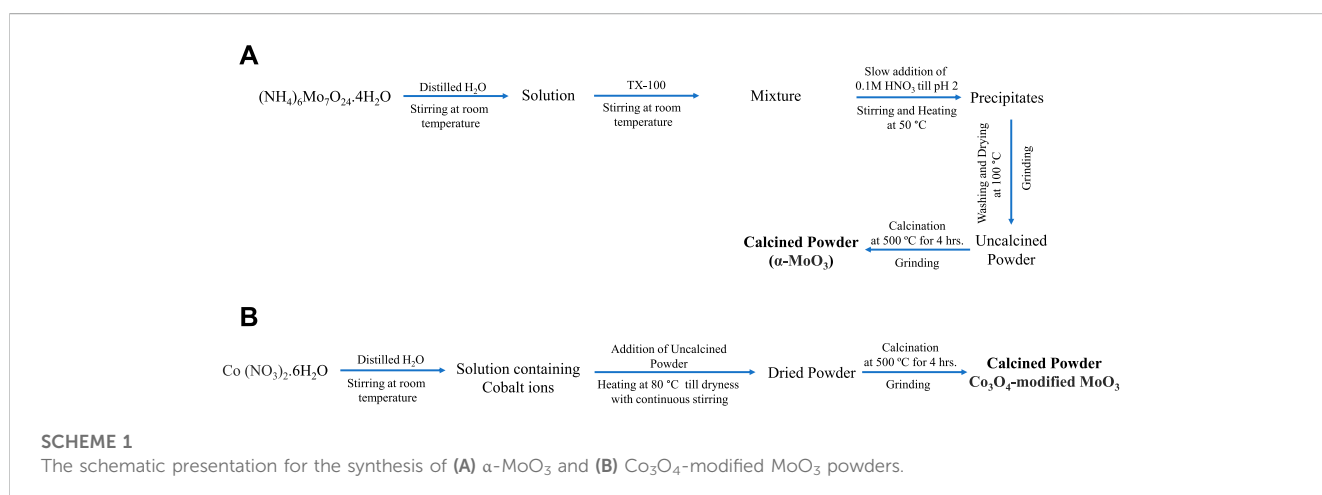
for the removal of imidacloprid over MoO<sub>3</sub>-based photocatalysts (Adabavazeh et al., 2021; Zhang et al., 2021). However, there is no investigation is present yet for the removal of imidacloprid and Greeda over Co<sub>3</sub>O<sub>4</sub>-modified orthorhombic MoO<sub>3</sub> under the illumination of natural sunlight.

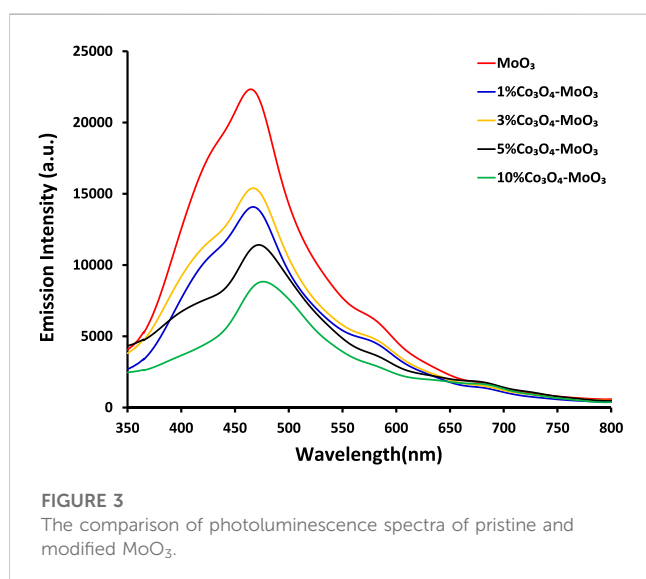
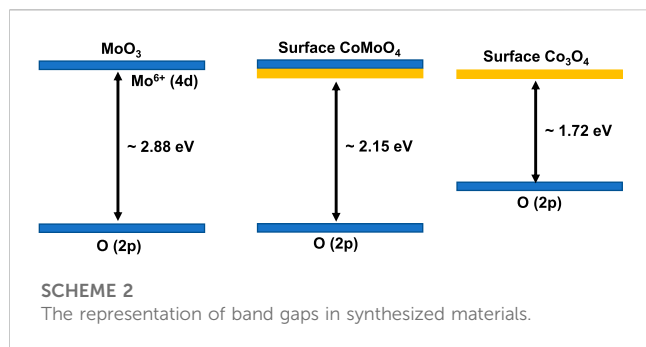
## Experimental

Orthorhombic MoO<sub>3</sub> was prepared using co-precipitation method. In this context, 12.35 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Sigma-Aldrich, ≥99%) was dissolved in distilled water with continuous stirring for an hour at room temperature. Then 2 mL Triton X-100 (Sigma-Aldrich, laboratory-grade) was added to the clear solution. The mixture was then acidified with slow addition of 0.1 M HNO<sub>3</sub> (Sigma-Aldrich, 70%) to attain the pH of the solution to 2 with constant heating at 50°C till the formation of precipitates. The precipitates were separated from the mixture through filtration, washed, and dried in an oven at 100°C. The dried precipitates were calcined at 500°C for 4 h at 10°C/min in a Vulcan D-550 muffle furnace. The calcined material was ground using mortar and pestle to get powder of α-MoO<sub>3</sub> photocatalyst.

The Co<sub>3</sub>O<sub>4</sub>-modified MoO<sub>3</sub> was synthesized using the wet-impregnation method (Scheme 1). The composite of 1 wt% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> was prepared by dissolving 0.15 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich, ≥99%) in distilled water in a beaker (100 mL) with continuous stirring at room temperature. Then, 3.0 g pre-synthesized α-MoO<sub>3</sub> was added to the cobalt nitrate solution under continuous stirring at 80°C. The mixture was kept on a hot plate till complete dryness at 80°C. The dried material was collected and calcined at 500°C for 4 h at 10°C/min in a Vulcan D-550 muffle furnace. The calcined material was ground using mortar and pestle to get powder of 1 wt% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> photocatalyst. Moreover, a similar procedure was adopted to synthesize 3, 5, and 10 wt% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> by using 0.45, 0.75 and 1.5 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, respectively.

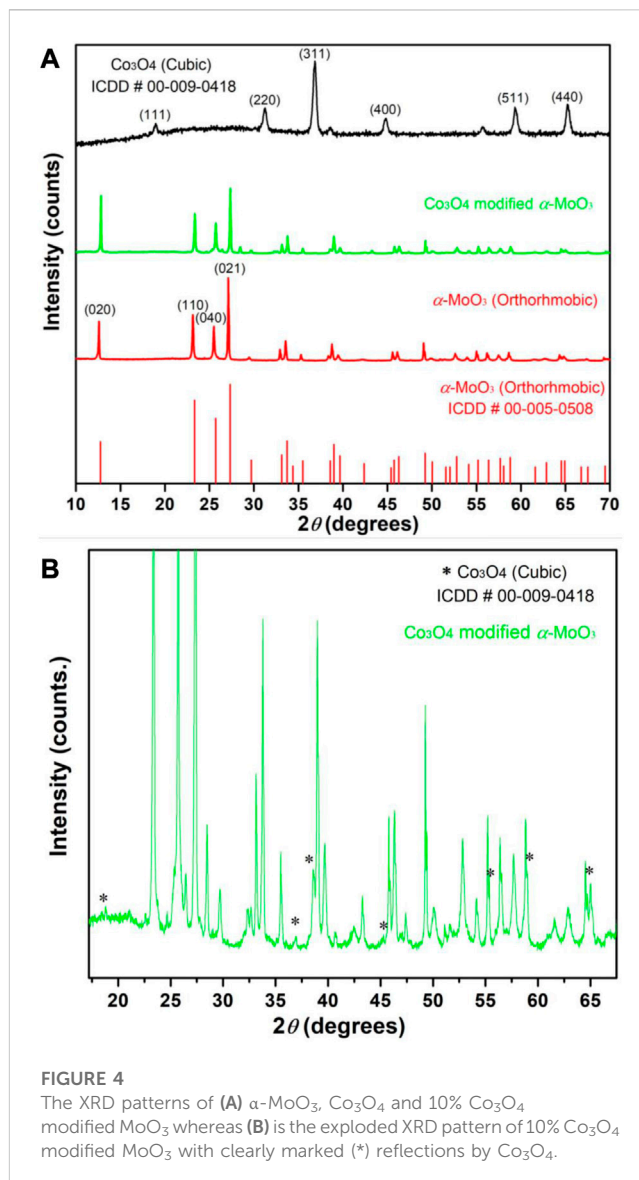
The synthesized materials were characterized using optical, structural and morphological techniques. The solid-state absorption spectra were recorded in the 200–850 nm range using Perkin Elmer UV-visible diffuse reflectance spectrophotometer whereas the band gap energy of the synthesized materials was





estimated using Kubelka-Munk,  $F(R)$ , the transformation of reflectance (%). The change in photo-excitons recombination was noticed from the photoluminescence response of the materials acquired from fluorescence spectrometer, RF-5301 PC, Shimadzu, Japan, at 200 nm excitation wavelength. The XRD patterns were recorded from 5 to 90 with  $0.02^\circ$  step size by X'pert X-ray powder diffractometer (Philips PW1398) having  $\text{Cu K}\alpha$  radiation source. Moreover, the morphology of the 10%  $\text{Co}_3\text{O}_4$ - $\text{MoO}_3$  was examined by field-emission scanning electron microscopy (Hitachi, SU8010, Tokyo, Japan).

The photocatalytic removal of 15 ppm imidacloprid (Merck, Analytical standard) was studied under the illumination of natural sunlight ( $900 \pm 50 \times 10^2$  lx). In a typical experiment, the optimized dose of pristine  $\text{MoO}_3$  (150 mg) was suspended in 100 mL 15 ppm imidacloprid aqueous solution and stirred for 10 min. The suspension was poured into a glass reactor of 14 cm (diameter) and 2 cm (height) and kept in dark for 30 min. After 30 min, the glass reactor was exposed to natural sunlight. The samples were collected after a regular time interval (light exposure) of 30 min and filtered using a  $0.20 \mu\text{m}$  syringe filter. The filtered samples were then subjected to a UV-visible spectrophotometer (UV-1800, Shimadzu, Japan) for the monitoring of imidacloprid removal while selecting its absorbance at a characteristic wavelength, i.e., 270 nm ( $\lambda_{\text{max}}$ )

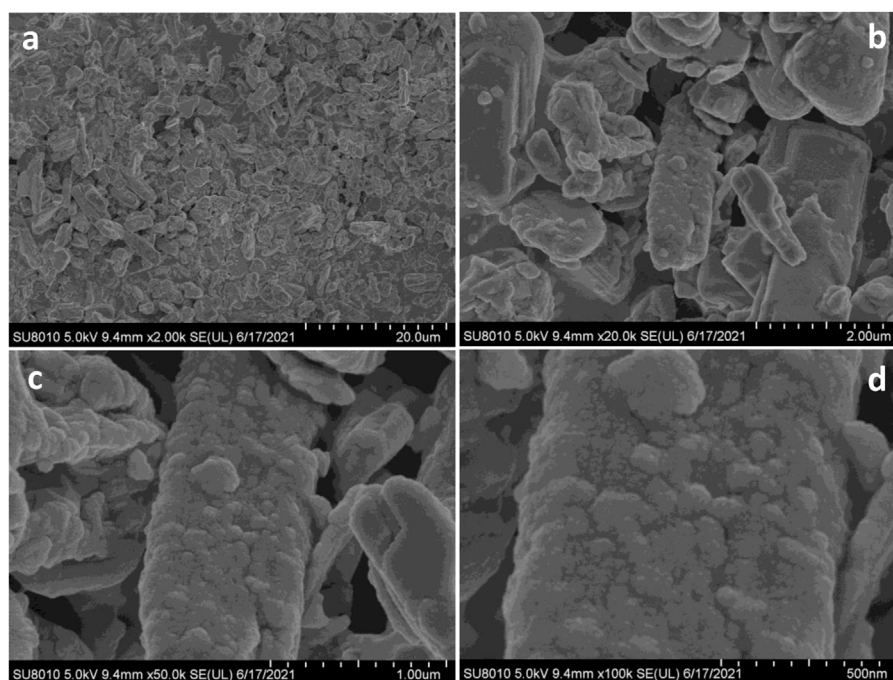


(Kanwal et al., 2018). The same procedure was adopted to monitor the removal of 15 ppm imidacloprid over other synthesized  $\text{Co}_3\text{O}_4$ -modified  $\text{MoO}_3$  composites.

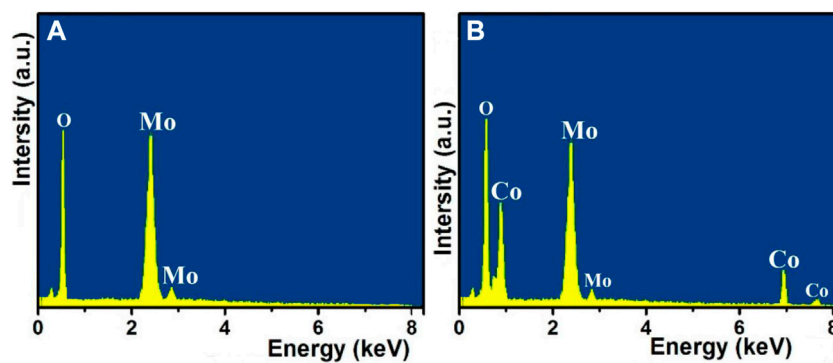
In order to study the removal of imidacloprid from the polluted water, the samples were collected using a syringe filter from the suspension exposed to the light after a regular interval and were subjected to UV-visible spectrophotometer for the determination of the concentration of removed pollutant which ultimately led to the % removal of imidacloprid by the photocatalyst under the exposure of light using the following equation (Garg et al., 2021).

$$\% \text{ removal} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Here,  $C_o$  is the pollutant initial concentration whereas  $C_t$  is the concentration of the pollutant after exposure time 't'. Moreover, the validity of Langmuir Hinshelwood (L-H) kinetic models was also studied using the following equation to evaluate the kinetics of



**FIGURE 5**  
The scanning electron micrographs of 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  at (A) 2.0 k (B) 20.0 k (C) 50.0 k and (D) 100 k magnifications.



**FIGURE 6**  
The EDX spectra of (A) pure  $\text{MoO}_3$  and (B) 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$ .

photocatalytic removal of organic pollutants under the exposure of light (Alhogbi et al., 2020).

$$\ln \frac{C_0}{C_t} = k \times t \quad (2)$$

Here,  $k$  is the rate constant which was determined from the slope by plotting  $\ln \frac{C_0}{C_t}$  vs  $t$ .

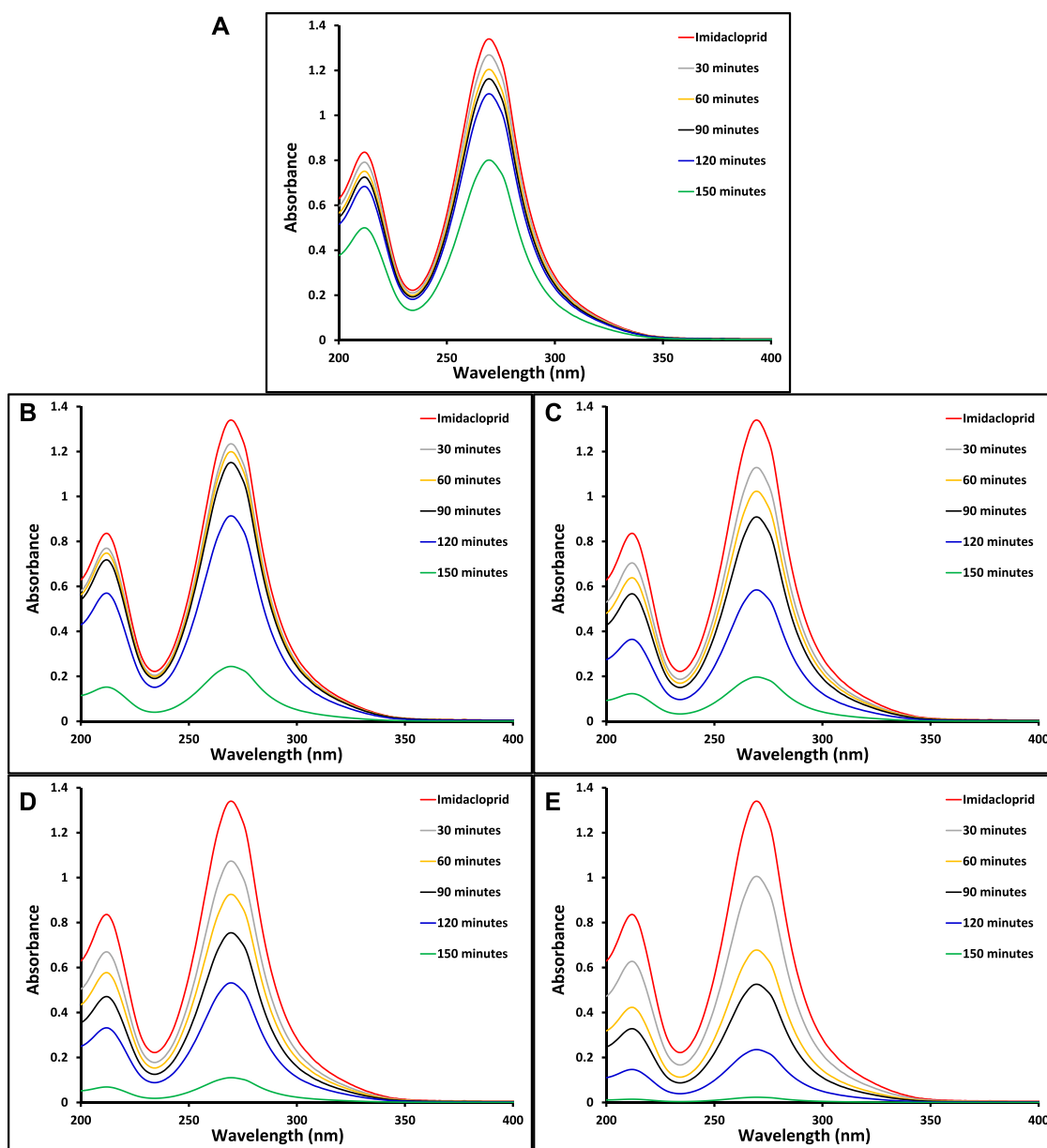
Moreover, the photocatalytic removal of 15 ppm Greeda (Agricom international, Jiangsu Pesticide Research Institute, Jiangsu, China), a commercially available insecticide in the

agriculture field, over 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  was also investigated under the illumination of natural sunlight.

## Results and discussion

The comparison of solid-state absorption spectra of  $\text{MoO}_3$  and its composites is presented in Figure 1 Which indicates the beneficial role of  $\text{Co}_3\text{O}_4$  in increasing the absorption cross-section of  $\text{MoO}_3$ . Wherein, maximum effect



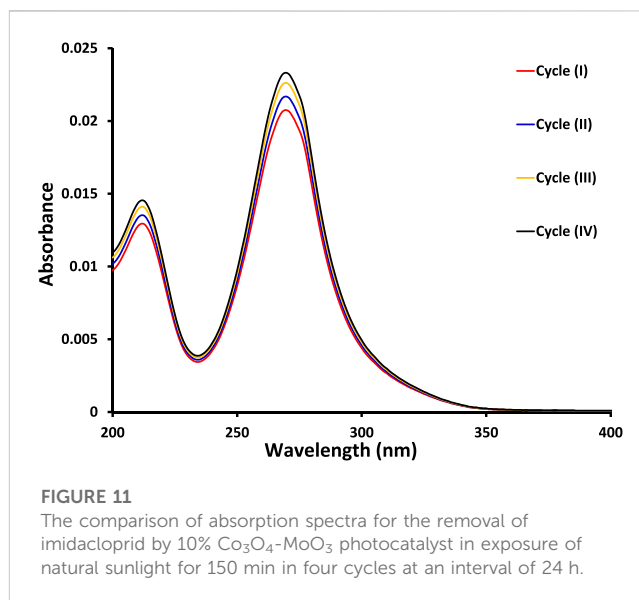
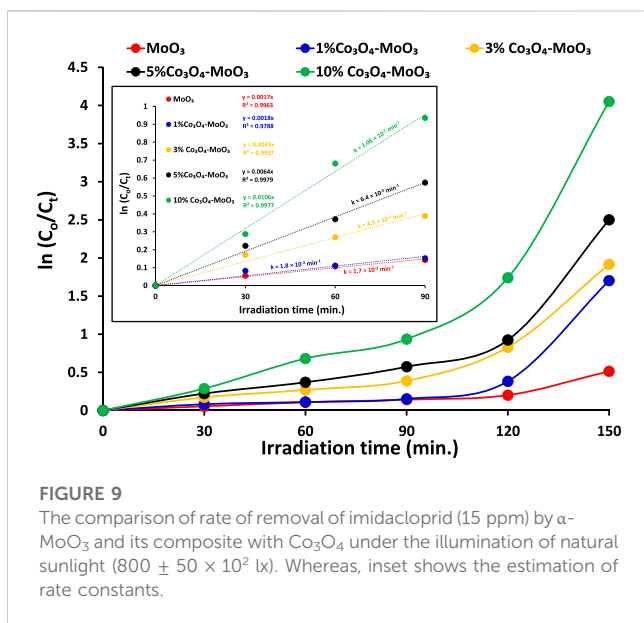
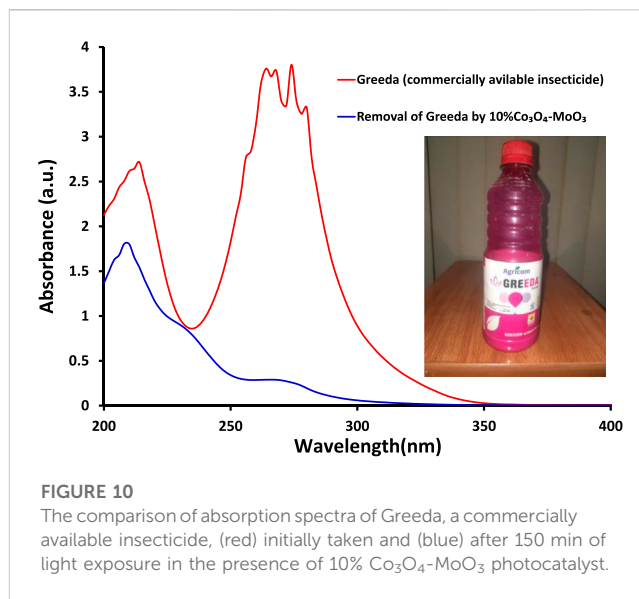
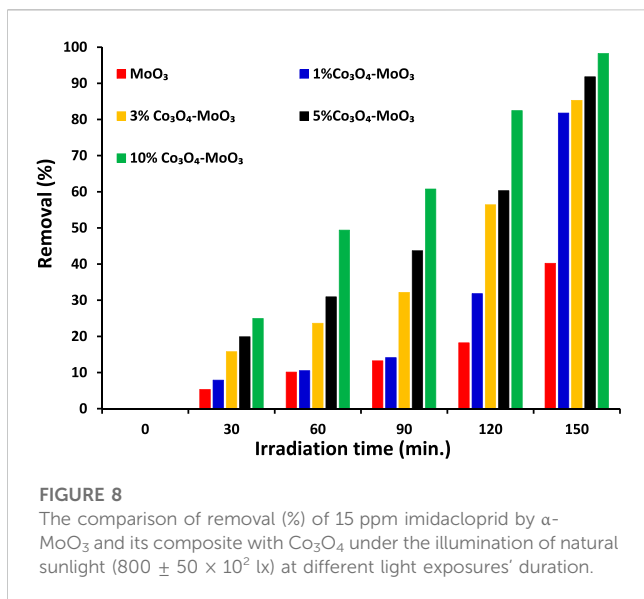


**FIGURE 7**

The comparison of absorption spectra for the removal of imidacloprid by (A) pristine MoO<sub>3</sub> (B) 1% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> (C) 3% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> (D) 5% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> and (E) 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> at different light exposure time.

in enhancing the absorption response was noticed for 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> composite. Moreover, the presence of distinct absorption due to Co<sub>3</sub>O<sub>4</sub> (encircled in Figure 1) in addition to the major absorption corresponding to MoO<sub>3</sub> confirms the composite nature of the synthesized materials. Band gap energy of the synthesized materials has been estimated by plotting  $(F(R) \times h\nu)^{1/n}$  versus  $h\nu$  (eV). Here, “n” can be ½ or two which corresponds to direct or indirect band gaps evaluation, respectively and F(R) is Kubelka–Munk function. The direct and indirect band gap evaluations (Figures 2A,B) reveal a lowering in the band gap energy of composite materials as compared to

pristine MoO<sub>3</sub>. The evaluated indirect band gap (~2.88 eV), as shown in Figure 2B has close agreement with literature values for MoO<sub>3</sub> which is mainly due to the excitations of the electron from O (2p) to Mo (4d) (Qamar et al., 2017). Whereas, the decrease in band gap energy of the composite than pristine MoO<sub>3</sub> is attributed to the introduction of cobalt (3d) orbitals below in the vicinity of the MoO<sub>3</sub> conduction band as shown in Scheme 2. The indirect band gap energies, estimated by extrapolating  $(F(R) \times h\nu)^{0.5}$  vs.  $h\nu$  curves to the horizontal axis were ~2.70 eV, ~2.68 eV, ~2.16 eV and ~2.15 eV for 1%, 3%, 5% and 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub>, respectively as shown in Figure 2B. The

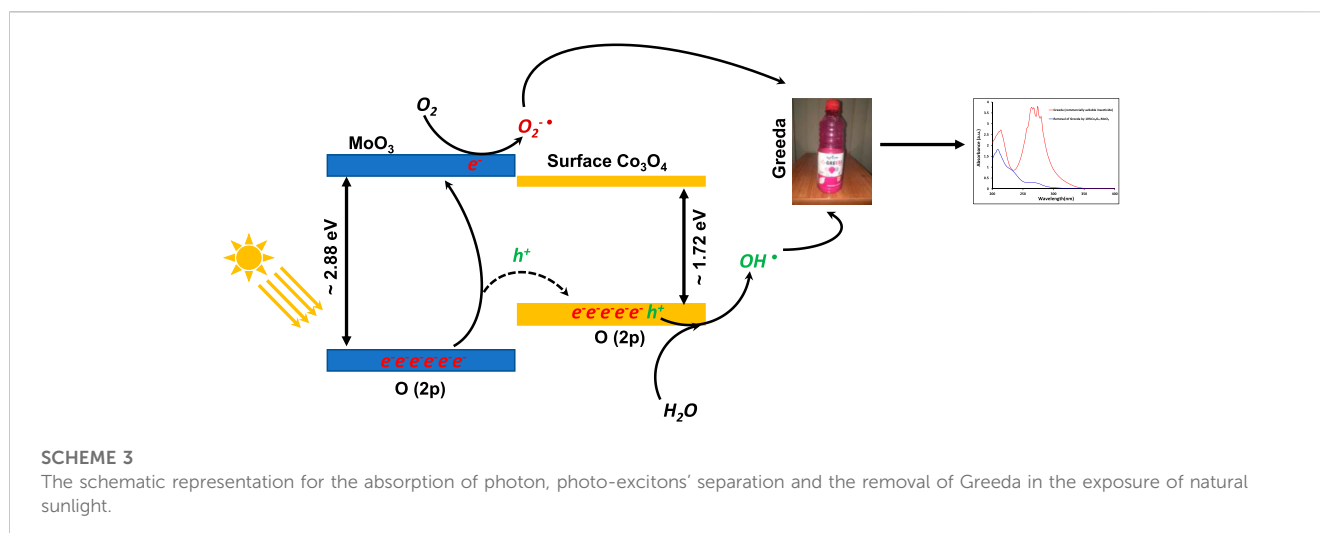


prominent multiple band edge near  $\sim 1.7$  eV was also noticed at higher loading (5% and 10%) of Co<sub>3</sub>O<sub>4</sub> in composites, which is in accordance with band gap energy of Co<sub>3</sub>O<sub>4</sub> presented in literature (Bhargava et al., 2018; Anuradha and Raji, 2020). Hence, the presence of these multiple edges in modified MoO<sub>3</sub> confirms the composite nature of the synthesized photocatalyst.

Figure 3 depicts the comparison of photoluminescence spectra of synthesized photocatalysts, where a successive decrease in emission intensity was noticed for all composites as compared to pristine MoO<sub>3</sub> indicating the supporting role of Co<sub>3</sub>O<sub>4</sub> in lowering the recombination process. Among composites, 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> showed the smallest photo-excitons ( $e^-h^+$ ) recombination which favors the fruitful use of photo-excitons in photocatalytic removal of target pollutant, i.e., insecticide.

Moreover, a  $\sim 60\%$  decrease in emission intensity was observed for 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> whereas  $\sim 31$ ,  $\sim 37$  and  $\sim 49\%$  decrease in emission intensity was noticed for 1, 3, and 5% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> composites, respectively.

The comparison of x-ray diffraction patterns of the synthesized MoO<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and 10% Co<sub>3</sub>O<sub>4</sub> modified MoO<sub>3</sub> is presented in Figure 4. An orthorhombic phase of the synthesized  $\alpha$ -MoO<sub>3</sub> with lattice parameters ( $a = 3.9620$  Å,  $b = 13.8580$  Å,  $c = 3.6970$  Å and  $\alpha = \beta = \gamma = 90^\circ$ ) and cubic phase of Co<sub>3</sub>O<sub>4</sub> having lattice parameters ( $a = b = c = 8.0840$  Å and  $\alpha = \beta = \gamma = 90^\circ$ ) was confirmed by matching diffractions patterns with ICDD# 00-006-0508 and 00-009-0418, respectively as shown in Figure 4A. The XRD pattern of 10% Co<sub>3</sub>O<sub>4</sub> modified MoO<sub>3</sub> in Figure 4A, clearly shows the dominance of diffraction peaks arising due to the MoO<sub>3</sub> as compared to the additional peaks due to the presence of cubic Co<sub>3</sub>O<sub>4</sub> which have been marked by (\*) in Figure 4B.



The presence of additional peaks due to cubic  $\text{Co}_3\text{O}_4$  in the XRD pattern of orthorhombic  $\text{MoO}_3$  confirms the composite nature of the newly synthesized photocatalysts. In addition to the presence of cubic  $\text{Co}_3\text{O}_4$  (ICDD# 00–009–0418) as the major phase in  $\alpha\text{-MoO}_3$ , a couple of low-intensity reflections also specified the occurrence of monoclinic  $\text{CoMoO}_4$  (ICDD# 00–021–0868). The existence of  $\text{CoMoO}_4$  may be attributed to the attachment of Cobalt with the surface oxygen shared by Mo. The average crystallite sizes of the pristine  $\text{MoO}_3$  and 10%  $\text{Co}_3\text{O}_4$  modified  $\text{MoO}_3$  were calculated using reflections at  $2\theta$  values of  $12.68^\circ$ ,  $23.27^\circ$ ,  $25.87^\circ$  and  $27.25^\circ$  with the help of the Debye–Scherrer equation. Wherein a mild increase in crystallite size for the composite sample was noticed as compared to pure  $\text{MoO}_3$ . The estimated average crystallite sizes of  $\alpha\text{-MoO}_3$ , 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  and  $\text{Co}_3\text{O}_4$  powders were  $\sim 54.42$  nm,  $\sim 58.43$  nm and  $\sim 20.63$  nm, respectively. Average crystallite size of  $\text{Co}_3\text{O}_4$  powder was evaluated using reflections at  $2\theta$  values of  $31.25^\circ$ ,  $36.84^\circ$  and  $65.22^\circ$ .

Moreover, the morphology of 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  was also explored at different magnification as shown in Figure 5 wherein the presence of  $\text{Co}_3\text{O}_4$  were noticed on the surface of orthorhombic  $\text{MoO}_3$ . The orthorhombic morphology of  $\text{MoO}_3$  was in accordance with XRD diffraction pattern of  $\text{MoO}_3$  (ICDD# 00–021–0868). The observed homogeneous distribution of  $\text{Co}_3\text{O}_4$  on the surface of  $\text{MoO}_3$  verifies the composite form of the synthesized photocatalysts and the distributed  $\text{Co}_3\text{O}_4$  played a significant role in enhancing the absorption of light and then increasing the photocatalytic efficiency of  $\alpha\text{-MoO}_3$  in natural sunlight.

Energy-dispersive X-ray spectroscopy was used to further determine the composition and element distribution of the  $\text{MoO}_3$  that had been synthesized in its as-prepared state (Figure 6A) and the 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  (Figure 6B). According to the findings, which are displayed in Figure 6B, the 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  composites displayed a spatial distribution of O, Mo, and Co species. The high intensity of the detection of O, Mo, and Co showed that each element was spread out evenly in the 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  composites.

The ultimate goal of this study was to investigate the removal of imidacloprid and Greeda under the illumination of natural sunlight. Before the exposure of suspension containing photocatalyst and imidacloprid to light as mentioned in the experimental section, the suspension was kept in dark for

30 min to establish an equilibrium between pollutant and catalyst. The photolysis of imidacloprid was also evaluated by recording the absorption spectrum of the substrate after 150 min of light exposure without the presence of a photocatalyst. The amount of photocatalyst was also optimized (150 mg of photocatalyst) while studying the photocatalytic removal of 15 ppm imidacloprid with varying doses of  $\text{MoO}_3$  catalyst under the illumination of natural sunlight. The comparison of absorption spectra of imidacloprid's removal over pristine and modified  $\text{MoO}_3$  under the illumination of sunlight ( $800 \pm 50 \times 102$  lx) is provided in Figure 7 at different exposure times. Moreover, higher photodegradation ( $\sim 98\%$ ) was noticed for 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  followed by 5%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  ( $\sim 92\%$ ), 3%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  ( $\sim 85\%$ ) and 1%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  ( $\sim 81\%$ ) and  $\text{MoO}_3$  ( $\sim 41\%$ ) after 150 min of sunlight exposure. As shown in Figure 8 The decreasing trend of removal efficiency (%) of the photocatalysts is given below.

$$10\% \text{Co}_3\text{O}_4\text{-MoO}_3 > 5\% \text{Co}_3\text{O}_4\text{-MoO}_3 > 3\% \text{Co}_3\text{O}_4\text{-MoO}_3 > 1\% \text{Co}_3\text{O}_4\text{-MoO}_3 > \text{MoO}_3$$

The kinetic study reveals that the photocatalytic removal of imidacloprid by newly synthesized materials did not follow the Langmuir Hinshelwood (L-H) kinetic model throughout light exposure from 0 to 150 min as shown in Figure 9. However, in the initial 90 min the rate of removal followed Langmuir Hinshelwood (L-H) kinetic model and the estimated rate constants are  $1.7 \times 10^{-3} \text{ min}^{-1}$ ,  $1.8 \times 10^{-3} \text{ min}^{-1}$ ,  $4.5 \times 10^{-3} \text{ min}^{-1}$ ,  $6.4 \times 10^{-3} \text{ min}^{-1}$  and  $1.1 \times 10^{-2} \text{ min}^{-1}$  by  $\text{MoO}_3$ , 1%  $\text{Co}_3\text{O}_4\text{-MoO}_3$ , 3%  $\text{Co}_3\text{O}_4\text{-MoO}_3$ , 5%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  and 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$ , respectively as provided in the inset of Figure 9. The higher removal efficiency of  $\text{Co}_3\text{O}_4\text{-MoO}_3$  as compared to pristine  $\text{MoO}_3$  may be attributed to the synergic role of  $\text{Co}_3\text{O}_4$  in increasing the life span of photo-excited electrons by lowering the charge recombination process (Figure 3), which ultimately leads to the higher removal of imidacloprid. In order to assess the application of an efficient photocatalyst declared in this study, i.e., 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  for the removal of insecticide, Greeda (a commercially available frequently applied insecticide in the agriculture field) was chosen. Figure 10 shows that  $\sim 93\%$  of Greeda was removed by 10%  $\text{Co}_3\text{O}_4\text{-MoO}_3$  in 150 min of



natural sunlight exposure. Previously, the photocatalytic removal of imidacloprid was explored previously using iron-based catalysts, ZnO, TiO<sub>2</sub>, SnO<sub>2</sub> ternary nanocomposites, g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> under the exposure of UV and visible light, however, studies pertaining to the removal of Greeda and Imidacloprid using Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> photocatalysts are not evident from the literature. (Guzsvány et al., 2010; Derbalah et al., 2019; Yari et al., 2019; Sudhaik et al., 2020; Li et al., 2022; Faisal et al., 2023). The efficiency of 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> photocatalyst after four cycles was also investigated and a minor decrease in efficiency was noticed for the removal of imidacloprid as shown in Figure 11. Moreover, the mechanism for the removal of Greeda in the exposure of natural sunlight by Co<sub>3</sub>O<sub>4</sub> modified MoO<sub>3</sub> composite is provided in Scheme 3.

## Conclusion

The successful synthesis of Co<sub>3</sub>O<sub>4</sub>-modified MoO<sub>3</sub> composites through the wet-impregnation method and their photocatalytic activities lead to the following conclusions.

- The successfully distributed Co<sub>3</sub>O<sub>4</sub> on the surface of orthorhombic MoO<sub>3</sub> played a significant role in improving the spectral response and lowering the bandgap energy of  $\alpha$ -MoO<sub>3</sub> from ~2.88 eV to ~2.15 eV.
- The higher  $e^-h^+$  recombination in  $\alpha$ -MoO<sub>3</sub> was successfully suppressed by modifying MoO<sub>3</sub> with Co<sub>3</sub>O<sub>4</sub>.
- All modified MoO<sub>3</sub> photocatalysts presented higher photocatalytic activity for the removal of imidacloprid under the illumination of natural sunlight due to the synergic effect of Co<sub>3</sub>O<sub>4</sub>.
- A commercially available insecticide (Greeda) was successfully removed (~93%) by 10% Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub> in 150 min of natural sunlight exposure.

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## Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

## Author contributions

The manuscript was written with the contributions of all authors. All authors have approved the final version of the manuscript.

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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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