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PROLIFIC FABRICATION OF LANTHANUM OXIDE WITH GRAPHITIC CARBON/GRAPHENE OXIDE FOR ENHANCING PHOTOCATALYTIC DEGRADATION OF CARBOFURAN FROM AQUEOUS SOLUTION

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ABSTRACT

Carbofuran insecticide is one of the most widely used low-cost carbamate pesticides because it effectively controls pests in agriculture fields and gardens. This study provides experimental results of the photocatalytic detoxification of Carbamate in wastewater using graphitic carbon nitride/GO/La_2O_3 nanocomposite nanoparticles. Calcination and hydrothermal technique were used to produce g-C_3N_4/GO/La_2O_3 nanocomposite. Furthermore, the photocatalytic detoxification of Carbofuran was investigated by numerous factors such as catalyst concentrations, irradiation period, and pH. According to the observation, the photo detoxification efficiency of Carbofuran pesticides rises as time increases. According to this study, g-C_3N_4/GO/La_2O_3 nanocomposite outperformed pure forms of g-C_3N_4, g-C_3N_4/GO, g-C_3N_4/La_2O_3 in degrading Carbofuran up to 80% and photo catalytically making it a potential alternative for wastewater treatment.

Keywords: Pesticide; Photocatalysis; Hydrothermal; Carbofuran; Lanthanum Oxide; g-C_3N_4.
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INTRODUCTION

Pesticides are frequently employed to enhance agricultural yields and get rid of destructive organisms. However, it is also reported that only 15% of applied pesticides truly achieve their goals, with the remainder damaging the ecosystem. These chemicals are persistent organic contaminants that accumulate in biota and sediments.[1-3] These are likely to travel over distances and, even at low concentrations, are intoxicating the environment, people, and other living matters.[4-5] Pesticide contamination comes largely from mining, urban and industrial operations, and agricultural field runoff.[3-6] More than 50 nations approximately, utilized 3.5 million tonnes of pesticides to promote agricultural production as of 2020.[9] These chemical exposures are the cause of a wide variety of diseases. Furthermore, insecticides in drinking and surface water can disrupt the endocrine system.[12,13] Carbofuran is effective against foliar pests that are present in fruit, vegetable, and forest crop production.[14] Carbofuran is a possible endocrine disruptor since it inhibits acetylcholinesterase, an enzyme necessary for the proper operation of the controlled nervous system. Additionally, Carbofuran is highly mobile in soils and very soluble in water (700 mg/l). Many studies also reported evidence of Carbofuran in the open and groundwater.[14] Therefore, creating an effective and affordable treatment technique to eliminate Carbofuran from the aqueous system is decisive. The most effective ways to remove Carbofuran from the aqueous systems seem to be through hydrolysis and microbial breakdown. However, the Carbofuran degradation via these processes takes a long time.[16] The photocatalysis degradation of hazardous chemicals in aqueous media has multiple advantages over conventional treatment techniques.[6-17] Over the past two decades, this technique has been extensively investigated. These studies have established the photocatalytic degradation of several water-soluble compounds from diverse sectors.[15-17]

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Nonetheless, there is no data on the synthesis of g-C_3N_4/GO/La_2O_3 ternary nanocomposite material or their photocatalytic degradation of Carbofuran.

EXPERIMENTAL

Materials

Thiourea (99%), ethanol, Sodium hydroxide, without additional purification, hydrogen peroxide, potassium permanganate, sodium nitrate, graphite flakes, and hydrochloric acid were obtained from Loba Chemie PVT.LTD. Deionized water was used throughout the research phase. A Carbamate insecticide, Carbofuran, was bought from a local farmer's market in Punjab, India.

Synthesis of the Photocatalyst

Thiourea was heated for two hours at 550° C at the thermal heating of 3° C/min to create bulk g-C_3N_4 in a crucible and put in a furnace. When it has reached room temperature after being removed from the muffle furnace, it is crushed into a powder in an agate mortar. The GO was synthesized following a modified Hummers method. A 500ml beaker containing an ice bath was initially filled, following which 0.5 g of graphite powder, 23 ml H_2SO_4, and 30 minutes of 500 rpm agitation were added. The solution was also stirred continuously for 60 minutes at a speed of 600 rpm after adding (0.5 gm) $NaNO_3$. Keeping the solution at 15ºC, 3 grams of $KMnO_4$ was gently added. The solution's temperature was gradually increased to 35º. After adding 50 ml of DI water to the mixture, the temperature was raised to 95 degrees Celsius for thirty minutes. Finally, the process was stopped with the addition of a 50 ml mixture of DI water and H_2O_2 (1.5 ml). Centrifuged at 3000 rpm for 7 min, rinsed with hydrochloric acid and DI water to remove metal ions and acid residues before drying at 70º. For the synthesis of g-C_3N_4/GO was dissolved in 100ml deionized water and stirred together for 1 hour. The solution was into an autoclave, sealed tightly, and heated at 200° C for 12 hours. The product was centrifuged, washed, and oven-dried at 80º C. In deionized water g-C_3N_4, GO and La_2O_3 was dissolved and stirred for 2 hours. The mixture was put in an autoclave and heated for 10 hours at 200°C. the resulting light-yellow precipitate was filtered and washed with ethyl alcohol and double distilled water before being dried in an oven.

RESULTS AND DISCUSSION

Material Characterization

X-Ray Diffraction Analysis

The amorphous carbon contained in GO is shown by the wider diffraction peak at 2θ=11.4$^{o11\text{-}15}$ .g-C_3N_4 and GO-related diffraction peaks are shown in Fig.-1 emerge in the GO/g-C_3N_4 nanocomposite, suggesting that nanocomposites were successfully formed. It is also clear that in g-C_3N_4/La_2O_3, the 2θ peaks of g-C_3N_4 detected at 13º vanished a little bit, whilst the 2θ peaks at 27º combined with typical peaks of La_2O_3 oxide. As a result, it was established that the hydrothermal process caused La to be infused with triazine structures of g-C_3N_4 to produce nanocomposite materials.

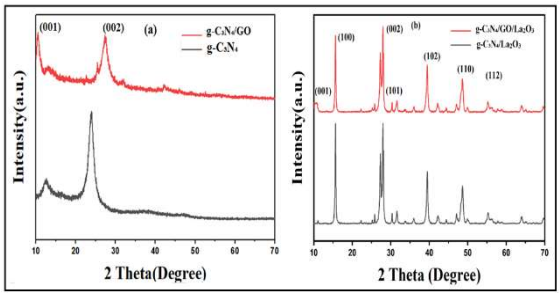

Fig.-1: XRD Pattern of (a) g-C $_3N_4$, g-C_3N_4/GO, and (b) g-C_3N_4/La_2O_3, g-C_3N_4/GO/La_2O_3 Nanocomposite

FT-IR Analysis

Figure-2 illustrates the FT-IR spectra of the g-C_3N_4, g-C_3N/GO, and g-C_3N_4/GO/La_2O_3 nanocomposites as they were produced. Peaks in the 1200-650 cm^{-1} region of pure g-C_3N_4 FT-IR spectra (curve a) were attributed to heterocycles' characteristic C-N stretching mode. The CN stretching vibration that resulted in the formation of the sp^2 hybridized network in the g-C_3N_4 network is responsible for the absorption band that can be seen at 645 cm^{-1}. The aromatic C-N stretching is responsible for peaks at 1240, 1351, 1417, and

15 78 cm^{-1}.[15] The band at 811 cm^{-1} exhibits the typical stretching vibration of s-triazine rings.[19] It is possible to attribute the wide absorption band of g-C_3N_4 at a wavelength of 3176 cm^{-1} to the characteristic stretching vibration modes of terminal NH_2 or NH bonds.[10-11] The peaks of GO at 1039, 1230, and 1727 cm^{-1} were connected to the stretching vibrations of the g-C_3N_4, respectively.[16] The FTIR spectra of the nanocomposite were shown in Fig.-2 and they included all of the typical peaks for g-C_3N_4 and La_2O_3. The FTIR spectra of g-C_3N_4 nanoflakes and g-C_3N_4/GO/La_2O_3 nanocomposite were found to be significant. The La-O stretching caused the medium to strong absorption bands at 445 cm^{-1}. [15] Therefore, the bands stated above demonstrate that La_2O_3 and GO are present in the nanocomposite of g-C_3N_4/GO/La_2O_3.

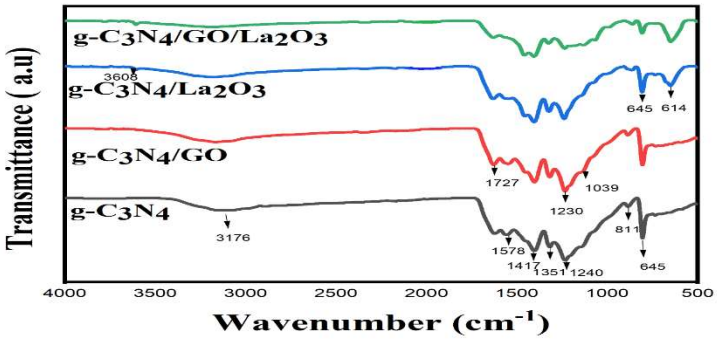

Fig.-2: FT-IR Pattern of g-C_3N_4, g-C_3N_4/GO, g-C_3N_4/La_2O_3, g-C_3N_4/GO/La_2O_3 Nanocomposite

FESEM Analysis

By using scanning electron microscopy, the morphologies of the g-C_3N_4, g-C_3N_4/GO, g-C_3N_4/La_2O_3, and g-C_3N_4/GO/La_2O_3 nanocomposite were clarified (SEM). Figure-3(a) illustrates an uneven platelets-like plane structure of g-C_3N_4 and a monolayer wrinkled 2-D sheet-like morphology owing to exfoliation.[15] The SEM pictures clearly show that the nanocomposite contains g-C_3N_4 nanoflakes that are embedded with La_2O_3 and GO nanoparticles. Also, sponge-like agglomerations were seen with various holes and spaces. The spectrum of EDX indicated that GO/La_2O_3 was effectively infused into the g-C_3N_4 nanocomposites, which are key components of nanocomposite material.[16-17]

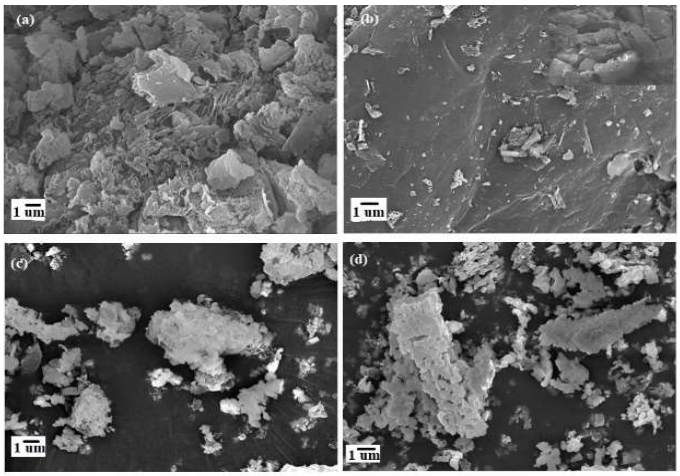

Fig.-3: FESEM Morphological Image of (a) g-C_3N_4(b) g-C_3N_4/GO (c) g-C_3N_4/La_2O_3 (d) g-C_3N_4/GO/La_2O_3

Photocatalytic Activity

pH Effect

The result of pH on the photo-catalytic detoxification was studied by adjusting the pH value of the Carbofuran solution while holding all other experimental conditions constant. The elimination efficacy of Carbofuran increased with increasing pH in the pH range of 1 to 7.0 but reduced when pH was elvatedfurtherfrom7.0 to 9.0. The ideal pH value was found to be 7.0, with the maximum Carbofuran removal efficiencies of 53.75,62.5, 67.5, and 80% in the visible region with g-C_3N_4, g-C_3N_4/GO, g-

C_3N_4/La_2O_3, and g-C_3N_4/GO/La_2O_3 photocatalytic nanocomposite, respectively. Carbofuran may be protonated at the carbonyl oxygen at pH 7. Electrostatic repulsion may occur from such protonation.[20]

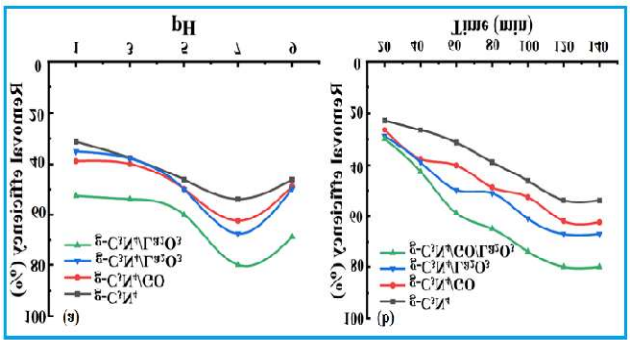

Fig.-4: Degradation of Carbofuran Pesticide (a) pH and (b) Time

Irradiation Study

The influence of contact (irradiation) time is shown in Fig.-4. (b). It has been demonstrated that removal effectiveness rises with exposure time. Figure- 4. (b) clearly illustrates that the degradation percentage for the as-produced nanocomposite rose from 24.52 to 80 % when the irradiation time interval was improved from 20 to 120 minutes. This might be ascribed to the fact that as the irradiation duration lengthens, the Carbofuran molecules have more opportunity to interact with the surface of the photocatalyst and generate hydroxyl radicals, which speeds up the photocatalytic reaction and hence increase the percentage of degradation.[17-19]

H_2O_2 effect

The ability of H_2O_2 to generate more OH radicals will enhance photocatalytic removal and create vibrant intermediates. Figure-5(a) shows the impact of H_2O_2 on the photocatalytic removal of Carbofuran by g-C_3N_4/GO/La_2O_3, where H_2O_2 was changed from 0.01 to 1%. The photo-degradation efficiency was 80% in the absence of H_2O_2. The elimination of Carbofuran by photocatalysis rose from 80 to 85.6 % when the concentration of H_2O_2 was increased from 0.01 to 0.1 %. However, as the H_2O_2 concentration was improved to 1%, the removal rate decreased to 73%. This drop was considered to be caused by an increase in H_2O_2 acting as an inhibitor when combined with hydroxyl radicals. By encasing photoinduced e in H_2O_2, the coupled e/h+ may be stabilized. The product of the reaction between H_2O_2 and O_2 is the OH radicals. Subsequently, it was believed that by including H_2O_2 in the photocatalytic reaction, the system would enhance the removal of Carbofuran. This amount of H_2O_2 given lowered the amount of· OH, radicals that were able to eliminate Carbofuran by trapping the product· OH, radicals and changing them into weaker oxidants HO_2 radicals.

Effect of Photo-Catalyst Dose

When the photocatalyst is readily available in sufficient amounts, Carbofuran is metabolized more efficiently. Figure-5(b) illustrates how the photocatalyst's dosage affects the nanocomposites' photocatalytic activity. To find the most effective amount of photocatalyst, the concentration of graphitic carbon nitride, g-C_3N_4/GO, g-C_3N_4/La_2O_3, and g-C_3N_4/GO/La_2O_3 nanocomposite in 100 ml of Carbofuran solution with 0.1% H_2O_2 was changed from 0.1 to 0.5 g/L. When the photocatalyst dose was improved from 0.1 to 0.3 g/L, Carbofuran photocatalytic removal efficiency increased from 46.37 to 80 % shown in Fig.-5(b). However, increasing the dosage had no additional effect on elimination efficiency. This result indicated that the photocatalyst's higher suspension caused a reduction in light penetration in the presence of a substantial amount of photocatalyst.[16-17]

Photocatalyst Regeneration

To increase the viability of the catalyst from an economic perspective, the synthesized photocatalyst should be recycled for 'n' cycles. For regeneration, the used photocatalyst was treated with 0.1 g/10ml of a solution of 30% H_2O_2, while being stirred for an hour. The efficiency of Carbofuran removal peaked at 48% in the

fifth cycle and then gradually decreased over the course of the subsequent regeneration cycles until the fifth cycle. Based on earlier reports the possible pathway is projected as shown in Fig.-6.

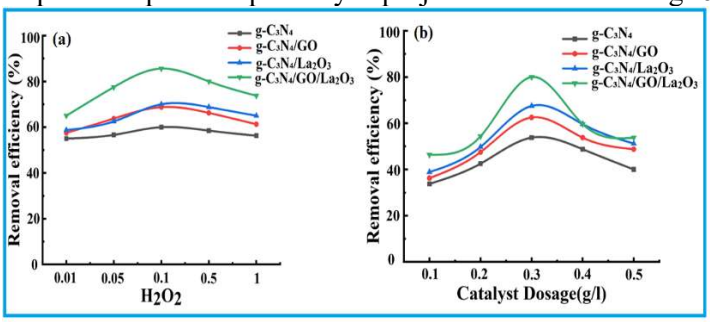

Fig.-5: Photocatalytic Degradation of Carbofuran Pesticide (a) Effect of H_2O_2 (b) Effect of Photocatalytic Dose on Degradation

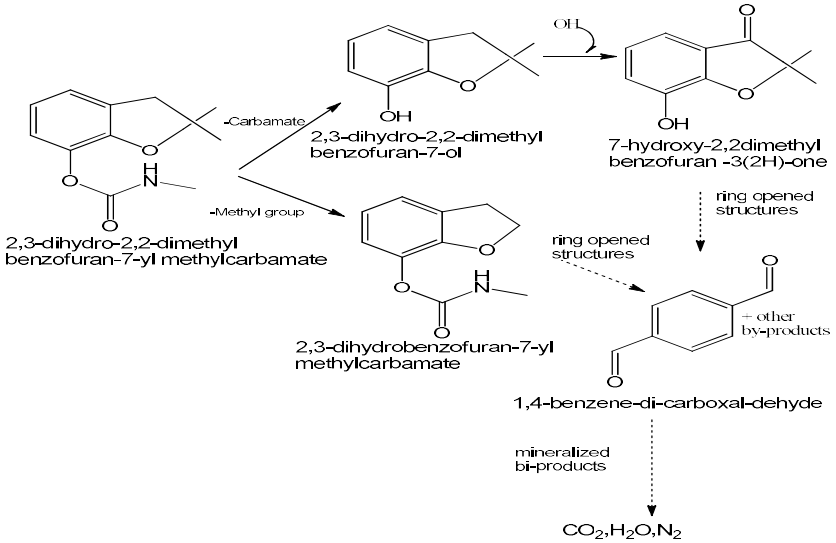

Fig.-6: Degradation Pathway of Carbofuran using g-C_3N_4/GO/La_2O_3 Nanocomposite

CONCLUSION

A robustly reusable dual photocatalyst that is g-C_3N_4/GO/La_2O_3 has been synthesized and used for the degradation of Carbofuran pesticide. To characterize the nanomaterial that was synthesized, XRD, FT-IR, and SEM were used. Under the influence of light, the nanocomposite that was created has a remarkable photocatalytic activity for the destruction of the pesticide known as carbofuran. After 120 minutes of light irradiation, Carbofuran photocatalytic degradation was achieved by 80 % and by using H_2O_2 at 85.6%. In comparison, the photocatalytic degradation using g-C_3N_4, g-C_3N_4/GO, and g-C_3N_4/La_2O_3 were just 53.75 and 62.5, and 67.5% respectively. This ternary nanocomposite can effectively limit the photo-induced electron-hole pairs recombination in addition to being able to absorb more visible light. Furthermore, ternary photocatalysts exhibit outstanding sustainability and recyclability in the photocatalytic degradation of carbofuran after five times, with a 48 % efficiency.

CONFLICT OF INTERESTS

This is certifying that; No conflict of interest between all authors S. Tabasum, A. Sharma, S. Rani, S. Chaudhary, A. Q. Malik, D. Kumar, T. Deshpande, all authors agree to submit and all authors contributed to the work.

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AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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