

Photocatalytic Degradation Of Aldrin Under The Influence Via Ozonation In The Presence Of Ag₂O/SmFeO₃ Under Visible Light

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Abstract: The photocatalytic degradation of aldrin, a hugely toxic and commonly used pesticide was studied using Ag doped SmFeO₃ as a heterogenous catalyst under ozonation reaction. Various photocatalytic nano particles were prepared with varied dopant percentage (1%, 2.5% and 5%) which were characterised using various analytical and morphological techniques. A magnificent degradation of aldrin up to 99.9% was achieved using 50 mg/L of 5% Ag₂O/SmFeO₃. It was observed that the degradation was highly efficient at a basic pH of 11 leading to mineralisation of any intermediates produced in the process within 2 h. The extent of degradation was monitored by GC-MS and TLC. Overall mineralisation was tracked using TOC value. The catalyst was easily separated from the reaction mixture using simple ultra filtration method. The separated catalyst was again washed and dried to be used for the next 7 cycles. This method has a promising scope with the development of such perovskite heterogenous photo catalyst for almost complete degradation of the hazardous chemicals released into water bodies such as aldrin.

Keywords: Aldrin; Advanced Oxidation Process; Photocatalyst; Ag₂O/SmFeO₃; Degradation.

1. Introduction

The release of toxic organic pollutants such as dyes, pesticides and herbicides, into natural water bodies has become a matter of great concern. Especially the agricultural pesticides that are commonly introduced into the water bodies through the untreated irrigation systems. Aldrin is a commonly used agricultural pesticide as it directly targets termites of rice, corn and cotton crops. Prolonged exposure to aldrin might cause serious effects in human such as headaches, nausea, dizziness and vomiting. Upon heavy exposure it might also lead to fatal death. Apart from human it also affects animals which might consume this chemical through water or while grazing. The most common animals that fall victims to this pesticide are cows, buffalos and goats which are sheltered alongside cropping fields. It is hard for aquatic fauna to metabolise and drain such pesticides from their systems without any adverse effects [1-2].

The resistance of these chemicals towards many archaic methods that have been in play for waste water treatment

makes it alarmingly necessary to discover and generate new methodologies for developing efficient water treatment systems. Many new approaches have been initiated to deal with the fall backs of the former techniques. Certain advances in this field include Advanced oxidation processes and adsorption protocols which are sometimes used in combination to achieve better results. Advanced oxidative processes include chemical oxidation in the presence of zone or hydrogen peroxide, photocatalytic oxidation using various heterogenous or homogenous catalysts, Fenton's chemistry and cavitation. The mix-and-match method of the above-mentioned techniques is an interesting field in green technology that is being investigated in the recent times. Photocatalytic degradation has been a hotspot of research for many environmental and chemical work in the recent years. The use of light for the degradation of harmful and hazardous chemicals from the environment without any or few value-added products have gained positive attention. Heterogenous photocatalysts help in capturing the light energy making it available for the necessary degradation reaction in an eco-friendly manner [3].

Several metal oxides such as TiO₂, ZnO and BiO have been used till date for creating photocatalytic nanoparticles. However, their large band gap sets a huge set-back for using it in its pure form. Therefore, certain oxides of perovskite systems with huge surface area and high electron-hole mobility have been a promising solution. SmFeO₃ is a rare-earth perovskite that is being actively investigated as a cathode in fuel cells, superconductors, gas sensitising agents, polymers and catalysts. Ag₂O acts as a p-type semi-conductor with a band gap of 2.1 eV exhibiting competent photoconductivity and photo voltaic properties. Although its band gap shines bright light on its photocatalytic abilities the quick recombination of the photogenerated holes and electrons need assistance in prolonging the life of holes. Coupling is a new approach that helps in extending the life of photogenerated holes, which in turn improves the performance of the photocatalyst [4-5].

Ozonation is an emerging methodology used in the water treatment to eliminate toxic organic chemicals. While many of the conventional methods suffice when the concentration of the pollutants are in high concentrations, the use of ozone is found to be powerful to eliminate them while they are at a very minimal concentrations by

converting them into value added products and mineralisation. This method has been accredited for its clean and safe degradation without any secondary pollutants. It is believed to be a revolutionary tool in combination with photocatalyst to remove minute traces of toxic chemicals from water, which might lead to magnification in a long run. In this work we aim at degrading a common and most toxic chemical aldrin from waste water using $\text{Ag}_2\text{O}/\text{SmFeO}_3$ as a photocatalyst [6-8].

2. Materials And Method

2.1 Photocatalytic Ozonolysis Experiment

Xenon lamp of 500W was used as a light source along with UV filter to maintain UV rays at a shorter wavelength of > 420 nm. Ozone was generated by fisher ozone generator 500 which was pumped into the reaction medium using long sintered glass with a constant flow rate of 10mL/min. was used. The reactor was maintained at room temperature (25 ± 1) °C using water circulation through a double walled pipe system. A magnetic stirred was employed to ensure even distribution of the ozone and the catalytic surface over the reaction system. For each run 50mL of water sample consisting of aldrin was tested within a range of 10-50mg of the photocatalyst prepared. KI test kit was used to determine the ozone concentration through the oxygen stream which was maintained constant at 0.05M. Multiple runs of each batch were carried out to obtain precise results.

2.2 Synthesis of $\text{Ag}_2\text{O}/\text{SmFeO}_3$ nanoparticles.

Sol gel method was employed for the preparation of SmFeO_3 perovskites. The nitrates of samarium ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and iron ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in equivalent ratio cautiously to attain nanoparticles in 20ml of ethyl glycol with under constant stirring for 4-5h. To this mixture calculated amount of AgNO_3 (i.e 1%, 2.5% and 5% of Ag doping) was added and stirred for one hour. The solution was maintained at a basic pH of 11 throughout using NaOH to avoid any unnecessary reversibility or side reactions. The solution was heated upto a temperature of 80°C-90°C, allowing the excessive water to evaporate slowly till a quasi-gel was attained. The gel was oven heated for more than half a day at 150°C to remove the remnant water in the gel till a non-hygroscopic brownish mixture was obtained. It was later subjected to calcination at 500°C and raised to 800°C for 4h to eliminate any nitrates present in the compound.

2.3 Instrumentation

The morphology of the catalyst was assessed using various analytical methods such as PXRD, BET, ICP, PL, SEM-EDX, and TEM. The reaction mechanism followed through the degradation of aldrin was conjectured by the intermediates identified using ^1H and ^{13}C NMR along with GC-MS and FTIR spectral studies.

3. Results And Discussion

3.1. BET Surface and elemental analysis

The surface area and its structural porosity of $\text{Ag}_2\text{O}/\text{SmFeO}_3$ were determined using nitrogen adsorption studies carried out on the prepared hybrids and comparing

them with pure SmFeO_3 . These isotherms represent a H3 hysteresis loop of type IV isotherm. The surface area of pure SmFeO_3 was measured to be 28.53 m^2/g which increased up to 67.25 m^2/g till 5% doping of Ag_2O . It is noteworthy that further increase in the dopant concentration started clogging the pores on the surface leading to decrease in surface area to 65.47 m^2/g .

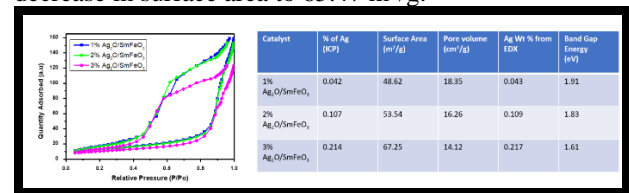


Figure 1: BET Surface area, Elemental analysis and Band gap of $\text{Ag}_2\text{O}/\text{SmFeO}_3$

3.2. UV-DRS:

The band gap values of pure Ag_2O and SmFeO_3 were measured and compared with the prepared hybrid composite as reflected in the adsorption spectra in Figure 2(a). The E_g value of pure Ag_2O and SmFeO_3 were found to be 1.58 eV (400-800nm) and 2.01 eV (300-600nm) while that of the hybrid was measured to be 1.91, 1.83 and 1.61 for 1% $\text{Ag}_2\text{O}/\text{SmFeO}_3$, 2.5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ and 5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ respectively. All the measurements were made within the range of 300-600nm and calculated using the following formula:

$$\alpha h\nu = B(h\nu - E_g)^{1/2}$$

Where α = adsorption co-efficient; h = Plank's constant; ν = Frequency of light; B = band gap energy; and E_g = Energy gap

3.3. Photoluminescence Spectra (PL)

The photoluminescent study was utilized to evaluate the photogenerated electron-hole junction. The PL studies indicate a peak at 370nm. The intensity of the peaks was observed to decrease with the increase in the dopant percentage which might be attributed to the slower recombination of electrons and holes. Therefore, 5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ might be expected to be a better photocatalyst compared to its lower concentrations as the rate of charge carrier recombination is low.

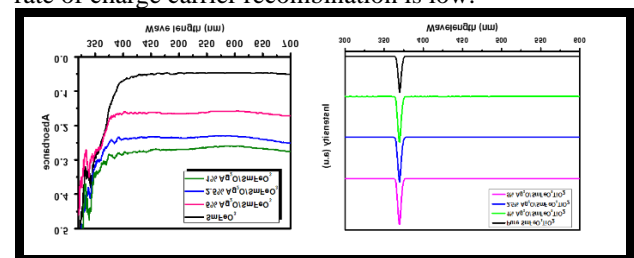


Figure 2 (a) UV DRS spectra (b) PL spectra

3.4. SEM and TEM

The SEM and TEM images supporting the morphology of the prepared $\text{Ag}_2\text{O}/\text{SmFeO}_3$ (1%, 2.5% and 5%) nanocomposites were displayed in Figure 3. The SEM and TEM images show that the Ag_2O on the surface is closely packed and agglomerated leading to the formation of pores as suggested by BET analysis. The agglomerations increased as the dopant percentage increased. The elemental analysis of the prepared composites was perceived by EDX studies. The TEM images represent

spherical particles with grain size ranging from 32.16 nm to 53.24 nm.

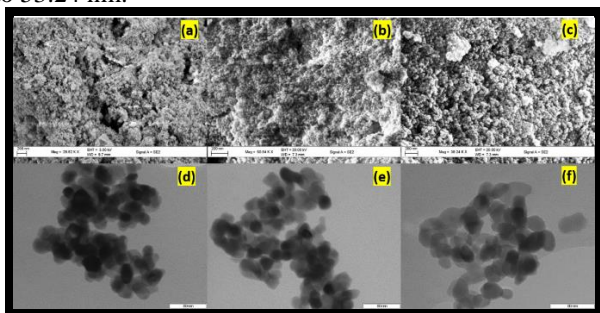


Figure 3: SEM of (a) 1% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ (b) 2.5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ (c) 5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ TEM of (d) 1% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ (e) 2.5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$ (f) 5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$

3.5. XRD analysis

The X-ray Diffraction patterns of Pure Ag_2O and SmFeO_3 were compared with varied dopant hybrids in Figure..... The peaks at Ag_2O at $2\theta = 26.7^\circ, 32.55^\circ, 37.89^\circ, 54.88^\circ, 65.52^\circ$ and 69.04° represent Ag_2O (JCPDS 041-1104) suggesting a FCC crystallinity, whereas peaks at $2\theta = 25.57^\circ, 31.93^\circ, 34.04^\circ, 39.81^\circ, 48.35^\circ, 53.24^\circ, 59.09^\circ$ and 68.47° represents pure SmFeO_3 (JCPDS card No. 39-1490). The hybrid composites of $\text{Ag}_2/\text{SmFeO}_3$ show a combination of pure crystalline phases of the parent compounds.

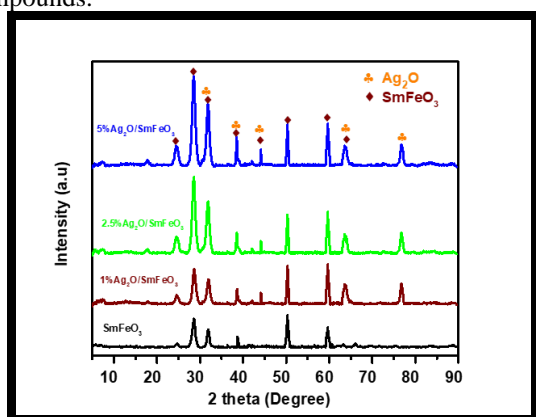


Figure 4: PXRD of (1%, 2.5% and 5%) $\text{Ag}_2\text{O}/\text{SmFeO}_3$

3.6. Effect of pH

The degradation of aldrin was observed at varied pH states starting from acidic to basic (pH = 3, 7, and 11). The patterns of degradation are portrayed in Fig..... depicting that at an acidic pH the degradation was barely satisfactory and it increased along the pH scale. At an acidic pH the only reactive species is ozone which might have experienced degradation stress while ozone being unstable. As we move towards the basic pH secondary oxidising agents such as hydroxyl radicals are generated at an enhanced rate. Hydroxyl free radicals are highly reactive ensuring faster and efficient degradation of aldrin at a basic pH of 11.

3.7. Effect of catalyst concentration

To determine the optimum catalytic dosage samples were prepared with catalytic concentrations ranging from 10 mg/L to 80mg/L. It was observed that the degradation efficiency increased up to 50mg/L and further increase in the catalyst dosage did not show any further increase but

instead deteriorated in efficiency. This might be credited to the increase in the active sites as the catalytic dosage increased allowing greater amount of light passage. When the dosage overpassed through the optimum amount the excessive particles might create obstruction to the light from entering the reaction medium, thus, lowering the degradation efficiency.

3.8. Effect of Ag_2O doping concentrations

As the concentration of the dopants increased the active sites that lower the activation energy for the degradation reaction also increase. As suggested in the morphological studies such as BET, SEM and TEM the agglomeration of the dopants increased as the dopant percentage increased creating porous surface. The degradation efficiency of the catalyst kept improving till 5% $\text{Ag}_2\text{O}/\text{SmFeO}_3$, and no further improvement was observed for higher dopant concentrations. Therefore, it might be suggested that 5% dopant percentage is an operative percentage at optimum conditions.

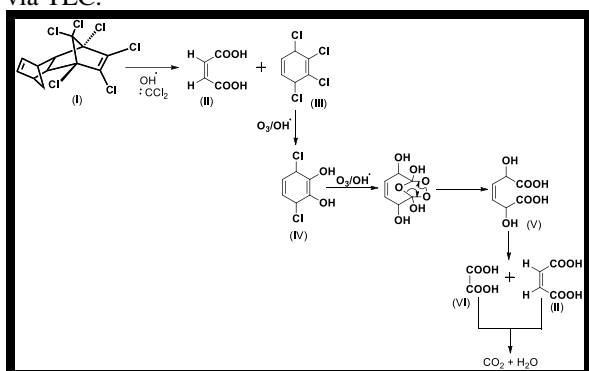
3.9. Catalyst testing and product identification

The photocatalytic degradation of aldrin was accompanied by ozonation under visible light. The reaction mixture was analysed at stipulated intervals of time (20mins) to separate the organic phase. The organic phase was separated and analysed to study the intermediates gathered during the degradation process. The revealed intermediated paved path for constructing the degradation pathway of aldrin in the reaction mixture. Several intermediates were identified using GC-MS. The peaks of the intermediates were observed within a retention time of 8.00 to 18.00 representing various carboxylic acid products. The identified were subjected to TLC and the sample was striped off from the TLC plate to gather the pure intermediate. The intermediate was further analysed using various spectral studies such as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, mass and FT-IR spectra. Further a qualitative test using lime water was carried out to test the release of CO_2 in support to the mineralisation of aldrin in ozone mediated photocatalytic degradation. The intermediates observed were identified to be Fumaric acid (FA), Oxalic Acid (OA), (Z)-2,5-dihydroxyhex-3-enedioic acid (DHHA), 3,6-dichlorocyclohexa-1,4-diene-1,2-diol (DCC), 1,2,3,6-tetrachlorocyclohexa-1,4-diene (TCC), and 9-hydroxyaldrin (HA) respectively which are evident from GC-MS.

3.10. Reaction mechanism

The photocatalyzed degradation pathway for aldrin under ozonation was proposed upon careful observation and investigation of the obtained intermediates. Highly active oxidizing species are generated during the ozonation process such as hydroxyl free radical (OH^\cdot) and dichlorocarbene ($:\text{CCl}_2$). These free radicals play an important role in the generation and separation of electrons and holes. The key oxidizing species in this degradation process is assumed to be OH^\cdot , which attributes to the dichlorination of the intermediates and ozonation process. The most important aspect in the ozonated photo-catalyzed degradation is the stability of the generated oxidizing agents, and the surface-active sites of the heterogenous photocatalyst. It is interesting to note that the first intermediate observed in the degradation process was 9-

hydroxyaldrin (HA), which supports our notion of OH[•] free radical domination in the degradation process. It is a known fact that the string electron density is a pre-requisite for the photolytic ozone induced electrophilic reactions. The presence of electron withdrawing groups such as (-Cl) are highly vulnerable to photo-ozonation reactions especially at ortho and para positions. Therefore, the presence of chloride in aldrin enables certain preferable sites for the radical attack to initiate degradation process. Further, this attack leads to ring opening and oxidation reactions leading to the formation of carboxylic groups (-COOH). With these factors into consideration the intermediates identified using various spectral analysis were assembled to propose a possible reaction pathway. With the hydroxyl interaction of aldrin a primary intermediate i.e 9-hydroxyaldrin (HA) with good concentration was obtained which releases two active oxidising agents OH[•] and :CCL₂ leading to the formation of fumaric acid (FA) and 1,2,3,6-tetrachlorocyclohexa-1,4-diene (TCC). Mineralisation of fumaric acid might lead to generation of CO₂ and H₂O, while TCC further dechlorinated to form 3,6-dichlorocyclohexa-1,4-diene-1,2-diol (DCC) which upon ozonation produces 2,5-dihydroxyhex-3-enedioic acid (DHHA). The C=C bond of DHHA was broken by further ozonation leading to the formation of common intermediates fumaric acid and oxalic acid (OA) which finally mineralise to form CO₂ and H₂O. All the intermediates mentioned in the reaction pathway are supported by the GC-MS analysis along with independent spectral data for each intermediate separated via TLC.



Scheme 1: Degradation pathway for Aldrin via photocatalytic degradation in the presence of ozone.

4. Conclusions

The present study addresses the easy synthetic protocol for the synthesis of Ag₂O/SmFeO₃ using sol-gel method. Simple careful steps allow a good dispersion of the desired dopant (in this case Ag₂O on SmFeO₃). The prepared catalyst was characterised using BET, SEM and TEM to understand the external morphology of the nanocatalyst, while the photoconduction efficiency of the catalyst was determined using ICP and PL studies. The catalyst was then examined for its efficiency in the degradation of aldrin, a harmful pesticide that reaches water bodies near the agricultural fields. The catalyst was found to be highly functional in the degradation of aldrin in combination with ozonation under visible light. The pathway of aldrin degradation was constructed by the information gathered by the separation of the intermediates and their identification. Although six intermediates (FA, OA, TCC, DCC, DHHA and HA) were identified during

the degradation process all of them were fated to be mineralised producing CO₂ and H₂O. Finally, a complete degradation was obtained with any traces or secondary pollutants using Ag₂O/SmFeO₃ photocatalyst in combination with ozone under visible light. This process is sustainable, and economical process with excellent results.

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