PHOTOCATALYTIC INVESTIGATION OF BIVO4/BIOBR/LFO MAGNETIC BASED TERNARY NANOCOMPOSITE AND BIODIESEL PRODUCTION FROM USED COOKING OIL

Project Reference No.: *47S_MSC_0156*

College *: M.S. Ramaiah University of Applied Sciences, Bengaluru*
Branch *: Department of Chemistry*
Guide(s) *: Dr. N. Manikanda Prabu*
Student(S) *: Ms. Diya Rose Davis*
Mr. Kethernath R.

Key words: $BiVO_4$, BiOBr, $Li_{0.5}Fe_{2.5}O_4$, Nanocomposite, Biodiesel, Transesterification

Introduction:

The extensive use of synthetic dyes in various industries, including textiles, leather, furniture, and plastics, has led to a significant concern regarding dye contamination in wastewater. A substantial portion of these dyes remains unutilized during the dyeing process, resulting in their discharge into industrial effluents and this poses a threat to both human health and the environment.

Conventional wastewater treatment methods such as membrane separation, coagulation, filtration, ion exchange and adsorption etc. have been employed for dye removal. However, Advanced Oxidation Processes (AOPs) has emerged as a promising technique, particularly since the latter half of the 20th century. This approach effectively degrades large dye molecules into smaller by inhibiting the recombination of electron – hole pairs for a long time, thereby producing environmentally benign by products such as water, carbon dioxide, and minerals.

AOPs play a critical role in photocatalytic dye degradation due to their ability to generate highly reactive species, particularly hydroxyl radicals ($OH^{\bullet}$) and superoxide radicals ($O_2^{\bullet-}$). The effectiveness of AOPs in dye degradation stems from the strong oxidative power of the generated radicals, allowing for the efficient breakdown of a wide range of organic pollutants. This approach offers a promising solution for wastewater treatment, contributing to environmental sustainability.

$BiVO_4$, BiOBr, and $Li_{0.5}Fe_{2.5}O_4$ are used in photocatalytic degradation of dyes due to their suitable bandgaps for visible light absorption, high photocatalytic activities, stability in aqueous environments, and, in the case of $Li_{0.5}Fe_{2.5}O_4$, additional magnetic properties that facilitate easy recovery and reuse. These characteristics make them effective and practical choices for environmental remediation applications.

Objectives:

The objectives of this work include,

- Synthesis of magnetic ternary nanocomposite and its characterization using powder X – Ray Diffraction (XRD), Diffuse Reflectance Spectroscopy (DRS), Scanning Electron Microscopy & Energy Dispersive Spectroscopy (SEM – EDS), Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometry (VSM) and UV – Visible spectroscopy
- Photocatalytic investigation on Congo red dye solution
- Investigation and reusability of the magnetic ternary nanocomposite
- Production of biodiesel from used cooking oil using magnetic ternary nanocomposite

Methodology:

The ternary magnetic nanocomposite was synthesized combining weight percentages of 25% $BiVO_4$/50% BiOBr/25% $Li_{0.5}Fe_{2.5}O_4$ and the schematic illustration is depicted below.

- **Synthesis of $BiVO_4$:**

Method: Hydrothermal route

Materials required: Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$), Ammonium metavanadate (NH_4VO_3), Teflon lined stainless steel autoclave

Procedure: The stoichiometric ratio of $Bi(NO_3)_3.5H_2O$ and NH_4VO_3 are dissolved in minimum amount of distilled water at 50℃. The combined solution undergoes hydrothermal reaction at 180℃ for 12 hours and the product is finally filtered and dried.

- **Synthesis of BiOBr**

Method: Co - precipitation

Materials required: Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$), Potassium bromide (KBr), Glycerol, Ethanol, Sonicator

Procedure: The separate solutions of $Bi(NO_3)_3.5H_2O$ in glycerol/water (1:1) and KBr in distilled water are prepared. Then, the KBr solution is added to the $Bi(NO_3)_3.5H_2O$ solution and stirred for 21 hours to induce precipitation. The precipitate is filtrated and dried at 90℃ for 6 hours.

- **Synthesis of $Li_{0.5}Fe_{2.5}O_4$**

Method: Auto combustion

Materials required: Ferric nitrate ($Fe(NO_3)_3.9H_2O$), Lithium nitrate ($LiNO_3$), Glycine, Sonicator

Procedure: Iron and lithium nitrate slats are dissolved along with glycine in minimum amount of distilled water and sonicated for 5 minutes. After sonication and stirring, the mixture is heated until it become a viscous gel. This gel ignites itself and transforms into the desired ferrite powder. The powder is then collected and grinded for further processing.

- **Synthesis of $BiVO_4$/BiOBr/$Li_{0.5}Fe_{2.5}O_4$ magnetic nanocomposite**

Method: Solid State

Materials required: Bismuth vanadate ($BiVO_4$), Bismuth oxybromide (BiOBr), Lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$), Acetone, Muffle furnace

Procedure: Weigh 25%$BiVO_4$,/50% of BiOBr/25%$Li_{0.5}Fe_{2.5}O_4$ in a mortar pestle and grind for 30 minutes in acetone medium. Transfer the compound to a clean crucible and calcinate in a muffle furnace at 350℃ for 4 hours. Weigh and transfer the composite to the sample holder.

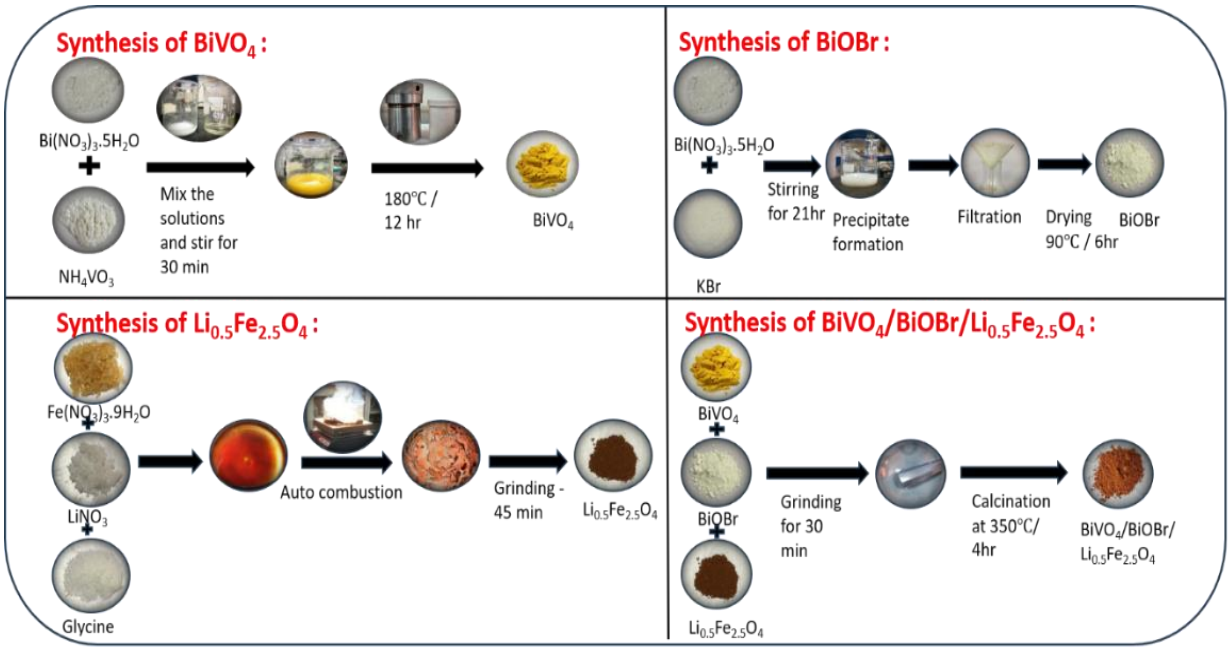

Figure 1. Schematic illustration of synthesis

Results and Discussions:

The magnetic ternary nanocomposite was synthesized and characterized using powder XRD, DRS, SEM, TEM, and VSM (other characterizations are going on).

- **Powder X – Ray Diffraction Analysis**

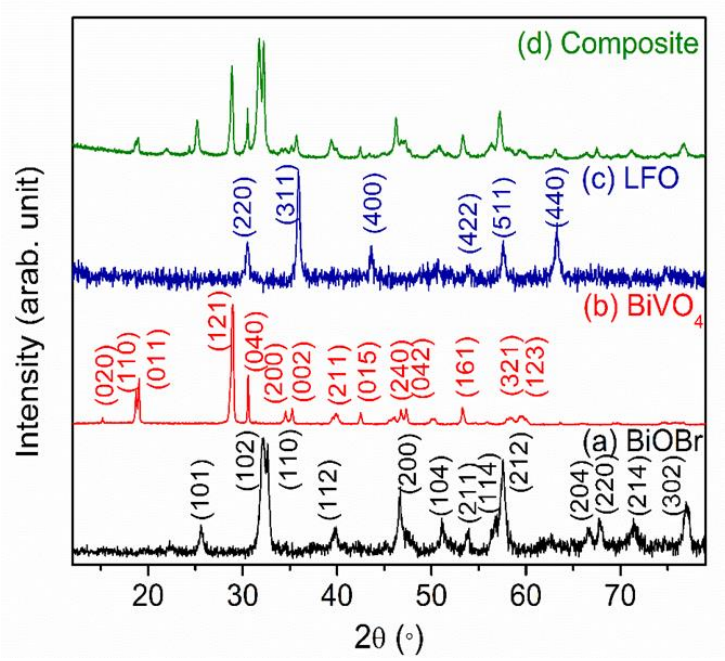

Figure 2. XRD pattern of the samples

The XRD pattern of the samples indicates the formation of single phase of compounds without any impurity. $BiVO_4$ is assigned to monoclinic structure with JCPDS No:14-0688, BiOBr is assigned to tetragonal phase with JCPDS No:09-0393 and for $Li_{0.5}Fe_{2.5}O_4$ is assigned to cubic spinel-phase lattice structure with JCPDS No: 38-0259. The crystallite size of the compounds are calculated using Scherrer formula, $D = (k \lambda) / (\beta \cos\Theta)$ and found that the $BiVO_4$ is 24 nm, BiOBr is 16 nm, $Li_{0.5}Fe_{2.5}O_4$ is 11 nm and the composite is 19 nm.

- **Band gap studies**

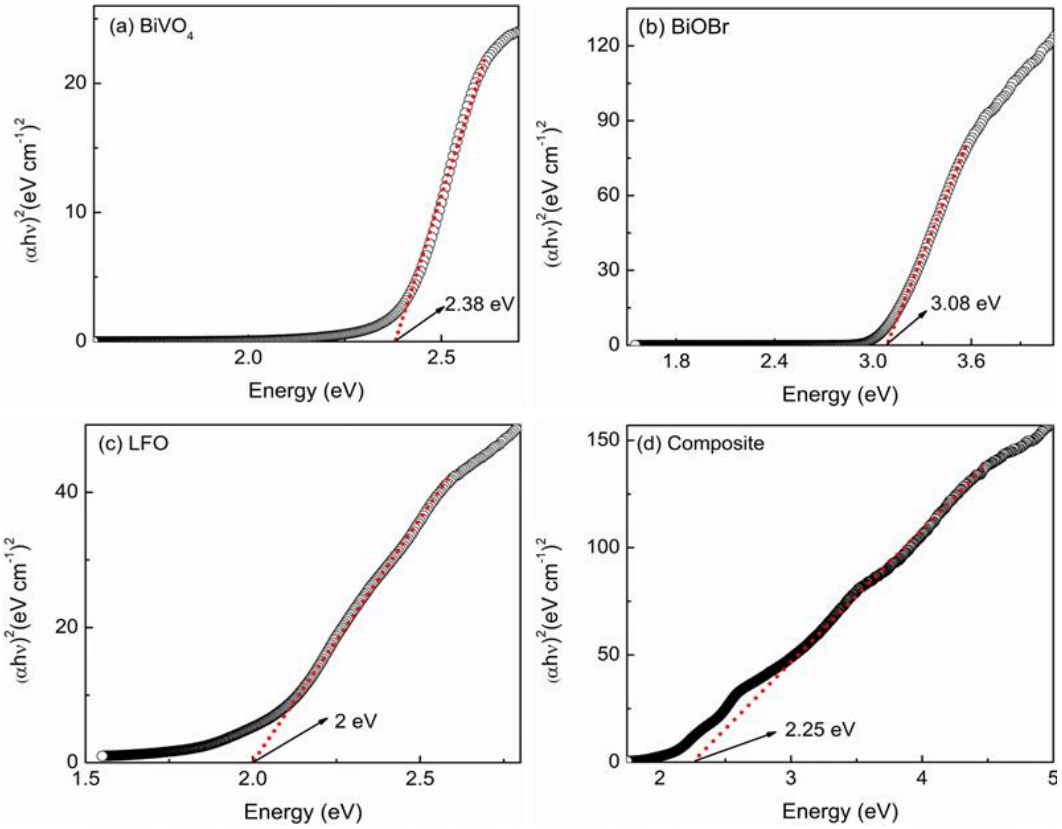

Figure 3. DRS of (a) $BiVO_4$ (b) BiOBr (c) $Li_{0.5}Fe_{2.5}O_4$ (d) Composite

Diffuse Reflectance Spectroscopy is a method used to identify the optical band gap of the nanomaterials. The indirect band gap is measured by extrapolating the linear region of the absorption curve to the x axis, and variation of this method is Tauc plot method. From the graph it's found that the band gap of $BiVO_4$ is 2.38 eV, BiOBr is 3.08 eV, $Li_{0.5}Fe_{2.5}O_4$ is 2 eV and for the composite is 2.25 eV.

- **Surface morphology analysis**

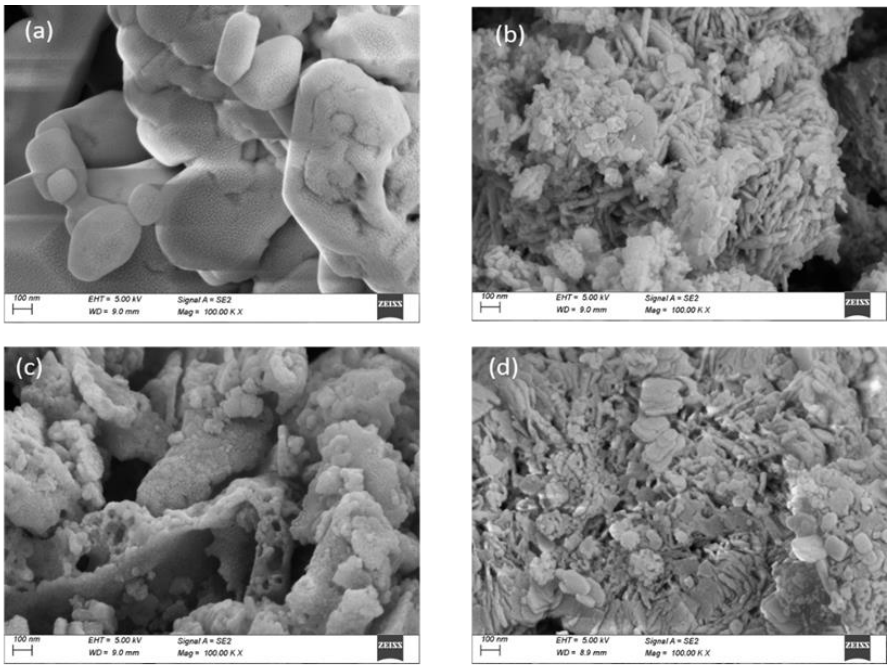

Figure 4 SEM images of (a)$BiVO_4$ (b)BiOBr (c)$Li_{0.5}Fe_{2.5}O_4$ (d) Composite at 100 nm scale

The SEM images of BiVO4, BiOBr, Li0.5Fe2.5O4 and the composite at 100 nm scale is depicted in the figure 19. It can be seen from SEM image of BiVO4 sample that most of the sample exhibit cuboidal and irregular shape and in the case of BiOBr, it exhibits rod like structure. Similarly, most of the ferrite particles are irregular in shape and agglomerated. And the composite is showing the mixed structure of all the parent compounds.

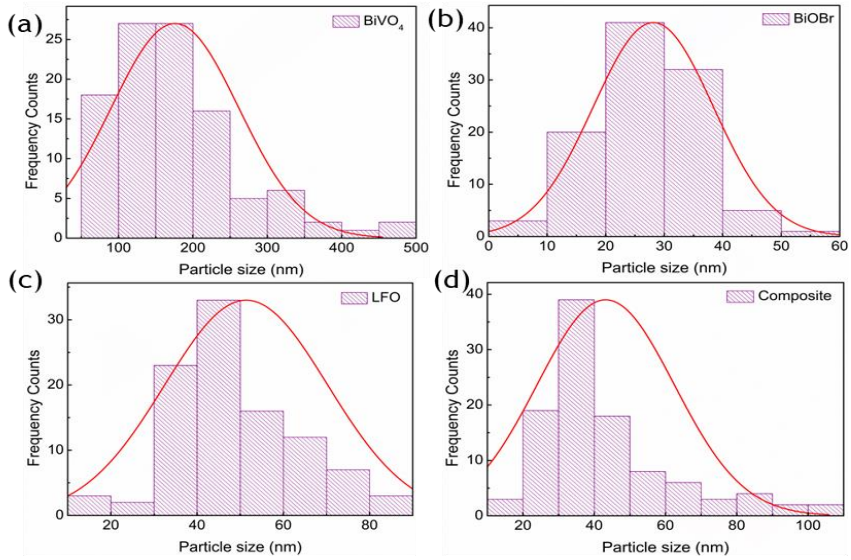

Figure 5 Histograms of (a)$BiVO_4$ (b)BiOBr (c)$Li_{0.5}Fe_{2.5}O_4$ (d) Composite

From the histograms it found that the average size of the $BiVO_4$ is 175 nm, BiOBr is 28 nm, $Li_{0.5}Fe_{2.5}O_4$ is 51 nm and for the composite is 44 nm.

- **Transmission Electron Microscopy**

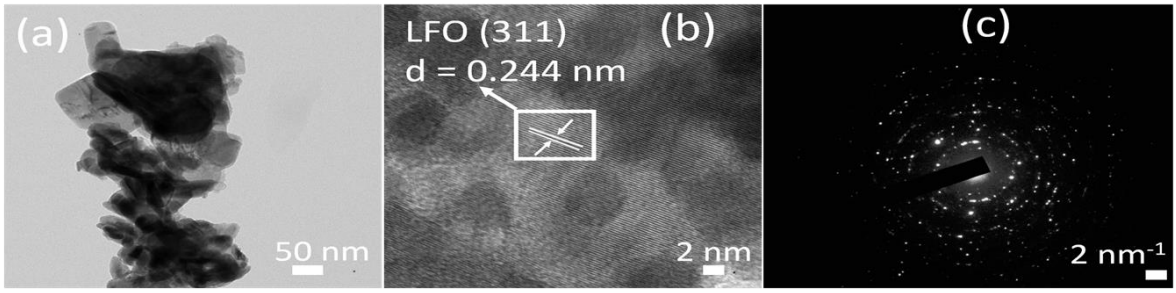

Figure 6. (a)TEM at 50 nm scale (b) HR-TEM at 2 nm scale (c)SAED at 2 nm-1 scale of composite

The TEM image of the composite is depicted in the above fig. 6. From the figure, it found that the d – spacing of the two consecutive planes are found to be 0.244 nm which corresponds to LFO (311). The SAED images shows that the composite is polycrystalline in nature

- **Magnetic property**

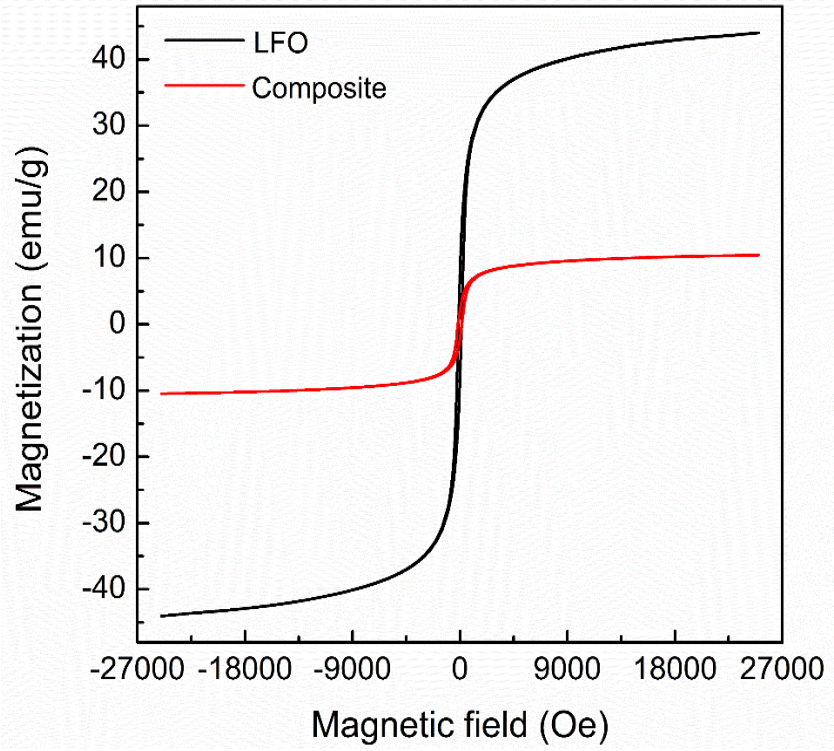

Figure 6. Magnetic loops of the $Li_{0.5}Fe_{2.5}O_4$ and composite

Measurements of a solid's or liquid's magnetic characteristics are made with a vibrating sample magnetometer (VSM). With an applied magnetic field, the magnetometer calculates the magnetic moment. From the graph, the magnetization value of composite is 11 emu/g and $Li_{0.5}Fe_{2.5}O_4$ is 44 emu/g. The magnetization value of the composite is lower than $Li_{0.5}Fe_{2.5}O_4$ the due to non – magnetic nature of $BiVO_4$ and BiOBr.

- **Photocatalytic studies**

Photocatalysis is a type of advanced oxidation process (AOP) that harnesses light to drive chemical reactions on the surface of a semiconductor photocatalyst. Light absorption by the photocatalyst excites electrons, creating electron-hole pairs that participate in redox reactions with adsorbed molecules on the catalyst's surface.

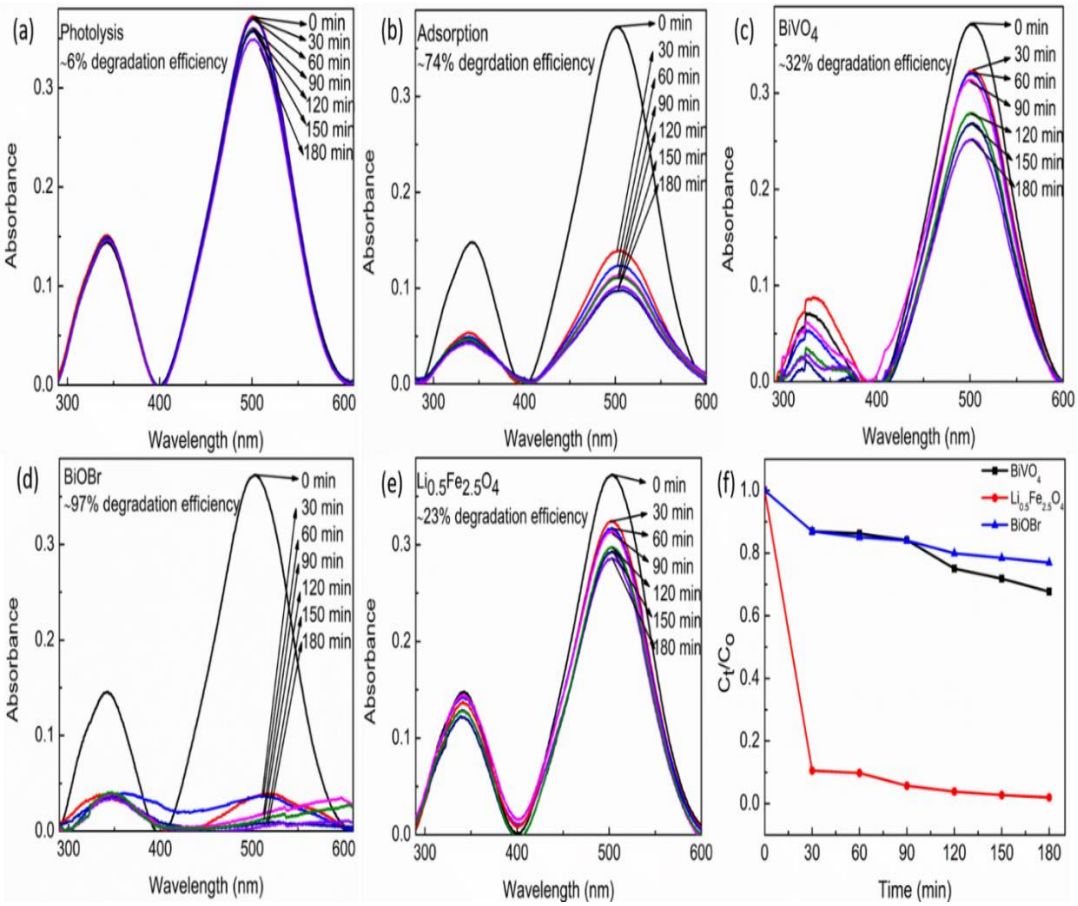

Figure 7. UV-Vis spectra of Congo red (a) Photolysis (b) Adsorption (c)$BiVO_4$ (d) BiOBr (e) $Li_{0.5}Fe_{2.5}O_4$ (f) C_t/C_o of $BiVO_4$, BiOBr, $Li_{0.5}Fe_{2.5}O_4$

- **Photocatalytic Degradation of Congo red Dye Solution**

The experiment investigated the visible-light driven photodegradation of Congo red dye using $BiVO_4$/BiOBr/$Li_{0.5}Fe_{2.5}O_4$ composites. A photodegradation setup equipped with a 250 W high-pressure mercury lamp served as the light source. A 10 ppm Congo red solution (250 mL) was prepared and stirred in the dark with 0.05 g of the composite catalyst and magnetic beads for 30 minutes to establish adsorption-desorption equilibrium. The solution was then exposed to the visible light source for consecutive 30-minute intervals over a total duration of 180 minutes. Samples were collected after each interval for UV analysis. The experiment was repeated using 0.15 g and 0.25 g of the composite catalyst to evaluate the effect of catalyst loading.

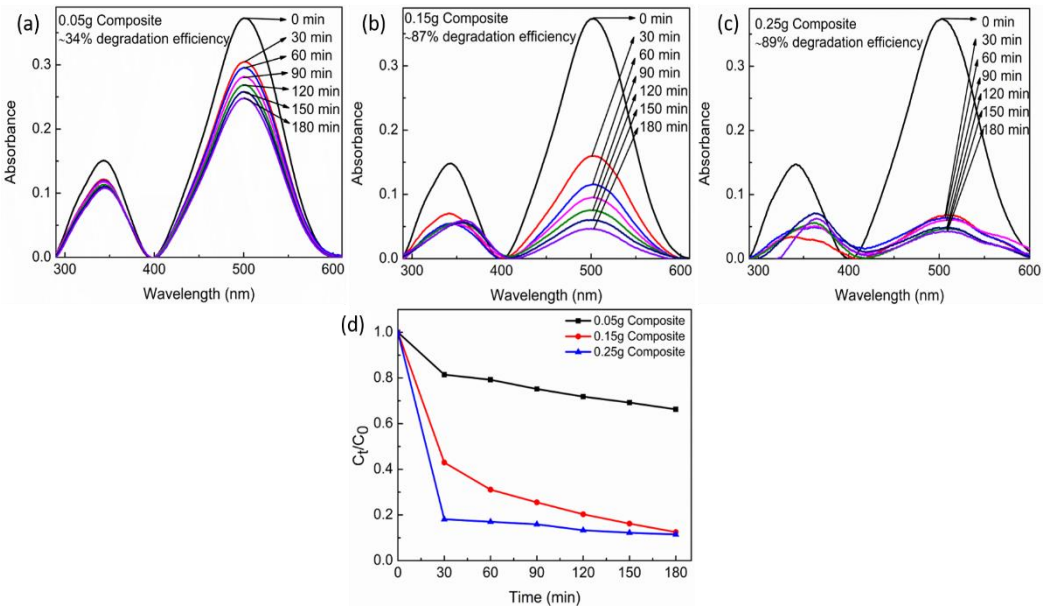

Figure 9. UV - Vis spectra of Congo red at 10 ppm concentration with (a) 0.05 g (b) 0.15 g and (c) 0.25 g composite and (d) C_t/C_o plot

From the UV – Vis, it found that the dye solution with 0.25 g of composite showed more degradation ~89%. So, 0.25 g of composite is used for further studies with 5 ppm, 10 ppm, 15 ppm, 20 ppm dye concentration.

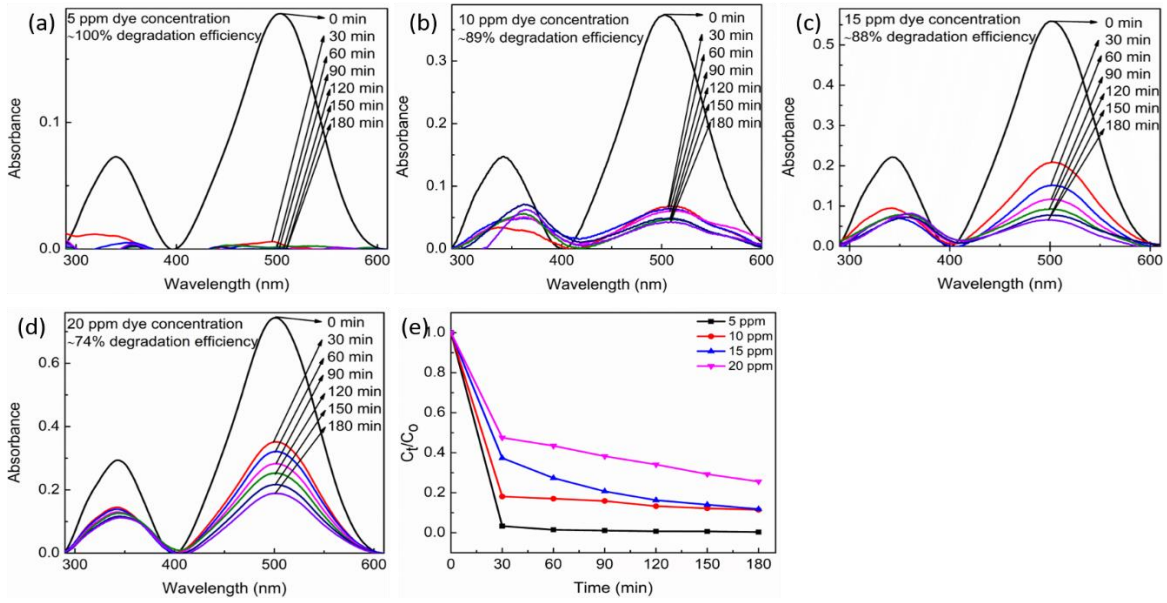

Figure 10. UV - Vis spectra of Congo red at (a) 5 ppm (b) 10 ppm (c) 15 ppm (d) 20 ppm with 0.25 g of composite and (d) C_t/C_o plot for 5, 10, 15 and 20 ppm

After the series of studies with 0.25g composite and different dye concentrations, it is noted that the dye with 5 ppm concentration dye showed more degradation i.e., ~100% at 180 min.

- **Reusability Studies**

A critical factor in optimizing the photocatalytic process is the reusability of the catalyst. The incorporation of $Li_{0.5}Fe_{2.5}O_4$ into the $BiVO_4$/BiOBr composite imparts magnetic properties, facilitating catalyst separation using an external magnet. This magnetic separation allows for efficient recovery of the catalyst particles after each reaction cycle. The recovered catalyst can then be washed with water and reused in subsequent degradation experiments without compromising its activity.

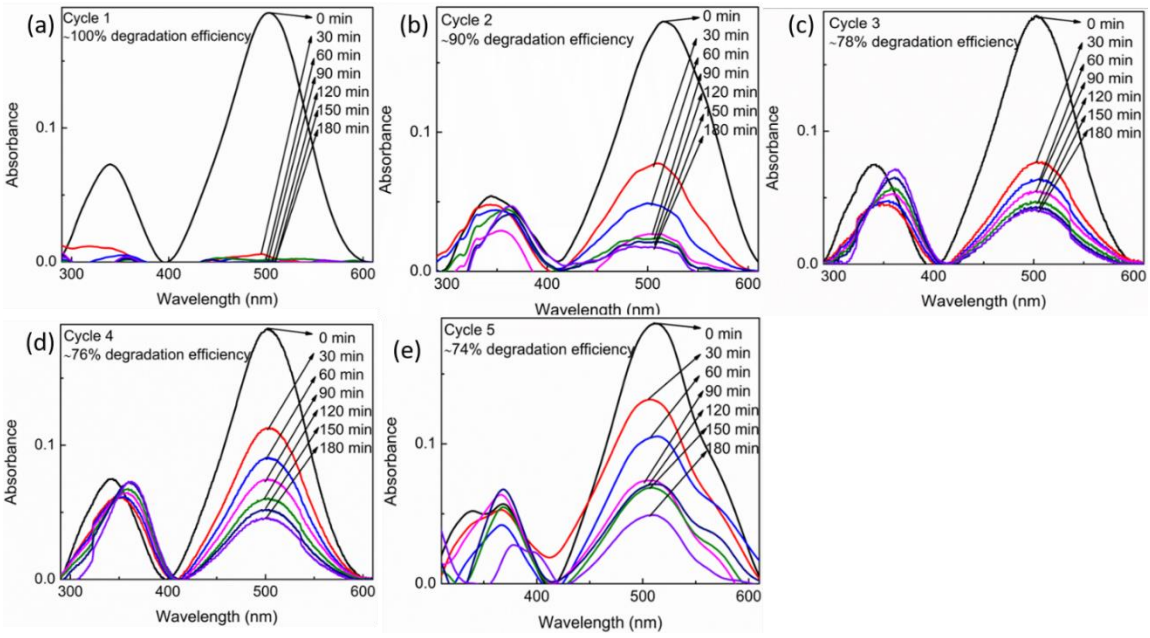

Figure 11. Reusability of the composite (a) Cycle 1 (b) Cycle 2 (c) Cycle 3 (d) Cycle 4 (e) Cycle 5

From the UV-Visible spectra (fig.11), we can see that the activity of the composite was decreased. This is because the active sites of the composites are occupied by the dye molecules.

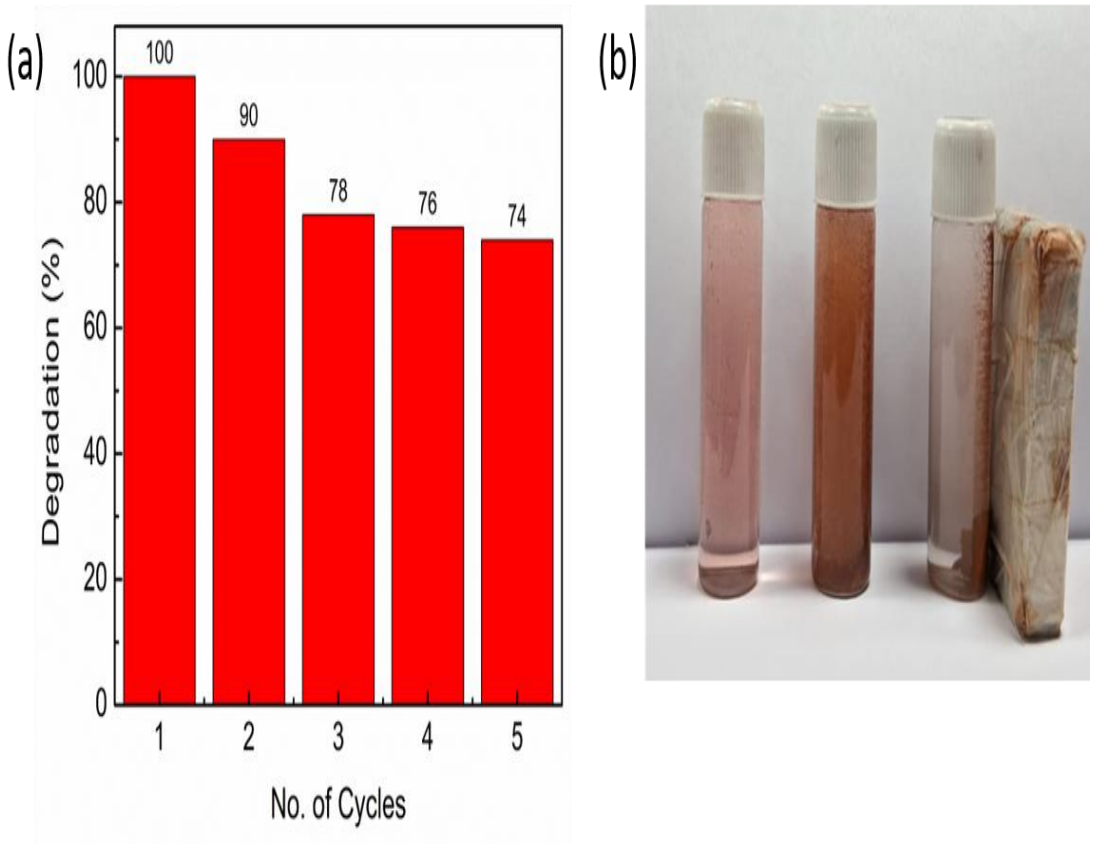

Figure 128.(a)Bar diagram of reusability of composite (b) Separation of composite using magnet

Table 1. Degradation (%) in consecutive cycles

No. of Cycles	Degradation (%)
1st cycle	100
2nd cycle	90
3rd cycle	78
4th cycle	76
5th cycle	74

The X-Ray Diffraction of the used samples were taken and identified that there is no change in the structure throughout the consecutive cycles.

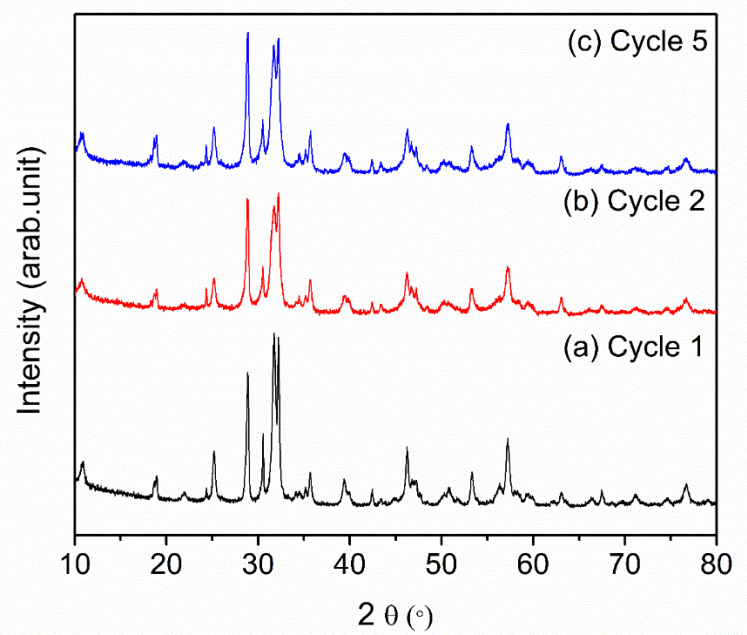

Figure 13.XRD pattern of the reused composite

Mechanism

- **Electron Trap**

The photocatalytic degradation experiment was modified to assess the influence of electron on Congo red dye degradation. To the 250 mL of 5 ppm Congo red solution, 0.25 g of composite and 0.0022 g of Silver Nitrate ($AgNO_3$) were added before exposure to the visible light source. The photocatalytic reaction was then carried out as previously described, with samples collected every 30 minutes for UV-Vis analysis. This modification allows for investigation of the potential role of electron in enhancing or altering the photodegradation efficiency of the composite catalyst.

- **Proton Trap**

The photocatalytic degradation experiment was modified to assess the influence of proton on Congo red dye degradation. To the 250 mL of 5 ppm Congo red solution, 0.25 g of composite and 0.0420 g of Disodium Ethylene Diamine Tetra Acetic acid (2Na – EDTA) were added before exposure to the visible light source. The photocatalytic reaction was then carried out as previously described, with samples collected every 30 minutes for UV-Vis analysis. This modification allows

for investigation of the potential role of proton in enhancing or altering the photodegradation efficiency of the composite catalyst.

- **Superoxide Trap**

The photocatalytic degradation experiment was modified to assess the influence of superoxide radicals on Congo red dye degradation. To the 250 mL of 5 ppm Congo red solution, 0.25 g of composite and 0.0440 g of Ascorbic acid were added before exposure to the visible light source. The photocatalytic reaction was then carried out as previously described, with samples collected every 30 minutes for UV-Vis analysis. This modification allows for investigation of the potential role of superoxide radicals in enhancing or altering the photodegradation efficiency of the composite catalyst.

- **Hydroxyl Trap**

The photocatalytic degradation experiment was modified to assess the influence of hydroxide radicals on Congo red dye degradation. To the 250 mL of 5 ppm Congo red solution, 0.25 g of composite and 2.5 ml of Isopropanol were added before exposure to the visible light source. The photocatalytic reaction was then carried out as previously described, with samples collected every 30 minutes for UV-Vis analysis. This modification allows for investigation of the potential role of hydroxyl radical in enhancing or altering the photodegradation efficiency of the composite catalyst.

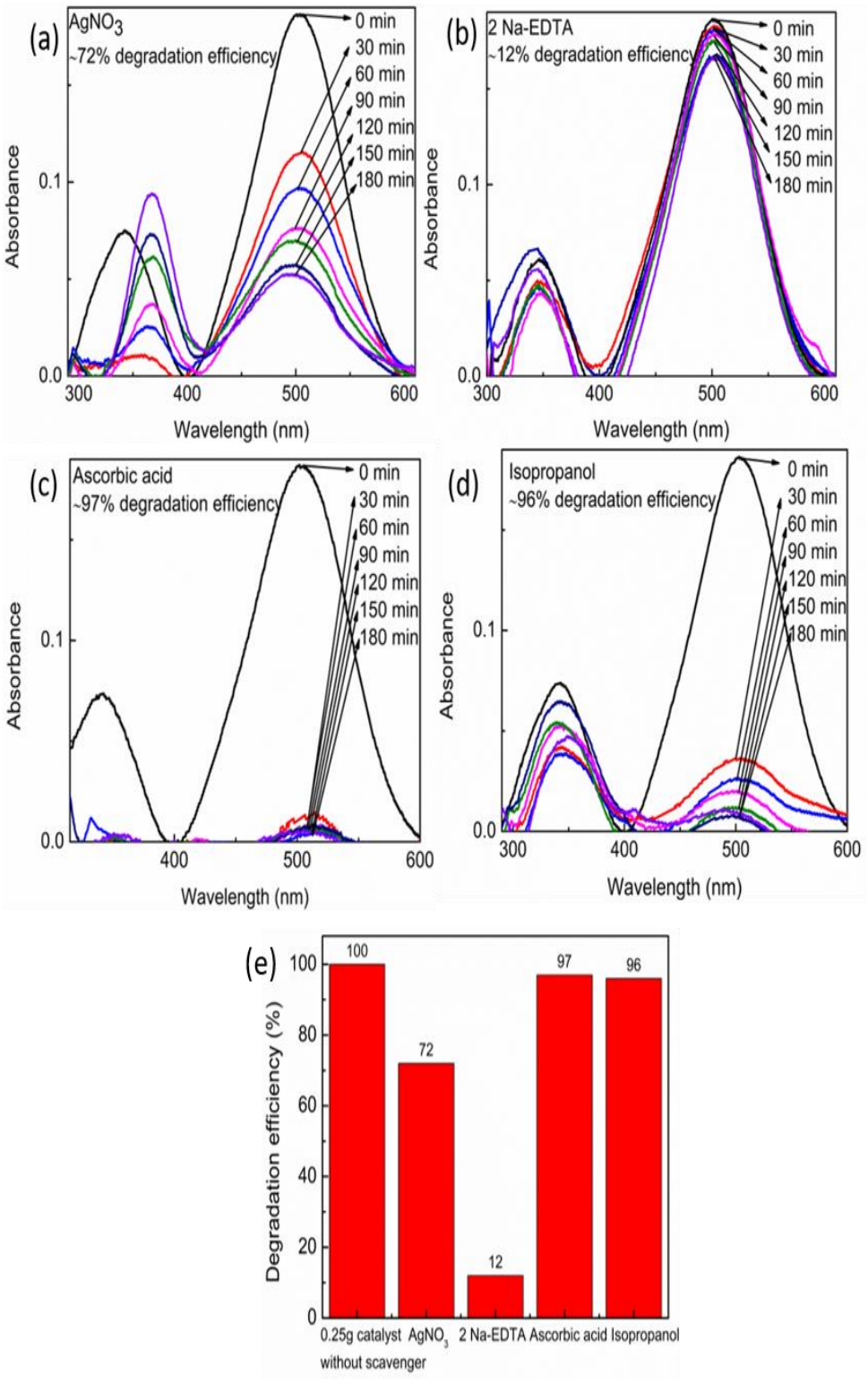

Figure 14. UV-Vis spectra of Congo red's mechanism with of (a)Electron trap (b)Proton trap (c)Superoxide trap (d)Hydroxide trap and (e) bar diagram for the mechanism

- **Biodiesel Production**

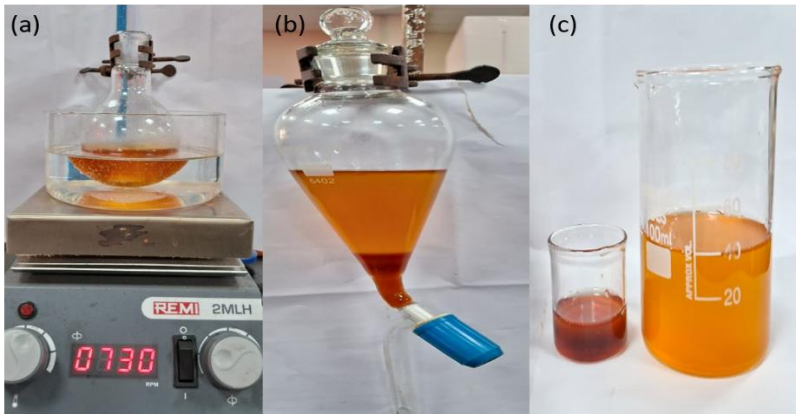

Figure 15. (a) Transesterification (b) Separation of biodiesel and glycerol (c) Glycerol and Biodiesel

Conclusions

A series of parent compounds (BiVO4, BiOBr, Li0.5Fe2.5O4) and a composite material were synthesized and characterized using various techniques (XRD, DRS, SEM, VSM, UV-Vis spectroscopy). The photocatalytic activity of these materials was evaluated for Congo red degradation, revealing that a 5 ppm concentration resulted in the highest degradation rate. The reusability of the catalyst was examined, and a decrease in degradation efficiency was observed, possibly due to the blockage of active sites by dye molecules. The mechanistic investigation suggests that holes play a dominant role in the degradation process. Furthermore, the synthesized materials were employed for biodiesel production, achieving a yield of 15% without the composite and a significant increase to 42% upon incorporation of 0.25 g of the composite catalyst.

Innovation of the Project:

A novel composite was synthesized in order to check the photocatalytic activity in the Congo red dye solution and in the biodiesel production with enhanced yield. The magnetic nature of the composite, due to the presence of $Li_{0.5}Fe_{2.5}O_4$ is helpful for the recyclability and reusability of the composite for consecutive cycles.

The successful development of this novel composite photocatalyst holds promise for a sustainable and efficient solution to wastewater treatment challenges. The combination of enhanced photocatalytic activity and magnetic separation capability paves the way for a practical and reusable technology for dye removal from wastewater.

The synergistic interaction between these components is expected to significantly enhance the photocatalytic performance of the composite. By promoting efficient charge separation and minimizing electron-hole recombination, the composite is anticipated to exhibit superior photocatalytic activity compared to individual components and this composite can be used as photocatalyst as well as catalyst in reactions.

Scope for future work:

- By strategically reducing the band gap of nanocomposites, it aims to suppress the recombination of photogenerated electron-hole pairs, ultimately enhancing the degradation rate of organic pollutants.
- The magnetic nature of the composite holds promises for applications beyond organic pollutant degradation. Its incorporation might enhance the activity and yield in biodiesel production processes.
- The magnetic property would allow for easy catalyst recovery after each production cycle, simplifying downstream processing and potentially reducing overall production costs.
- By tailoring the composition of the nanocomposite, researchers can engineer its band gap, magnetic properties, and ultimately, its degradation efficiency for organic pollutants.
- It paves the way for the development of robust and sustainable AOP technologies with a focus on reusability and broader applicability, including biodiesel production.
- $Li_{0.5}Fe_{2.5}O_4$ can be further modified to enhance the photocatalytic property of the nanocomposite for the efficient treatment of waste water.
- Photocatalytic activity can be improved by varying the composition of the parent compounds.