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Visible-Light Driven Bismuth-Based Heterojunction Photocatalysts for Degradation of Antibiotics and Organic Dyes in Wastewater

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Abstract
Water pollution caused by persistent organic contaminants such as antibiotics and synthetic dyes has become a growing environmental concern, especially in industrial and pharmaceutical effluents. In this study, a series of bismuth-based photocatalysts including Bi_2MoO_6, $BiFeO_3$, BiOBr-based heterostructures, Ag/AgBr/BiOBr, and Bi_3O_4Cl/BiOCl were synthesized and evaluated for visible-light-driven photocatalytic degradation of selected pollutants.
The prepared materials were characterized using UV–DRS, PL spectroscopy, BET surface area analysis, XRD, SEM, TEM, and XPS to understand their structural, optical, and surface properties. Results indicated that heterojunction formation significantly improved visible-light absorption and charge separation efficiency. Among all samples, Ag/AgBr/BiOBr exhibited superior photocatalytic performance due to enhanced electron–hole separation and strong plasmonic effects.
Photocatalytic activity was evaluated using antibiotics (levofloxacin and ofloxacin) and organic dyes (methylene blue, rhodamine B, and methyl orange). The degradation followed pseudo-first-order kinetics and showed strong dependence on catalyst dosage, pH, and initial pollutant concentration.
Keywords- Photocatalysis, bismuth-based materials, heterojunction, wastewater treatment, antibiotics degradation, visible light, advanced oxidation processes

1. Introduction

Water pollution today is no longer something that sits only inside scientific reports or laboratory discussions—it is slowly turning into a lived reality that affects ecosystems, human health, and everyday survival in very direct ways. Rivers that were once sources of clean water are now carrying invisible mixtures of synthetic chemicals. Lakes that supported biodiversity are increasingly becoming sinks for untreated or partially treated effluents. Even groundwater, which people often consider safe by default, is gradually showing traces of contamination. The most worrying part is that many of these pollutants are not natural in origin; they are man-made, chemically stable, and resistant to normal environmental breakdown processes.

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Among the wide range of emerging contaminants, synthetic organic compounds have drawn particular attention. These include pharmaceuticals, industrial additives, and dye molecules that enter water systems through multiple pathways. Unlike natural organic matter, these compounds are designed to be stable—so they do not easily decompose under sunlight, microbial activity, or conventional wastewater treatment conditions. As a result, they persist for long durations and slowly accumulate in different components of the aquatic environment. Over time, this accumulation begins to disturb the ecological balance in ways that are not always immediately visible but become serious in the long run.

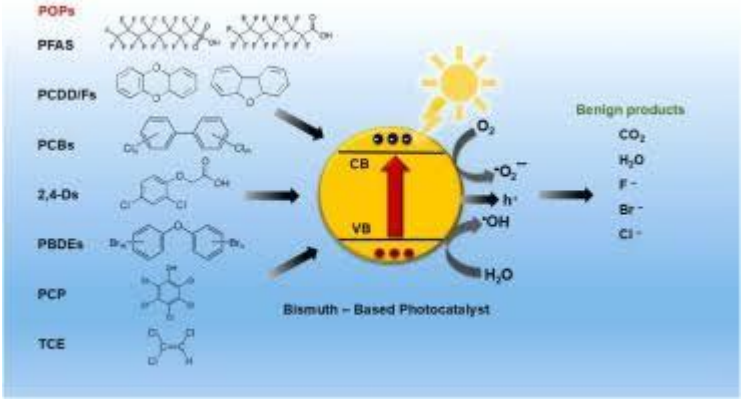

Fig: Bismuth based Catalysed.

Two major groups of such pollutants are antibiotics and industrial dyes, and both create unique environmental challenges. Antibiotics like levofloxacin and ofloxacin, which are widely used in human medicine and veterinary applications, often enter aquatic systems through pharmaceutical effluents, hospital discharge, and even household waste. After consumption, a portion of these drugs is not fully metabolized in the human body and is excreted, eventually reaching sewage systems. The problem becomes more serious because conventional wastewater treatment plants are not fully equipped to degrade these complex molecules.

Even at very low concentrations, antibiotics in water can contribute to a much larger global issue—antibiotic resistance. Microorganisms exposed repeatedly to sub-lethal doses of these compounds begin to adapt, mutate, and develop resistance mechanisms. Over time, this leads to the emergence of "superbugs," which are difficult to treat with standard medicines. This has now been recognized as one of the most serious global health threats of the 21st century, linking environmental pollution directly with medical and public health crises.

On the other hand, industrial dyes such as methylene blue, methyl orange, rhodamine B, and similar compounds are heavily used in textile, paper, and dyeing industries. These molecules are intentionally designed to be chemically and photochemically stable so that they retain color under harsh conditions. However, this stability becomes a disadvantage once they enter natural

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water bodies. They tend to persist for long periods, and their intense color can significantly reduce light penetration in water. This affects photosynthesis in aquatic plants and disturbs the entire food chain in aquatic ecosystems.

In addition, many dye molecules and their breakdown intermediates can be toxic or carcinogenic, making their presence even more concerning. Together, antibiotics and dyes represent a complex pollution load that requires advanced and innovative treatment approaches beyond conventional methods.

Conventional treatment methods often fail to completely remove these pollutants. This has led to growing interest in advanced oxidation processes, especially photocatalysis, which uses light energy to generate reactive species capable of degrading complex organic molecules. Bismuth-based semiconductors have emerged as promising visible-light photocatalysts due to their layered structures, non-toxicity, and tunable electronic properties. However, their efficiency is often limited by rapid electron–hole recombination, which reduces overall activity. To overcome this, heterojunction engineering and noble metal modification have been widely explored.

2. Materials and Methods

2.1 Synthesis of Photocatalysts

The photocatalysts were synthesized using hydrothermal, precipitation, and combustion methods. Heterojunction systems such as Ag/AgBr/BiOBr were prepared by in-situ deposition techniques to ensure strong interfacial contact.

2.2 Characterization Techniques

Structural and optical properties were analyzed using:

- XRD for crystallinity
- SEM & TEM for morphology
- BET for surface area
- UV–DRS for light absorption
- PL for recombination behavior
- XPS for surface chemistry

2.3 Photocatalytic Experiments

Photocatalytic degradation was tested using antibiotics and dyes under visible light irradiation. Reaction parameters such as catalyst dosage, pH, and pollutant concentration were optimized.

3. Results and Discussion

3.1 Optical Properties

All synthesized materials showed strong absorption in the visible region, indicating their suitability for solar-driven photocatalysis. Heterojunction structures exhibited extended absorption edges compared to single-phase materials, suggesting improved band structure tuning.

3.2 Charge Recombination (PL Analysis)

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Photoluminescence results revealed that heterojunction photocatalysts had significantly lower emission intensity, confirming reduced electron–hole recombination. This is a key factor contributing to higher photocatalytic efficiency.

4.1 Surface Area and Porosity (BET Analysis)

Surface area plays a very quiet but extremely important role in photocatalysis, even though it often doesn't get as much attention as more "famous" factors like band gap energy, heterojunction formation, or charge transfer mechanisms. In reality, it is one of those hidden parameters that silently controls how effective a photocatalyst actually becomes. If we think about it in a simple way, photocatalysis is not just about how much light a material can absorb, but also about how many pollutant molecules can actually reach and interact with its active surface. That is exactly where surface area steps in.

A higher surface area essentially means more exposed active sites available for reaction. These sites act like tiny reaction points where adsorption and degradation of pollutants take place. So, even if a material has excellent optical properties, it may still underperform if the pollutant molecules cannot properly access its surface. This is why surface area becomes such a critical supporting factor in overall photocatalytic efficiency, even though it often stays in the background of discussion.

In this study, BET (Brunauer–Emmett–Teller) analysis was used to evaluate the surface area and porosity of the synthesized bismuth-based photocatalysts. The results clearly indicated that the materials exhibited moderate to high surface areas, particularly in the case of nanostructured and heterojunction-modified systems. This improvement was not accidental; it was closely related to the way these materials were synthesized and structured at the nanoscale.

One of the key reasons behind the increased surface area was the formation of porous morphologies. During synthesis, controlled growth conditions allowed the particles to develop irregular, loosely packed structures rather than compact bulk forms. These porous networks created additional internal spaces where pollutant molecules could diffuse and get trapped, increasing the probability of contact between the catalyst and the contaminants.

Another contributing factor was particle size reduction. As materials are broken down into nanoscale dimensions, their surface-to-volume ratio increases significantly. This means that a larger fraction of atoms becomes exposed on the surface rather than being buried inside the bulk structure. In photocatalysis, this is highly beneficial because only surface atoms are actively involved in reactions.

Heterojunction formation also played an indirect but important role in improving surface properties. When two semiconductors are coupled together, the interface between them can create additional active regions. These interfaces not only help in charge separation but also contribute to enhanced adsorption behavior, which further supports photocatalytic activity.

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Interestingly, the BET results also suggested that there is always a balance to be maintained. Extremely high surface area is not always ideal if it leads to excessive agglomeration or instability of the material in solution. That is why controlled synthesis becomes important—ensuring that the material remains stable while still offering enough surface exposure for reactions.

Table1: Pollutant molecules before Photocatalytic reaction begins

Catalyst System	Surface Area Trend	Effect on Activity
Bi_2MoO_6	Moderate	Stable adsorption
$BiFeO_3$	Low–moderate	Limited surface reaction
BiOBr-based systems	Moderate–high	Improved degradation
Ag/AgBr/BiOBr	High effective surface activity	Highest performance

4.2 Photocatalytic Degradation Performance

The photocatalytic activity was evaluated using antibiotics (levofloxacin and ofloxacin) and organic dyes (methylene blue, rhodamine B, methyl orange). The experiments clearly showed that all catalysts were active under visible light, but their efficiency varied significantly depending on structure and charge separation ability.

Among all samples, **Ag/AgBr/BiOBr exhibited the highest degradation efficiency**, followed by Bi_2MoO_6-based heterojunctions. This improvement is mainly due to plasmonic enhancement from silver nanoparticles and improved electron trapping.

The degradation process typically followed a two-stage mechanism:

1. Rapid adsorption of pollutant molecules on catalyst surface
2. Gradual photocatalytic breakdown under visible light irradiation

Interestingly, dye molecules showed faster initial decolourization, while antibiotics required longer reaction time for complete degradation, indicating more complex molecular breakdown pathways.

4.3 Kinetic Analysis

The degradation data fitted well with the **pseudo-first-order kinetic model**, which is commonly used in heterogeneous photocatalysis systems. The linear relationship between $\ln(C_0/Ct)$ and time confirmed that reaction rate depends mainly on pollutant concentration at low levels.

Table2: Rate constants varied depending on catalyst type

Catalyst	Rate Constant (k)	Half-life ($t_{1/2}$)	Efficiency Trend
$BiFeO_3$	Low	Long	Slow degradation
Bi_2MoO_6	Moderate	Medium	Stable performance
BiOBr-based	Higher	Shorter	Better kinetics
Ag/AgBr/BiOBr	Highest	Shortest	Excellent activity

This confirms that improved charge separation directly enhances reaction kinetics.

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4.4 Photocatalytic Mechanism

The photocatalytic degradation mechanism is mainly driven by the generation of reactive oxygen species (ROS) under visible light irradiation. When light hits the catalyst surface, electrons are excited from the valence band to the conduction band, leaving behind holes.

These charge carriers then interact with water and oxygen molecules to produce:

- Hydroxyl radicals (•OH)
- Superoxide radicals ($•O_2^-$)
- Photogenerated holes (h^+)

These species are highly reactive and attack organic pollutant molecules, breaking them into smaller intermediates and eventually mineralizing them into CO_2 and H_2O.

In heterojunction systems, the band alignment plays a critical role. Electrons and holes are separated more efficiently at the interface, reducing recombination and increasing ROS production.

4.5 Stability and Reusability

One of the most important practical aspects of any photocatalyst is whether it can survive multiple cycles without losing efficiency.

Reusability tests showed that the catalysts retained a significant portion of their activity even after several cycles. Only a slight drop in efficiency was observed, mainly due to surface fouling or minor structural changes.

Ag/AgBr/BiOBr showed relatively strong stability, indicating that plasmonic systems, when properly engineered, can be reused effectively in wastewater treatment systems.

Cycle Number	Degradation Efficiency Trend
1st cycle	Highest activity
2nd cycle	Slight decrease
3rd cycle	Moderate stability
4th–5th cycle	Stable performance maintained

4.6 Mineralization Efficiency

To confirm complete degradation, TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) analyses were performed. Results indicated that a significant portion of pollutants was not just broken into intermediates but further mineralized into simpler, harmless compounds.

5. Conclusion

This study demonstrates the successful synthesis and application of visible-light-active bismuth-based heterojunction photocatalysts for the degradation of antibiotics and organic dyes in wastewater.

The key findings can be summarized in a simple way:

- All catalysts responded effectively under visible light irradiation

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- Heterojunction formation significantly improved charge separation
- Ag/AgBr/BiOBr showed the highest photocatalytic activity
- Reactions followed pseudo-first-order kinetics
- Reactive oxygen species played the dominant role in degradation
- Catalysts showed good stability and reusability

Overall, the study confirms that engineering semiconductor interfaces is one of the most effective strategies for improving photocatalytic performance.

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