4.1. Introduction

BiOBr is an important V-Vi-Vii ternary compound, and belongs to the family of main group multicomponent metal oxyhalides. It is known to exhibit good photocatalytic activity due to the hybridization between O 2p and Bi 6s states. It has a layered tetragonal matlockite (PbFCl) structure, and possess unique and excellent electrical, magnetic, optical, and luminescent properties. The presence of layered structure helps to polarize the related atoms or orbitals by providing enough large space. The induced dipole can then separate the electron-hole pairs efficiently, and improve the photocatalytic ability.

BiOBr has a unique sandwich like crystal structure consisting of tetragonal \([\text{Bi}_2\text{O}_2]^{+}\) slices sandwiched between two sheets of \(\text{Br}^{-}\) ions, forming a \([\text{Bi}_2\text{O}_2\text{Br}_2]\) layer unit. The \([\text{Bi}_2\text{O}_2\text{Br}_2]\) layer units are held by non-bonding (van der waals) interactions through Br atoms along the anisotropic growth direction, which is \(c\) axis. These nonbonding interactions help the layer units to stock together one by one in an orderly way. There exist strong internal electric field perpendicular to \(\text{Br}^{-}\) ions and Bismuth oxide layer in these sandwich like crystals. The presence of such strong internal electric fields are believed to enhance the effective separation and conduction of photoinduced electron-hole pairs, which facilitates the redox reaction on the surface of semiconductor, and thereby assist a high photocatalytic activity.

Bismuth oxybromide (BiOBr) has been recognised as one of the most promising photocatalysts owing to its lamellar structure, high photocatalytic activity, and photocorrosion stability. The good chemical stability and eco-friendly nature makes BiOBr as one of the choicest catalysts for degradation of toxic organic pollutants. To further enhance the photocatalytic activity of BiOBr for practical applications, it is important to decrease the electron-hole recombination to a higher rate. Some research has suggested that the electron-hole recombination in semiconductors can be retarded by constructing molecular electron relay semiconductor structures, or efficient electron transport matrices.
Some researchers have also reported that photocatalytic activity is related to the configuration of the photocatalysts, and therefore tuning of shape and structure could improve the photocatalytic ability of the photocatalyst.\textsuperscript{24,25} Moreover, it is notable that the band gap of BiOBr has been reported around (2.9 eV) which limits its absorption above 430 nm.\textsuperscript{26} Several strategies, such as impurity doping,\textsuperscript{27} surface decoration,\textsuperscript{28,29} (metal deposition or heterojunction), photosensitization,\textsuperscript{29} and morphology controlled synthesis\textsuperscript{30-34} have been employed to broaden the visible light absorption range of such photocatalysts. Though doping has proved to be effective in shifting the absorption edge into the visible range, but the sensitivity of photocatalysts to doping level and homogeneity makes it a less suitable method.\textsuperscript{35} Construction of heterostructures by combination of two semiconductors with matching band potentials, such as BiOCl/Bi\textsubscript{2}O\textsubscript{3},\textsuperscript{36} A\textsubscript{g}I/BiOCl,\textsuperscript{37} BiOCl/BiOI,\textsuperscript{38} BiOBr/BiOI,\textsuperscript{39-41} Bi\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}/BiOI,\textsuperscript{42} and Bi\textsubscript{2}S\textsubscript{3}/BiOI\textsuperscript{43} has turned out to be more flexible and effective strategy for broadening the visible light absorption of photocatalysts because heterojunction can effectively tune the electronic properties of composites,\textsuperscript{36} and are also less sensitive to component homogeneity. For an effective heterojunction with increased visible light absorption and efficient separation of photoinduced charge carriers, the semiconductors should have the matching band structure, requisite band gap energy, and suitable molar ratio.\textsuperscript{29,44-46}

4.2. Review of literature

To date, extensive efforts have been made focussing on the development of various synthetic methods for the synthesis of BiOBr and BiOBr based composites. Three dimensional (3D) nanostructured materials, such as nanosheets and nanoplates with large surface area, nearly perfect crystallinity, structural anisotropy, and quantum confinement effects have attracted much attention in recent years because it is believed that such structures could favour the decrease of electron-hole recombination and facilitate their transfer to the surface.\textsuperscript{47} Tian \textit{et al.}\textsuperscript{48} reported mesoporous 3D BiOBr microspheres with excellent visible light activity for the removal of bisphenol A. These mesoporous materials have ordered open pore frameworks and high surface area,\textsuperscript{49,2} which not only improves the contact of photocatalyst with organic pollutants, but also provides transport paths and more active sites in photocatalytic reaction. Further, these mesoporous materials can harvest visible light more efficiently due to the multiple scattering within the solid frame work.\textsuperscript{49,2} Similarly, Tang’s group\textsuperscript{50} reported three dimensional (3-D) microspherical BiOBr architectures assembled by nanosheets by employing ethylene glycol (EG) assisted solvothermal route. Various other morphologies
of BiOBr with improved catalytic ability have also been reported. For example, Wang et al.\textsuperscript{26} used hydrolysis method to synthesize highly efficient photocatalytic BiOBr powder using Bi$_2$O$_3$ and hydrobromic acid. Similarly, highly visible light active flower like BiOBr microspheres with excellent visible light activity were reported by Huo et al.\textsuperscript{30} Recently, ionic liquids (IL) have received considerable attention conducive to the synthesis of functional materials because IL is a good dispersing agent, solvent, and a template.\textsuperscript{51-54} Xia et al.\textsuperscript{55} reported a facile one pot solvothermal synthesis of highly visible light active Bi$_2$WO$_6$/BiOBr in presence of reactive ionic liquid [C16mim] Br. They reported that [C16mim] Br acts as solvent, reactant, and template at the same time.

In the recent past, microwave assisted synthetic routes have been reported to have several advantages\textsuperscript{56-59} including: (1) shorter reaction time; (2) easiness to tune compositions of the products; and (3) more uniform product dimensions and composition. Zhang et al.\textsuperscript{60} demonstrated the microwave assisted solvothermal route for the synthesis of BiOBr photocatalyst with strong adsorption, and excellent properties, using Bi (NO$_3$)$_3$.5H$_2$O, cetyltrimethylammonium bromide (CTAB) as bromine source, and diethylene glycol as solvent.

Carbon materials have been reported as efficient electron transport matrices. Song et al.\textsuperscript{1} reported a green single step microwave assisted strategy for the synthesis of BiOBr and BiOBr/graphene composites. According to them, microwave irradiation helps in selective activation of the target precursors to initiate nucleation and subsequent growth.

4.3. Present work

The most effective and simple strategy to improve the photocatalytic activity of a photocatalyst is the construction of heterostructure by coupling of two semiconductor photocatalysts, as it provides a feasible method to promote the separation of photogenerated electron-hole pairs, and also combining of two semiconductors with different band gaps is flexible for broadening the visible light absorption.\textsuperscript{61} P-n heterostructures with n- type ZnFe$_2$O$_4$ and p-type BiOBr were synthesized by Kong et al.\textsuperscript{61} via simple ultrasound deposition method. The introduction of ZnFe$_2$O$_4$ into BiOBr lead to the considerable extension of absorption edge of BiOBr, and the composite showed exceptional VLD photocatalytic activity. Similarly, many other coupled systems concerned BiOBr such as BiOCl/BiOBr,\textsuperscript{62} Ag/AgBr/BiOBr,\textsuperscript{63} (BiO)$_2$CO$_3$/BiOBr,\textsuperscript{64} and AgBr/BiOBr\textsuperscript{65} have been reported to have higher photocatalytic performance than individual BiOBr. Many other materials, such as Ag,\textsuperscript{66} Fe,\textsuperscript{33} or g-C$_3$N$_4$\textsuperscript{67} have been coupled with BiOBr to enhance the photocatalytic activity of BiOBr. All these above
mentioned literature reports motivated us to fabricate Ag₃PO₄/BiOBr heterojunctions with a hope of enhanced catalytic performance. Ag₃PO₄ is a visible light responsive photocatalyst, and exhibits extremely high photooxidative capability for O₂ evolution from water, and decomposition of organic dyes. Unfortunately, pure Ag₃PO₄ has low structural stability which limits its environmental applications. Ag₃PO₄ has been previously coupled with many semiconductors to improve their catalytic efficiency such as Ag₃PO₄/TiO₂, Ag₃PO₄/BiOI, Ag₃PO₄/CeO₂, Ag₃PO₄ loaded Bi₂MoO₆, Ag₃PO₄/MoS₂, Ag₃PO₄/BiPO₄, Ag₃PO₄/SnO₂, Ag₃PO₄/WO₃, CdS@Ag₃PO₄, Ag₃PO₄/ZnO, and Ag₃PO₄/BiOCl. To the best of our knowledge, no significant effort has been made for the preparation of Ag₃PO₄/BiOBr. The reason why we choose Ag₃PO₄ to couple with BiOBr is based on following considerations: (a) Ag₃PO₄ has a band gap of around 2.36-2.40 eV which enables it to absorb visible light up to 540 nm, and therefore can act as a sensitizer, and enhance the visible light absorption. (b) Considering the low structural stability of pure Ag₃PO₄ and its unique photo oxidative ability, coupling of Ag₃PO₄ with BiOBr could be a good strategy to develop efficient and stable photocatalyst. Therefore, herein an effective yet simple co-precipitation method has been reported to synthesize novel Ag₃PO₄/BiOBr heterojunction photocatalyst, and its photocatalytic activity was explored by decomposing refractory dye Rhodamine B. Various characterization techniques were used to study the structure, morphology, and optical properties of these heterojunctions. The photocatalytic experiment was performed in an immersion well reactor. The as synthesized composite system exhibited very high visible light induced photocatalytic activity. Scavenger experiments were carried out to investigate the primary reactive species involved in the photo decolourization of dye. Mineralization extent of dye was investigated by Chemical oxygen Demand (COD) technique. Photoluminescence (PL) analysis was used to confirm the effective separation of photoinduced charge carriers. The stability of the photocatalyst was investigated by repetition experiments.

4.4. Experimental

4.4.1. Preparation of BiOBr microspheres
The BiOBr microspheres were synthesized by simple precipitation method. 0.01 mol of Bi(NO₃)₃·5H₂O was dissolved in absolute ethanol. Subsequently, NaBr aqueous solution (molar ratio of Bi/Br = 1:1) was added drop wise, and pH of the resultant suspension was adjusted to 8 using 1.5 M aqueous ammonia solution. The resulting mixture was stirred
for 12 h at 85 °C. Finally, the product was separated by centrifugation, washed with deionized water and absolute ethanol, and then dried at 80 °C for 10 h.

4.4.2. Preparation of Ag$_3$PO$_4$/BiOBr heterostructures

For the preparation of Ag$_3$PO$_4$/BiOBr heterostructures, 1.0 g of BiOBr was dispersed in 20 mL of water by ultrasonication, and different quantities of AgNO$_3$ and Na$_3$PO$_4$ were added into the suspension, and stirred for 6 h at room temperature. Subsequently, the Ag$_3$PO$_4$/BiOBr microspheres were separated by centrifugation, and washed with deionized water followed by absolute ethanol, and then vacuum dried at 80 °C for 10 h. The samples with different Ag/Bi weight ratio of 0.1, 0.3, 0.5, 0.7, and 0.9 were noted as AB1, AB3, AB5, AB7, and AB9, respectively. For comparison, pure Ag$_3$PO$_4$ powders were prepared by referring to previous studies. 82

4.4.3. Characterization

The phase purity and the structural properties of the obtained samples were examined at room temperature by X-ray diffraction (XRD) using Shimadzu XRD-6100 X-ray diffractometer with Cu Kα radiation ($\lambda=1.5406$ Å) and a scanning speed of 10°/min in the 2θ ranges from 10° to 80°. The morphology was probed by Carl-Zeiss field-emission scanning electron microscope (FESEM) on which elemental analysis was also probed using EDS attachment. Transmission electron microscopy (TEM) studies were recorded on a TEM (JEM 2100F) instrument. The specific surface area was calculated by measuring N$_2$ adsorption and desorption isotherms on a Belsorp-Max and Belsorp-Aqua Porosimeter. UV-vis-NIR spectrophotometer (Perkin Elmer) equipped with an integrating sphere assembly was used to obtain UV-vis diffuse reflectance spectra (DRS) of the samples in the region of 300-800 nm. Fluorospectrometer was used to obtain the photoluminescence spectra (PL) of the samples.

4.4.4. Photocatalytic activity test and Chemical Oxygen Demand (COD) measurements

The visible light photocatalytic activities of pure BiOBr, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/BiOBr hybrids were evaluated by the photocatalytic degradation of Rhodamine B (RhB) dye and phenol aqueous solutions. The photocatalytic tests were performed in an immersion well photoreactor (consisting of inner and outer jacket) made of pyrex glass equipped with a magnetic bar, a water circulating jacket, and an opening for molecular oxygen. Visible light halogen linear lamp (500 W, 9500 Lumens) was used to carry out irradiations. The reaction temperature was kept constant at 20±0.3 °C using refrigerated circulating liquid bath. Prior to the illumination, the suspension containing 100 mL of dye with appropriate quantity of the catalyst (1 gL$^{-1}$) was magnetically stirred, while the solution was purged...
continuously with atmospheric air for at least 30 min. in the dark to attain adsorption-desorption equilibrium between photocatalyst and pollutant. 5mL of sample suspensions were collected at 3 min. interval, centrifuged, and then analysed with (Shimadzu UV-Vis 1601) spectrophotometer. The change in absorbance of the dye was followed at its $\lambda_{\text{max}}$ (554 nm) as a function of irradiation time. The observed absorbance is proportional to Beer-Lambert Law in the range of studied dye concentration. The concentration of dye was calculated by standard calibration curve obtained from the absorbance of the dye at different known concentrations. To investigate the effect of relevant reactive oxygen species, appropriate quantity of various quencher species were added in the reaction system in a manner similar to the photocatalytic experiment. The dosage of quenchers was referred to the previous studies.\textsuperscript{83,84} COD was estimated before and after the irradiation in accordance with standard APHA method.\textsuperscript{85,86}

4.5. Results and discussion

4.5.1. Structural characterization

Fig. 4.1 shows the XRD patterns of pure BiOBr, Ag\textsubscript{3}PO\textsubscript{4}, and Ag\textsubscript{3}PO\textsubscript{4}/BiOBr microspheres. All the detectable peaks in pure BiOBr can be assigned to the tetragonal primitive crystal structure of BiOBr.\textsuperscript{87} The characteristic peaks of Ag\textsubscript{3}PO\textsubscript{4} are in good accordance with the body centred cubic structure of Ag\textsubscript{3}PO\textsubscript{4}.\textsuperscript{82} The Ag\textsubscript{3}PO\textsubscript{4}/BiOBr hybrids exhibit a coexistence of Ag\textsubscript{3}PO\textsubscript{4} and BiOBr phases, with diffraction peaks corresponding to both Ag\textsubscript{3}PO\textsubscript{4} and BiOBr. For all the composites the intensity of Ag\textsubscript{3}PO\textsubscript{4} diffraction peaks increases with increase in its content.

The crystallite sizes of pure BiOBr and composite catalysts were calculated by the Scherer formula\textsuperscript{41} (Equation 4.1)

$$D = \frac{K \lambda}{\beta \cos \theta_B} \quad [4.1]$$

Where D is taken as crystallite size, K is a constant, $\beta$ is the FWHM measured in radians on the 2θ scale, and $\theta_B$ is the Bragg angle for diffraction peaks. The crystallite sizes of pure BiOBr and composite catalysts are given in Table 4.1. It can be inferred from the Table 4.1, that the loading of Ag\textsubscript{3}PO\textsubscript{4} does not affect the crystallite size of BiOBr microspheres.
Fig. 4.1: XRD patterns of: BiOBr, AB1, AB3, AB5, AB7, AB9, and Ag₃PO₄.

Table 4.1. Crystallite size of pure and hybrid composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOBr</td>
<td>16.49</td>
</tr>
<tr>
<td>AB1</td>
<td>14.61</td>
</tr>
<tr>
<td>AB3</td>
<td>14.63</td>
</tr>
<tr>
<td>AB5</td>
<td>17.95</td>
</tr>
<tr>
<td>AB7</td>
<td>19.21</td>
</tr>
<tr>
<td>AB9</td>
<td>18.91</td>
</tr>
</tbody>
</table>

4.5.2. Morphological characterization

The detailed morphology and composition of Ag₃PO₄/BiOBr were investigated by SEM and EDS, as shown in Fig. 4.2 and Fig. 4.3, respectively. The SEM image in Fig. 4.2 (a) shows that the pure BiOBr is made up of flower shaped microspheres with smooth surfaces. Fig. 4.2 (b-f) presents the SEM images of Ag₃PO₄/BiOBr hybrids. The
morphology of BiOBr and Ag₃PO₄/BiOBr hybrids is similar except for small Ag₃PO₄ particles formed on the surface of BiOBr.

Fig. 4.2: SEM images of: (a) BiOBr, (b) AB1, (c) AB3, (d) AB5, (e) AB7, and (f) AB9.

Because, it is not clear to distinguish between BiOBr and Ag₃PO₄/BiOBr hybrids, EDS spectrum of BiOBr and hybrids was collected, and is shown in Fig. 4.3. The EDS spectrum of pure BiOBr (Fig. 4.3 (a)) shows the presence of Bi, O, and Br elements whereas the hybrids (Fig. 4.3 (b-f)) show the presence of Ag and P in addition to Bi, O, and Br elements. Further, with increase in content of Ag₃PO₄, the amount of Ag and P as detected by EDS also increases. This clearly proves the formation of Ag₃PO₄ particles. Moreover, the Ag/Bi weight ratios in hybrids
obtained from EDS results is virtually identical or very close to the theoretical Ag/Bi ratios. All these results clearly prove the formation of Ag₃PO₄ in hybrids.

**Fig. 4.3:** EDS spectrum of: (a) BiOBr, (b) AB1, (c) AB3, (d) AB5, (e) AB7, and (f) AB9.

TEM was used to further investigate the structure and morphology of the sample. The TEM image of pure BiOBr microsphere (Fig. 4.4 (a)) shows that it has a spherical structure with smooth surface, whereas that of Ag₃PO₄/BiOBr hybrid (Fig. 4.4 (b)) depicts lot of subtle Ag₃PO₄ particles grown on the surface of BiOBr microspheres indicating the formation of composite.

**Fig. 4.4:** TEM images of the samples: (a) BiOBr, (b) AB7.
4.5.3. FTIR Study

Fig. 4.5 displays the FT-IR spectrum of BiOBr and Ag₃PO₄/BiOBr composite (AB7). The band at 1627 cm⁻¹ in the spectrum of BiOBr is attributed to OH stretching vibrations of water molecule. The absorption band at 522 cm⁻¹ is ascribed to the Bi–O stretching mode. The absorption bands at 1022 cm⁻¹, 1070 cm⁻¹, and 550 cm⁻¹ in the spectrum of Ag₃PO₄/BiOBr (AB7) correspond to the P-O stretching vibrations of PO₄⁻.

![FTIR spectra of BiOBr and AB7.](image)

4.5.4. BET analysis

Fig. 4.6 presents the N₂ adsorption-desorption isotherms of pure BiOBr and AB7 respectively. According to IUPAC classification, both BiOBr and AB7 exhibit type III isotherms. Both BiOBr and AB7 in the low pressure region have quite gentle curves. With increase in \( P/P₀ \), the adsorption increases slowly and show a sudden jump around 0.9-1.0, which may be attributed to the capillary condensing phenomenon of N₂ in the mesoporous pressure region. The curves of both BiOBr and AB7 are similar indicating that the morphology and pore size of both these samples is more or less identical. The Brunauer–Emmett–Teller (BET) surface area of AB7 (35.30 m²g⁻¹) was found to be higher than BiOBr (15.8 m²g⁻¹) which may be beneficial in reducing the electron-hole recombination.
4.5.5. DRS

The optical absorbance of obtained samples was measured by UV–vis. diffuse reflectance spectra (DRS). As shown in the Fig. 4.7, BiOBr has an absorption edge around 430 nm, while Ag₃PO₄ has absorption edge around 520 nm. As can be seen from the figure, Ag₃PO₄/BiOBr composites have better visible light absorption compared to pure BiOBr, with AB7 having absorption edge around 503 nm. Therefore, light absorption of composites is enhanced to a large extent through the introduction of Ag₃PO₄.

As reported by the Butler, the band gap energy of semiconductor is calculated by Equation 4.2.

\[(hv \cdot \alpha) = (Ahv - Eg)^{n/2} \quad \text{(4.2)}\]

Since \(\alpha\) is proportional to kubelka–munk function \(F(R)\), the expression becomes

\[hv \cdot F(R) = (Ahv - Eg)^{n/2} \quad \text{(4.3)}\]

where \(h\) is planck’s constant, \(v\) is the light frequency, \(F(R)\) is the kubelka–munk function, \(A\) is the proportional constant, and \(Eg\) is the Band gap energy. The value of ‘\(n\)’ is determined by the type of optical transition (\(n=1\) for direct transition and \(n = 4\) for indirect transition). From the experimental data, the \(Eg\) of BiOBr and Ag₃PO₄ were determined from the plot of \((F(R) \cdot hv)^{1/2}\) vs. \(hv\) (Fig. 4.8 (a)) and \((F(R) \cdot hv)^2\) vs. \(hv\) (Fig. 4.8 (b)) respectively. The band gaps for BiOBr and Ag₃PO₄ were estimated to be 2.74 eV and 2.36 eV respectively.
Fig. 4.7: DRS of BiOBr and Ag$_3$PO$_4$/BiOBr hybrids.

Fig. 4.8: (a) Plot of $(F(R).hv)^{1/2}$ versus energy $(hv)$ for the band gap energy of BiOBr, and (b) $(F(R).hv)^2$ versus energy $(hv)$ for Ag$_3$PO$_4$. 
4.5.6. PL spectra

The activity of a photocatalyst, and the subsequent quantum yield of the reaction are largely determined by the life time of the electron-hole pairs. Since the electron-hole recombination is mainly responsible for PL emissions, therefore, the PL spectra was used to investigate the recombination of photoinduced charge carriers. The low intensity of PL emission implies the lower rate of recombination of photoinduced charge carriers. Fig. 4.9 presents the PL spectra of BiOBr, Ag₃PO₄, and AB7. The BiOBr shows only one emission peak centred around 435 nm, whereas Ag₃PO₄ shows two emission peaks centred around 480 nm and 550 nm. AB7 presents the lowest emission peaks centred around 437 nm and 540 nm suggesting that the electron-hole recombination is lowest in AB7 which results into the weak intensities of PL emissions in AB7, compared with pure BiOBr and Ag₃PO₄. The most probable reason for this kind of behaviour is the effective separation of photoinduced charge carriers in AB7 as a result of heterojunction.

![PL spectra of the samples](image)

**Fig. 4.9:** PL spectra of the samples ($\lambda_{exc} = 400$ nm).

4.5.7. Photocatalytic properties

The photocatalytic activities of the as prepared Ag₃PO₄/BiOBr samples were evaluated by the degradation of RhB under visible light irradiation. Fig. 4.10 (b) presents the variations of the RhB concentration ($C_t/C_0$) over different samples as a function of irradiation time. Prior to the irradiation, the dark adsorption was checked for 30 minutes. As can be seen from the Fig. 4.10 (b), the adsorption is almost insignificant, and hence can be neglected. Fig. 4.10 (b) shows that all Ag₃PO₄/BiOBr hybrids exhibit higher photocatalytic
activities, compared to pure BiOBr and Ag$_3$PO$_4$. The photocatalytic activities of composites enhance with increasing amounts of Ag$_3$PO$_4$. Among the heterojunctions, the highest photocatalytic activity is achieved for AB7 with nearly 97.5% of RhB removal after 21 min. of visible light irradiation. The two important factors responsible for the enhanced visible light activity of heterojunctions are: (a) increased surface area of the composites which prevents the electron-hole recombination, and (b) the formation of heterojunction with natural energy bias which facilitates the transfer of photoinduced charge carriers, and hence impedes the electron-hole recombination. The photocatalytic activity of the composites is related to the amount of Ag$_3$PO$_4$ loading, and the activity sequence is in the order: AB7 > AB9 > AB5 > AB3 > AB1 > BiOBr > Ag$_3$PO$_4$. Fig. 4.10 (a) depicts the change in visible spectrum of RhB solution at different time intervals of irradiation using the hybrid AB7 as photocatalyst. It is well known that the photocatalytic decolourization of most of the dyes follow pseudo-first order kinetics model, and therefore, to understand the reaction kinetics of RhB degradation, the apparent pseudo-first order kinetics model given by Equation 4.4, was applied in experiments.

\[
\ln\left(\frac{C_0}{C_t}\right) = K_{app}t
\]  

[4.4]

Where $K_{app}$ is apparent pseudo first order rate constant. The values of $K_{app}$ for all the composites were calculated via the first order linear fit from the data of Fig. 4.10 (c), and are given in Table 4.2. The value of $K_{app}$ increases with increase in the content of Ag$_3$PO$_4$, and the highest $K_{app}$ is observed for AB7 composite. The degradation constant of AB7 (0.17 min$^{-1}$) is found to be about 3.81 times that of BiOBr (0.0446 min$^{-1}$), and 5.24 times that of Ag$_3$PO$_4$ (0.0324 min$^{-1}$).

Table 4.2: Pseudo-first order rate constants ($K_{app}$) of different photocatalysts for the decolourization of RhB calculated from the plots of $\ln\left(\frac{C_0}{C_t}\right)$ versus irradiation time.
Fig. 4.10: (a) Change in UV-vis spectra of RhB aqueous suspension in the presence of AB7 at different irradiation times, (b) Change in concentration ($C_t/C_0$) of RhB in the presence of $\text{Ag}_3\text{PO}_4$, BiOBr, and $\text{Ag}_3\text{PO}_4$/BiOBr hybrids under visible light, and (c) $\ln(C_0/C_t)$ versus irradiation time for different catalysts.
To further confirm the mineralization, the COD removal during the photocatalytic reaction was carried out in accordance with standard APHA method. The decrease in the value of COD signifies the extent of mineralization of organic species. As shown in the Fig. 4.11, the COD value decreases substantially with irradiation time. After 21 minutes the COD is reduced to about 96% of initial value. The photodegradation efficiency was calculated by the Equation 4.5.

\[
\text{Efficiency(\%)} = \frac{\text{Initial (COD)} - \text{Final (COD)}}{\text{Initial (COD)}} \times 100 \quad [4.5]
\]

![Graph showing variation of COD with irradiation time and percent efficiency.](image)

**Fig. 4.11:** Variation of COD with irradiation time and percent (\%) efficiency.

The photocatalytic activity of as prepared Ag\textsubscript{3}PO\textsubscript{4}/BiOBr heterojunctions was compared to the previously reported visible light activity of various BiOBr heterojunctions, as shown in Table 4.3. From Table 4.3, it is clear that the Ag\textsubscript{3}PO\textsubscript{4}/BiOBr heterojunctions show enhanced visible light activity compared to the previously reported other heterojunctions.
Table 4.3. Visible light percent (%) decolourization of RhB over previously reported BiOBr heterojunctions and Ag₃PO₄/BiOBr heterojunction.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Catalyst</th>
<th>% Decolourization of RhB</th>
<th>Irradiation Time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS₂ coupled BiOBr</td>
<td>100%</td>
<td>170</td>
<td>[95]</td>
</tr>
<tr>
<td>2</td>
<td>BiOBr/ montmorillonite</td>
<td>98.96%</td>
<td>120</td>
<td>[96]</td>
</tr>
<tr>
<td>3</td>
<td>BiOBr/Fe₂O₃</td>
<td>97.8%</td>
<td>120</td>
<td>[97]</td>
</tr>
<tr>
<td>4</td>
<td>BiOBr/Fe₃O₄</td>
<td>100%</td>
<td>60</td>
<td>[62]</td>
</tr>
<tr>
<td>5</td>
<td>BiOCl-BiOBr</td>
<td>99%</td>
<td>30</td>
<td>[33]</td>
</tr>
<tr>
<td>6</td>
<td>Fe- doped BiOBr</td>
<td>73%</td>
<td>40</td>
<td>[67]</td>
</tr>
<tr>
<td>7</td>
<td>Ag Modified BiOBr</td>
<td>100%</td>
<td>40</td>
<td>[66]</td>
</tr>
<tr>
<td>8</td>
<td>BiOBr-TiO₂</td>
<td>100%</td>
<td>20</td>
<td>[98]</td>
</tr>
<tr>
<td>9</td>
<td>Ag₃PO₄/BiOBr</td>
<td>97.5%</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

4.5.8. Discussion of Degradation mechanism

4.5.8.1. Formation of reactive species

Various scavengers of the reactive species were added to the reaction system to investigate the type of reactive species (such as 'OH, h⁺, H₂O₂ and O₂⁻) produced, and contribute maximum towards the decolourization of RhB during the photocatalytic process. Benzoquinone (BQ) was added as a superoxide radical (O₂⁻) scavenger, ammonium oxalate (AO) as h⁺, and tert-butylalcohol (TBA) as a hydroxyl radical ('OH) scavenger. As shown in the Fig. 4.12, AO and TBA inhibits the removal efficiency of RhB and the K_{app} value decreases significantly, indicating that h⁺ and 'OH are the primary reactive species in the photodegradation process of RhB using Ag₃PO₄/BiOBr composite. The addition of BQ in the reaction system has no obvious effect on the photodegradation process of RhB and K_{app} value, suggesting that O₂⁻ is not the primary reactive species in the photocatalytic degradation process of RhB.
4.5.8.2. Origin of reactive species

Photocatalytic mechanism and photosensitization are the two possible reaction mechanisms responsible for the origin of reactive species. Phenol, which is visible light inactive, was used as a model pollutant to ensure that the reactive species originate from the photocatalytic process of the Ag$_3$PO$_4$/BiOBr, and not from the sensitization of dye under visible light irradiation. Fig. 4.13 (a) presents the variations of the phenol concentration ($C_t/C_0$) over BiOBr, Ag$_3$PO$_4$, and AB7 samples as a function of irradiation time. Prior to the irradiation, dark adsorption was checked for 30 min and was found to be negligible. Fig. 4.13 (a) displays that concentration of phenol decreases slightly with increasing irradiation time in presence of pure Ag$_3$PO$_4$ and BiOBr, whereas there is a sharp decrease in the concentration of phenol in presence of AB7. The values of $K_{app}$ for the degradation of phenol in the presence of BiOBr, Ag$_3$PO$_4$, and AB7 were calculated via the first order linear fit from the data of Fig. 4.13 (b). The value of $K_{app}$ for AB7 (0.0957 min$^{-1}$) is found to be 3.5 times higher than that of BiOBr (0.0272 min$^{-1}$) and 5.5 times higher than that of Ag$_3$PO$_4$ (0.0174 min$^{-1}$). These results clearly indicate that the reactive species originate from the photocatalytic process of the Ag$_3$PO$_4$/BiOBr composites under visible light, and rules out the possibility of photosensitization by dye molecules.
4.5.8.3. Possible photocatalytic mechanism

The photocatalytic activity of a heterojunction in a hybrid semiconductor is directly related to the electronic band structure of individual components and the fate of the photoinduced charge carriers.\(^{10}\) To fully understand the photocatalytic mechanism, the band edge position of the valence band and the conduction band of Ag\(_3\)PO\(_4\) and BiOBr was determined by using the empirical Equation 4.6:\(^{29}\)

\[ E_{\text{VB}} = X - E_c + 0.5E_g. \]  \[4.6\]

Where \(E_{\text{VB}}\) is the energy of VB edge potential, \(X\) is the electronegativity of semiconductor, and \(E_c\) is the energy of free electrons on hydrogen scale (4.5 eV). The top of the valence band \(E_{\text{VB}}\) of BiOBr and Ag\(_3\)PO\(_4\) were calculated to be 3.05 eV/NHE and 2.63 eV/NHE, respectively. Moreover, the conduction band edge potential \(E_{\text{CB}}\) can be determined by Equation 4.7.

Fig. 4.13: (a) Change in concentration \((C_t/C_0)\) of phenol in the presence of BiOBr, Ag\(_3\)PO\(_4\) and AB7 (b) Phenol degradation curves of \(\ln (C_0/C_t)\) versus irradiation time for BiOBr, Ag\(_3\)PO\(_4\) and AB7.
\[ E_{CB} = E_{VB} - E_g. \]  

The \( E_{CB} \) for BiOBr and \( \text{Ag}_3\text{PO}_4 \) were elicited as 0.31 eV/NHE and 0.27 eV/NHE, respectively.

From the calculated \( E_{VB} \) and \( E_{CB} \), we can draw a schematic diagram of band alignment of \( \text{Ag}_3\text{PO}_4/\text{BiOBr} \), as shown in Fig. 4.14. BiOBr has more positive VB and CB than \( \text{Ag}_3\text{PO}_4 \) which results in the generation of natural energy bias at heterojunction, and subsequent transfer of photoinduced charge carriers.\(^{102,103}\)

Under visible light irradiation, both \( \text{Ag}_3\text{PO}_4 \) and BiOBr generate electron-hole pairs. As shown in the Fig. 4.14, the photoexcited electrons on the less positive CB of \( \text{Ag}_3\text{PO}_4 \) will prefer to flow down to the more positive CB of BiOBr, while the photogenerated holes on the more positive VB of BiOBr will transfer to the less positive VB of \( \text{Ag}_3\text{PO}_4 \). This leads to the efficient separation of electron-hole pairs, and thus prolonged life of photoinduced charge carriers.

Although, the photogenerated electrons are capable of reducing \( \text{O}_2 \) to \( \text{O}_2^- \), but since the CB potential of BiOBr semiconductor is less negative than the standard reduction potential of oxygen (- 0.046 eV),\(^{104}\) sufficient potential cannot be generated by CB of BiOBr to reduce \( \text{O}_2 \) to \( \text{O}_2^- \). Thus, \( \text{O}_2^- \) is not involved in decolourization process of RhB.

At the same time the \( E_{VB} \) value of \( \text{Ag}_3\text{PO}_4 \) (2.63 eV) is more positive than the \( E^0 \) (\( \text{•OH}/\text{H}_2\text{O} \) = +2.27 eV), indicating that sufficient potential can be generated by \( h^+ \) on VB of \( \text{Ag}_3\text{PO}_4 \) to oxidize \( \text{H}_2\text{O} \) to \( \text{•OH} \).\(^{105}\)

Based on the above discussion, the mechanism for the photocatalytic degradation of RhB on \( \text{Ag}_3\text{PO}_4/\text{BiOBr} \) heterojunction may be proposed as described in Equation 4.8-4.12.

We propose that under visible light irradiation both \( \text{Ag}_3\text{PO}_4 \) and BiOBr are simultaneously excited and result into the formation of electron-hole pairs. The electrons from the CB of \( \text{Ag}_3\text{PO}_4 \) are injected into the CB of BiOBr, whereas holes from VB of BiOBr are injected into the VB of \( \text{Ag}_3\text{PO}_4 \). These holes on the VB of \( \text{Ag}_3\text{PO}_4 \) then combine with water and oxidize it into \( \text{•OH} \). The \( \text{•OH} \) radicals then react with RhB and decompose it into intermediate products. The mechanism is well supported by the results of DRS, PL studies, and the effect of scavengers.
Fig. 4.14: Schematic diagram of electron-hole pair separation and the possible reaction mechanism over Ag₃PO₄/BiOBr photocatalyst under visible light irradiation.

4.5.9. Stability of catalyst

The stability of the silver based catalyst is always of vital consideration because there are fair chances of reduction of Ag⁺ into Ag⁰ metal by the excited electrons.⁷⁰,⁸² Therefore, repeatability experiments of the RhB degradation over AB7 were taken to investigate the stability of the Ag₃PO₄/BiOBr catalyst. As shown in the Fig. 4.15 (a), the degradation of RhB by AB7 is maintained at 95 % after 6 recycling runs suggesting that Ag₃PO₄/BiOBr has high stability under visible light irradiation. The XRD results of used AB7 after 6 recycling runs (Fig. 4.15 (b)) reveals that the structure and the phase remains intact with no peak detection for Ag⁰ metal. Thus, reason for the stability of the catalyst is the efficient separation of photogenerated electron-hole pairs, and the fast transfer of excited electrons from the conduction band of Ag₃PO₄ to the conduction band of BiOBr.
4.6. Conclusion

Efficient visible light active Ag$_3$PO$_4$/BiOBr microspheres were synthesized via simple co-precipitation method. The as prepared hybrids showed enhanced visible light absorption, and exhibited better photocatalytic activity on the degradation of RhB and phenol, compared to pure BiOBr and Ag$_3$PO$_4$ samples under visible light irradiation. The optimal content of Ag$_3$PO$_4$ in the Ag$_3$PO$_4$/BiOBr catalyst was found to be Ag/Bi weight ratio of 0.7. The photocatalytic activity did not show any significant decrease after 6 recycling runs. On the basis of experimental and theoretically calculated results, the reactive holes were suggested to play critical role in the photodegradation of RhB over the
Ag₃PO₄/BiOBr catalyst. Considering the facile and environment friendly route for the synthesis of Ag₃PO₄/BiOBr hybrids, and the enhanced visible light absorption of Bismuth Oxybromide due to the introduction of silver based compound, it is possible to widely apply these highly efficient Ag₃PO₄/BiOBr hybrids in various fields such as waste water treatment.
References