Preparation, Characterization and Photocatalytic Application of Novel Bismuth Vanadate/ Hydroxyapatite Composite

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**ABSTRACT**

BiVO₄/Hydroxyapatite (HAP) composite was synthesized successfully by combining co-precipitation process and wet-chemical method. Three composites have been prepared by varying the molar concentration of BiVO₄ and HAP and were named as 1:1-BHC, 1:2-BHC and 2:1-BHC respectively. These composites were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM and TEM images of as prepared composites revealed the BiVO₄ nanorods enclosed with HAP nanoflakes while XRD and FTIR results confirmed the formation of nano composites. The composites were then used as photocatalyst for the photocatalytic degradation of malachite green (MG) dye and the photocatalytic activities were compared with that of BiVO₄. The 2:1-BHC showed best MG photodegradation, better than BiVO₄ itself due to synergistic effects of adsorption of dye particles by HAP and subsequent photocatalytic degradation by BiVO₄. The optimum catalyst dose for 2:1-BHC was found to be 0.1 g per 100 mL of 10 ppm dye concentration with initial pH of solution being 6. These results revealed that BHC-composite did possess the features of visible light active photocatalyst and could be used for the degradation of organic pollutants like dyes.

**KEYWORDS**

Photocatalysis
BHC-composites
MG photodegradation
nanocomposite

**GRAPHICAL ABSTRACT**

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Introduction

In the recent decade, bismuth-based visible light-active photocatalysts have been extensively used for the removal of pollutants from water. Bi$_2$O$_3$[1,2], BiVO$_4$[3-7], Bi$_2$WO$_6$[8,9], BiPO$_4$ [1-11] with narrow band gap ($E_g$) have been investigated by many research groups. Among them, BiVO$_4$ ($E_g$=2.4 eV) is one of the widely studied efficient visible light active photocatalyst. It has been used in photocatalytic degradation of organic pollutants in wastewater as well as for photoelectrochemical water splitting resulting hydrogen and O$_2$ evolution under the sunlight irradiation [12,13].

In our previous work, BiVO$_4$ was used for photocatalytic degradation of the malachite green (MG) dye [14]. In the experiment, there was a problem of dispersion of BiVO$_4$ catalyst in the dye solution and was difficult to separate as well. Similar problems have been stated by other research groups [15]. Additionally, there was a problem of deviation of pH during photocatalytical degradation of MG dye. Therefore, control of pH during the photodegradation experiment is a great challenge. To overcome such problems, many research groups have used dopants or heterojunction with BiVO$_4$ [16]. However, the synthesis of composites with stable support was reported to be one of the most employed methods to improve the material performance. Literatures reported that a stable support can immobilize the active catalyst, increase the surface area of catalytic material, decrease the sintering as well as improve thermal, hydrolytic and chemical stability of the catalytic material [15,17-19]. In the present study, hydroxyapatite (HAP) has been chosen as a supporting material for BiVO$_4$ in form of BiVO$_4$/HAP composites.

The hydroxyapatite (HAP) Ca$_{10}$ (PO$_4$)$_6$(OH)$_2$ is one of the common supporting materials that has been used with different semiconductors such as TiO$_2$ [17,18,20], Ag$_3$PO$_4$ [21], AgBr/Ag$_3$PO$_4$ [21], and BiOCl [22]. HAP was reported to increase the surface area of catalytic material and adsorb pollutant particles for their faster degradation [22]. Yet, it had not been used with BiVO$_4$. In this work, it was used as supporting material with BiVO$_4$ on account of some common features of BiVO$_4$ and HAP such as: both can be synthesized at basic pH [5,21]; both exist in monoclinic forms [3,5,20]; both can be synthesized in nano sizes [5,20]; and both have been used separately in degradation of organic matter with initial solution pH 6 [14,23]. For synthesis of the composite, facile co-precipitation method for BiVO$_4$ [5] and wet-chemical method for HAP [21,24] have been chosen regarding their simplicity and compatibility.

To study the photocatalytic activity of as prepared BiVO$_4$/HAP composite, malachite green dye (MG) has been used as a model dye pollutant which can undergo photodegradation in presence of a suitable photocatalyst and visible light. Malachite green (MG), a triphenylmethane dye, is a cationic dye with molecular formula C$_{23}$H$_{25}$N$_2$Cl available as chloride salt. It has been used in dyeing paper, leather and silk. It is also utilized as a biological stain; as antibacterial, antiseptic, fungicidal, algicidal and parasiticidal in aquaculture. However, it has been proven to be toxic, irritant, mutagenic and carcinogenic to humans [25-27]. Among various methods of removal of this dye from polluted water, photocatalytic degradation has been proven to be most effective and economic [25]. This process degrades the toxic chemical into smaller eco-friendly products ensuring the complete removal of the dye pollutant [25]. In this study, we report the BiVO$_4$/HAP composites for the photocatalytic activity which is not reported so far and the results were compared with bare BiVO$_4$ to test its efficiency.

Experimental

Reagents

Analytical Reagent (AR) grade bismuth nitrate was purchased from the Merck
Specialties Private Limited, Mumbai and Laboratory Reagent (LR) grade ammonium vanadate (NH$_4$VO$_3$) from S.D. Fine Chem. Limited, Mumbai. Calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O) was obtained from the Rankem (product no. C0480). Di-ammonium hydrogen orthophosphate ((NH$_4$)$_2$HPO$_4$) was procured from Thomas Baker Chemicals Pvt. Ltd., India and LR grade 25% ammonia was purchased from Merck life Science private Limited, Mumbai. All the chemicals were used without further purifications.

**Instruments**

The X-ray diffraction patterns were recorded using Bruker D2 Phaser. A monochromatized Cu Kα (λ = 1.54 Å) radiation working at energy resolution of 180 eV was used. The surface morphology of the as-prepared BiVO$_4$ particles were obtained using mini SEM (Nanoeye, Co.) and those of composites were taken using SU-70, HI-0032. Magnified view of the composites was obtained using Transmission electron microscopy (TEM, model Sapera 1 with microscope H7650. The Fourier Transfer Infrared (FTIR) spectra were obtained by using Shimadzu IR Affinity-1 and were recorded from 4000-400 cm$^{-1}$ wavenumber.

**Methods**

**Preparation of BiVO$_4$**

BiVO$_4$ was prepared by facile co-precipitation method [5]. Bismuth nitrate solution was prepared by dissolving 1.498 g Bi(NO$_3$)$_3$.5H$_2$O in 100 mL (4M) HNO$_3$ solution at 70 °C. It was added dropwise in stirred condition to the ammonium vanadate solution prepared by dissolving 0.362 g NH$_4$VO$_3$ in 100 mL (2M) NH$_4$OH solution. After mixing, the solution pH was adjusted to 9 using (5M) NaOH solution. Then a yellow suspension was obtained. The solvent was evaporated slowly at 70 °C. After complete evaporation, it was calcined at 200 °C. Thus obtained dried material was ground to fine powder. Thus, BiVO$_4$ was prepared.

**Preparation of BiVO$_4$/HAP composite**

HAP was prepared by wet-chemical method [21]. First of all, the 15 mL of 0.003 mole of (NH$_4$)$_2$HPO$_4$ was added dropwisely to the 15 mL of 0.005 mole of Ca(NO$_3$)$_2$ solution with continuous stirring. A white colored precipitate started to form. After complete addition of (NH$_4$)$_2$HPO$_4$, the pH was adjusted to 9 using (2M) NH$_4$OH solution. Then, a white precipitate of HAP was obtained. As prepared BiVO$_4$ powder was then added slowly in small portions to the HAP containing solution with continuous stirring for 30 min. After addition, stirring was further continued for next 30 min and then left for aging for next 20 h. Then, the solvent was evaporated at 110 °C until all the water got evaporated leaving yellowish white powder. Thus BiVO$_4$/HAP composite was obtained.

Here, BiVO$_4$/HAP composites having three different molar ratios have been prepared. Table 1 shows the molar ratio composition of three different BiVO$_4$/HAP composites which were named as 1:1-BHC, 1:2-BHC, 2:1-BHC.

**Table 1. Molar ratio composition of BiVO$_4$/HAP composites**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BiVO$_4$</th>
<th>HAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 BHC</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1:1 BHC</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1:2 BHC</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
**Photocatalytic activity**

The photocatalytic activities of as-prepared BiVO$_4$ and BHC-composites were measured by degradation of malachite green dye (MG) at ambient temperature. Each degradation study was carried out three times (n=3). A low-cost light simulator was fabricated with a 500 W halogen lamp and was used as the irradiation source. The temperature of the reaction system was maintained at 20-25 °C. For the photocatalytic test, 100 mL of (10 ppm) dye solution was taken in 250 mL beaker. Then, 0.1 g as prepared BHC-composite photocatalyst was added, pH adjusted to 6 [14] and stirred for 15 min for adsorption-desorption process. After that, the solution containing beaker was kept in dark for 30 min for adsorption-desorption equilibrium. Before irradiation, 4 mL of solution was withdrawn for absorbance studies prior to irradiation of light. Then 4 mL of the solutions were pipetted out at every 30 min of irradiation and double centrifugation was done at 4000 rpm for 20 min. Then the absorbance was noted at 617 nm using visible spectrophotometer. Air supply was provided to the reaction system as per needed using air pump from the Silver Lake, model no. SL-2800.

**Results and discussion**

**Phase analysis by X-ray diffraction (XRD)**

The XRD patterns of BHCs and pure BiVO$_4$ powders are shown in Figure 1.

![Figure 1. XRD patterns of 1:2-BHC, 1:1-BHC, 2:1-BHC and BiVO$_4$](image1)

**Figure 1. XRD patterns of 1:2-BHC, 1:1-BHC, 2:1-BHC and BiVO$_4$**

![Figure 2. FTIR spectrum of 2:1-BHC](image2)

**Figure 2. FTIR spectrum of 2:1-BHC**
In the XRD patterns of all four prepared catalysts, one can see the major peaks at 30° (121), 33° (040), 40° (211), 49° (116) of 2θ degrees. These peaks are assigned for BiVO₄ according to JCPDS card no. 14-0688 [28]. In the BHCs, some new peaks could be observed. These additional peaks at 26° (002), 28° (210), 31.9° (211), 32° (112), 39.5° (310), 47.16° (222), 49.8° (213) of 2θ degrees can be indexed according to JCPDS card no. 09-0423 which corresponds to HAP. These peaks are present along with the peaks of BiVO₄ which suggest the coexistence of both BiVO₄ and HAP of composite. However, the peaks seem to be broadening with the increase in HAP content and there are some slight shifts in the BiVO₄ peaks with the addition of HAP. This may be due to the varying calcination temperature for bare BiVO₄ (200 °C) and BHCs (110 °C) [29,30]. According to the literature [30], the decreasing calcination temperature leads to broader peaks indicating decreasing crystallinity. Such shifts have been observed in other research works as well [17,31].

Fourier transform infrared spectroscopy (FTIR)

The composite formed between BiVO₄ and HAP was further investigated using FTIR analyses to get a better overview of the prepared samples. The FTIR spectrum of 2:1-BHC is shown in Figure 2.

As can be seen from the FTIR spectrum of 2:1-BHC, characteristic bands of phosphate bending at 1024 cm⁻¹ and 558 cm⁻¹ with a shoulder at 600 cm⁻¹ corresponding to PO₄³⁻ are present. Similarly, the band at 1338 cm⁻¹ can be assigned to P=O stretch. In additions to these, smaller bands could also be seen at 825 cm⁻¹ which corresponds to the asymmetric V-O stretch, at 669 cm⁻¹ which relates to VO₃⁻ and the one at 473 cm⁻¹ corresponds to weak Bi-O bond [14]. The bands at around 2327 cm⁻¹ and 2349 cm⁻¹ correspond to atmospheric/dissolved CO₂. These results are in correspondence with the available literature [31,32]. Hence, the BiVO₄ and HAP have been able to form a composite which was clearly observed in the FTIR spectra.

Surface analysis by scanning electron microscopy (SEM)

Surface morphology of the as prepared samples and its particle size were studied using the scanning electron microscopy (SEM). The SEM images of the BiVO₄ and BHCs are demonstrated in Figure 3.

Figure 3a shows the SEM image of prepared BiVO₄ before calcination at 200 °C. It revealed the rod-shaped structures along with some agglomerated structures. The rod-shaped structures are most probably of BiVO₄ and the presence of agglomerated structures probably belongs to the by-products and the non-crystallites. The length of the rods was found to be 1.5 µm and the thickness was found to be 0.5 µm. Such surface morphology was obtained in alkaline pH as per the literatures [4,22].

Figure 3b, c and d illustrates the SEM images of 2:1-BHC, 1:1-BHC and 1:2-BHC respectively. In images b, c and d, brighter rod-like structures were clearly seen which were found to be attached with lighter flake-like structures. The brighter rod-like structures are supposed to be BiVO₄ particles which were attached to the lighter HAP flake-like particles [24,33]. The number of dense rod-shaped particles was found to be decreased in SEM images b to d which may be due to decreasing molar ratio of BiVO₄. Here, the size of the composite particles was found to be in the nano-size range. The length of the rod-like BiVO₄ particles were measured to be 50 nm and width to be 10-20 nm while the size of HAP appears to be varying from 100-150 nm.
Figure 3. SEM images of as-prepared a) BiVO$_4$ b) 2:1-BHC c) 1:1-BHC d) 1:2-BHC

Transmission electron microscopy (TEM)

The TEM images of all the BHCs are shown in Figure 4 where distinct darker rod-like structures of BiVO$_4$ along with the lighter spread flake-like structures probably of HAP [24] could be clearly seen.

The BiVO$_4$ rod-like particles were found to be scattered in the 2:1-BHC while it was less scattered in 1:1-BHC and 1:2-BHC. In the 1:1 and 1:2 composites, the BiVO$_4$ rods were concentrated in few areas only. Therefore, more homogeneous distribution of BiVO$_4$ is seen in 2:1-BHC.

The distinctly observed denser rods and the lighter flakes leads to a presumption of true formation of composite as the two components are distinct from each other. Since the BiVO$_4$ nanorods are attached to and surrounded by HAP flakes, such attachment can make BiVO$_4$ particles less dispersed in water as HAP is insoluble in water. This result meets the objective of present research work to make the BiVO$_4$ less dispersed in the reaction system.

Photocatalytic degradation studies

In our previous study [14], BiVO$_4$ showed good photocatalytic performance when irradiation was coupled with air supply. Here, the synergistic effect of the lamp light irradiation along with air (O$_2$) supply led to faster formation of reactive oxygen species (•OH, h$^+$, •OOH or •O$_2^-$) responsible for faster
rate of dye degradation [14]. As described in previous literature, the electron-hole pair (e\(^-\)h\(^+\)) generated by action of visible light on BiVO\(_4\) undergo a series of reactions to generate reactive oxygen species. The reactive oxygen species then react with dye molecules and convert them to harmless products. At this stage, additional oxygen supply from outside accelerates the formation of superoxide anion (\(\text{O}_2^-\)) which takes part in faster MG degradation. In this study, as prepared BHCs were used in photocatalytic degradation of the MG under lamp light irradiation with air supply. Then, the results were compared with the photocatalytic degradation of MG by BiVO\(_4\) in similar physical conditions (Figure 5).

Figure 4. TEM image of a) 2:1-BHC, b) 1:1-BHC and c) 1:2-BHC in 200 nm and 100 nm resolution

Figure 5. Comparative study of photocatalytic degradation % of MG using BiVO\(_4\), 2:1-BHC, 1:1-BHC and 1:2-BHC as a function of time (min)

As can be seen in Figure 5, four different catalysts showed different rates of photodegradation of MG. The 1:2-BHC and 1:1-BHC showed less photocatalytic activity compared with that of the BiVO\(_4\) catalyst while 2:1-BHC displays better activity than BiVO\(_4\). In fact, BiVO\(_4\) degraded 73.53% of dye while 2:1-BHC degraded 80.20% of dye in 120 min of irradiation. A closer inspection reveals that the 2:1-BHC has degraded significant amount of dye (>50%) within 30 min of irradiation which is higher than any other photocatalysts.
In this experiment, HAP does not display any significant role as photocatalyst because the band gap of monophasic HAP lies in far UV region \( E_g > 6 \) eV \[20\]. Hence, the photocatalytic work is exclusively dependent on BiVO\(_4\). However, the presence of HAP in BHCs has some effect in the photocatalytic capability of the composites. This might be due to its characteristic adsorbing capability of HAP \[34\] which adsorbs the dye particles on the catalyst surface and facilitates BiVO\(_4\) to degrade dye molecules without itself actually participating in photodegradation of dye. In case of 2:1-BHC, the molar content of both components of the composite appears to be exactly right for the faster degradation of MG dye due to combined effect of adsorption and photocatalytic degradation. However, in case of 1:1-BHC and 1:2-BHC, the decreased molar content of BiVO\(_4\) photocatalyst might be the reason for slower degradation of dye.

Here, HAP also revealed the role of supporting material in immobilizing the BiVO\(_4\) particles leading to less dispersed BiVO\(_4\) particles into the solution.

Similarly, the pH of the solution before and after irradiation was measured (Table 2).

As shown in Table 2, the pH was constant in 2:1-BHC system. So, the spectrophotometric studies are most reproducible in 2:1-BHC composite compared to other prepared composites for the degradation of MG dye.

Therefore, 2:1-BHC demonstrated the best photocatalytic activity in the photodegradation of MG dye. Further studies were then conducted only in 2:1-BHC compared with BiVO\(_4\).

**Effect of catalyst dose**

For this study, the catalyst dose was varied from 0.05 g to 0.2 g with 10 ppm dye concentration, other physical conditions of irradiation, initial pH, air supply and temperature remaining constant.

### Table 2. pH of the test solutions before and after irradiation

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Initial pH</th>
<th>pH after 120 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO(_4)</td>
<td>6</td>
<td>7 (± 0.5)</td>
</tr>
<tr>
<td>1:2 BHC</td>
<td>6</td>
<td>6.5 (±0.3)</td>
</tr>
<tr>
<td>1:1 BHC</td>
<td>6</td>
<td>6.5 (±0.2)</td>
</tr>
<tr>
<td>2:1 BHC</td>
<td>6</td>
<td>6 (±0.0)</td>
</tr>
</tbody>
</table>

**Figure 6.** Effect of catalyst dose (g): (a) BiVO\(_4\), (b) 2:1-BHC on degradation % of MG
Figure 6 shows the curves of photodegradation rates of MG by BiVO₄ and 2:1-BHC as a function of catalyst dose.

As can be seen in Figure 6, both the BiVO₄ and 2:1-BHC demonstrated similar characteristics in terms of catalyst dose. The highest photodegradation rate was displayed by 0.1 g photocatalyst dose. Both 0.05 g and 0.2 g catalyst dose exhibited low photocatalytic activity. The decreased degradation rate in 0.05 g may be due to lesser amount of photocatalyst. On the contrary, in the case of 0.2 g catalyst dose, the decreased degradation rate may be due to the turbidity caused by higher dose of catalyst which leads to scattering of light and reducing light penetration to the bottom of the solution [14]. Hence, 0.1 g catalyst per 100 mL dye solution was found to be the optimum catalyst dose for the photodegradation of MG dye. Similar optimum conditions have been reported by other literature too [5,31-32].

Effect of dye concentration

Dye concentration of 10 ppm and 15 ppm were tested for their photodegradation by 0.1 g 2:1-BHC catalyst in 100 mL dye solution maintaining similar physical conditions.

Figure 7. Effect of MG dye concentration (ppm) on photocatalytic action of 2:1 BHC

Table 3. Photodegradation of MG dye for various catalysts

<table>
<thead>
<tr>
<th>Catalyst used</th>
<th>Irradiation source</th>
<th>Dye concentration (ppm)</th>
<th>Irradiation time (min)</th>
<th>Percentage degradation (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-doped ZnO(5% wt), K₂S₂O₈, 0.33 mmol</td>
<td>9W fluorescent visible lamp</td>
<td>0.1</td>
<td>120</td>
<td>90</td>
<td>[35]</td>
</tr>
<tr>
<td>Fe₇₃S₂Si₁₃₂B₃Cu₁Nb₃ metallic glass, K₂S₂O₈</td>
<td>300W simulated solar lamp</td>
<td>20</td>
<td>30</td>
<td>100</td>
<td>[36]</td>
</tr>
<tr>
<td>Naked Nb₂O₅</td>
<td>125W high pressure Hg lamp</td>
<td>5</td>
<td>60</td>
<td>53.25</td>
<td>[37]</td>
</tr>
<tr>
<td>Bi₂O₃/FeVO₄</td>
<td>500W Xe lamp</td>
<td>20</td>
<td>240</td>
<td>88.7</td>
<td>[38]</td>
</tr>
<tr>
<td>BiVO₄</td>
<td>500W halogen lamp</td>
<td>10</td>
<td>120</td>
<td>72.73</td>
<td>[14]</td>
</tr>
<tr>
<td>2:1 BiVO₄/Hydroxyapatite composite</td>
<td>500W halogen lamp</td>
<td>10</td>
<td>120</td>
<td>80.2</td>
<td>This work</td>
</tr>
</tbody>
</table>
As seen in Figure 7, the degradation rate for 10 ppm dye concentration is higher than that of 15 ppm dye concentration. This might be due to the high accumulation of dye particles in the solution which prevents the light to reach onto the catalyst surface. Consequently, the photocatalytic action could not be performed effectively for the degradation of dye.

Comparison with other works

The photocatalytic performance of 2:1-BHC on the photocatalytic degradation of MG dye can be compared with other reported works, as seen in Table 3.

Table 3 suggests that the results of the present work are comparable with previous other reports.

Conclusion

Nanoparticles BiVO₄ along with three BiVO₄/hydroxyapatite composites (BHCs) were successfully synthesized by co-precipitation method and wet-chemical method, respectively. The XRD, FTIR, SEM, and TEM analyses revealed proper formation of the nanocomposites. The photocatalytic activity of all four photocatalysts was studied for the MG dye photodegradation under 500W halogen lamp irradiation. The 2:1-BHC, consisted of two parts of the BiVO₄ and one part of HAP, showed best photocatalytic activity in degradation of MG dye. However, BiVO₄ showed better photocatalysis than 1:1-BHC and 1:2-BHC. The enhanced photocatalytic activity of 2:1-BHC might be due to combined activity of the BiVO₄ and HAP. Here, BiVO₄ acts as active photocatalyst which uses visible light for dye degradation. Supporting it is the HAP, which prevents the dispersion of BiVO₄ into the solution owing to the formation of composite. Moreover, HAP also facilitates BiVO₄ in faster degradation of dye by rapid adsorption of the dye molecules on the surface of the composite photocatalyst. Therefore, the 2:1 BHC composite exhibited better photocatalytic results. Hence it might be better photocatalyst for the degradation of dyes under visible light.

This study could provide a facile and economic approach to treat the organic pollutants using composites, photocatalysis, and adsorption.

Acknowledgement

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Disclosure statement

No potential conflict of interest was reported by the authors.

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