Synthesis and Characterization of BiVO₄ nanoparticles and its Photocatalytic Activity on Levofloxacin Antibiotics

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ABSTRACT
In this research, BiVO₄ photocatalyst was successfully synthesized through a facile chemical precipitation method. The as-synthesized photocatalyst was characterized using X-ray diffraction (XRD), scanning electron microscope accompanied with an energy-dispersive X-ray spectroscopy (SEM/EDS) and UV–Vis diffuse reflectance spectroscopy (UV–Vis/DRS). The photocatalytic activity of the as-synthesized photocatalyst was tested on the degradation of levofloxacin as a model pollutant. 85% degradation of 20 ppm levofloxacin was achieved within 90 min of visible light irradiation as compared with 18% using commercial photocatalyst P25, under the same experimental conditions. Such enhanced activity was attributed to higher absorption of visible light by the as-synthesized BiVO₄ that led to formation of a large number of reactive species. The kinetics of the photodegradation process was explained in terms of the Langmuir Hinshelwood model. The values of the kinetic rate constant (k) of the photodegradation were 2.52 x 10⁻³ min⁻¹, and 22.35 x 10⁻³ min⁻¹ for commercial P25 and the as-synthesized BiVO₄ photocatalysts, respectively. The investigation of the total organic carbon (TOC) indicated high mineralization of levofloxacin was achieved. Finally, the as-synthesized BiVO₄ photocatalyst was found to retain its high degradation efficiency even after 5 cycles, indicating its stability for repeated applications.

Keywords: Antibiotics, BiVO₄, Levofloxacin, Photocatalyst, Photodegradation

INTRODUCTION
Recent trends in environmental science have focused on the removal of pharmaceuticals and their metabolites in water bodies. The presence of pharmaceuticals in the environment can result in exposure to non-target organisms with wide ranging impacts. Extensive use of antibiotics and antimicrobial products has led to antibiotic-resistance in bacteria (Zaman, 2017). Moreover, a variety of aquatic organisms have shown accumulated levels of prescription hormones, antimicrobials, and antidepressants (Ferre et al., 2008). These drugs, which are up to 90 % excreted in its original form, after human consumption, can seep into surface and ground water from domestic wastewater besides some effluents (Daughton, 2010; William, 2005). Levofloxacin is a widely used second-generation fluoroquinolone antibiotic and is known for its broad-spectrum activity against gram positive and gram-negative bacteria (Lee et al., 2017; Sturini, et al., 2012). In addition to this, it has an excellent tissue penetration and is available in both oral and intravenous formulations. However, it may produce serious and life-threatening adverse reactions. According to the U.S Food and Drug Administration (FDA), levofloxacin may cause worsening of myasthenia gravis symptoms, including muscle weakness and breathing problems as well as spontaneous tendon ruptures (Kansal et al., 2014). After consumption, as much as 87% of levofloxacin was discharged in urine within 2 days (Lu et al., 2019). Therefore, levofloxacin is considered as a pollutant which needs to be removed from water bodies.

Conventional wastewater treatment methods are ineffective in removing antibiotics such as levofloxacin at trace levels (Safari et al., 2015). Hence, there is a considerable need for the efficient degradation of this harmful substance by exploring other potential technologies. Photocatalysis is one of the leading advanced oxidation processes (AOPs) that degrades various organic compounds and has been used extensively for the degradation of pharmaceutical compounds in aqueous solution (Lofrano et al., 2017; Kaur &Kansal, 2016; Aga, 2007). These compounds in the presence of this process are eventually converted to smaller moieties which are of less harmful in nature to the environment.

Attempt by various researchers have been made to develop various heterogeneous catalysts with increased oxidative power. These mostly include metal and non-metal doped catalysts (Qiao et al., 2017). Bismuth-based metal oxides such as BiVO₄, Bi₂WO₆ etc. have been reported as novel compounds which show enhanced photocatalytic efficiency and improved charge transfer (Pálmai et al., 2017; Chen et al., 2016). Bismuth vanadate
using BaSO4 as a reference standard. Total organic carbon (TOC) was measured with Shimadzu 5000 TOC Analyzer equipped with an autosampler.

Results and Discussion

The XRD pattern of the as-synthesized BiVO4 photocatalyst is presented in Fig. 1. It can be seen that all the diffraction peaks can be indexed to the monoclinic scheelite structure of bismuth vanadate (m-BiVO4) (JCPD file no: 14-0688). No peaks of any other phases were detected, indicating the purity of the sample. The crystallite size of the prepared samples as calculated using the Scherrer’s equation (3) (Du et al., 2016) is presented in Table 1.

\[ D = \frac{k\lambda}{\beta\cos\theta} \]  

Where, D is the crystal size, \( \lambda \) is the wavelength equal to 0.154 nm, k is a constant taken as 0.94, \( \beta \) is the peak full widths at half-maximum intensity (FWHM) and \( \theta \) is the Bragg angle of the actual peak.

The surface morphology of the as-synthesized BiVO4 photocatalyst was examined using a scanning electron microscope (SEM), and SEM images and Energy-dispersive X-ray spectroscopy (EDS) were obtained using a OneSight new wide-range high-speed detector.
the images are as shown in Fig. 2. It can be seen from the images that the as-synthesized m-BiVO₄ photocatalyst shows irregular sphere-like morphology. Bi, V, and O were the only elements which appeared in the EDS trace, which further confirmed the purity of the sample.

Fig. 1 XRD pattern of the as-synthesized BiVO₄

Fig. 2 SEM images at a) x400 b) x5000 magnification and c) EDS pattern of the as-synthesized BiVO₄

Fig. 3 presents the UV–vis spectra of the as-synthesize BiVO₄ photocatalyst. The sample show strong absorption in the visible light region in addition to that in the UV light zone. The band gap energy of photocatalysts can be calculated using Tauc’s equation (eq. 4) based on the DRS results (Tang et al., 2015).
\[ \alpha h\nu = A(h\nu - E_g)^n/2 \]  

where \( \alpha \) is the absorption coefficient, \( h \) is the Planck’s constant, \( \nu \) is the light frequency, \( A \) is the proportionality constant and \( E_g \) is the band gap. The value of \( n \) depends on the type of optical transition in the semiconductor, whether direct \( (n = 1) \) or indirect \( (n = 4) \) transition (Pirzada et al., 2015). The band gap energy of the as-synthesized BiVO\(_4\) photocatalyst was found to be 2.44 eV as estimated from the plot of \((\alpha h\nu)^2\) versus \(h\nu\) as shown in Fig. 3 (inset). The result indicated that the as-synthesized BiVO\(_4\) photocatalyst has appropriate band gap energy which is favorable for the photocatalytic decomposition of organic contaminants under visible light irradiation.

![Fig. 3 UV-Vis absorption spectrum and Tauc plot (inset) for the as-synthesized BiVO\(_4\)](image)

### Table 1: Crystallite size, surface area, pore volume and band gap energy of BiVO\(_4\) photocatalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO(_4)</td>
<td>26.88</td>
<td>0.9856</td>
<td>8.413</td>
<td>0.00142</td>
<td>2.44</td>
</tr>
</tbody>
</table>

### Photocatalytic degradation of levofloxacin

The catalytic activity of the as-synthesized BiVO\(_4\) photocatalysts was evaluated in the degradation of levofloxacin visible light illumination. Figure 4a is the plot of degradation efficiency of levofloxacin by the as-synthesized BiVO\(_4\) photocatalysts, where \( C_0 \) is the initial concentration of levofloxacin and \( C \) is the concentration during irradiation time \( t \). Before the introduction of the photocatalysts, blank studies were conducted, and the results revealed that the concentration of levofloxacin remains constant in the absence of catalyst, thus further indicating the stability of levofloxacin under visible light irradiation. As shown from figure 4a, about 85% of levofloxacin degradation was achieved after 90 min of visible light irradiation in the presence of the as-synthesized BiVO\(_4\) photocatalysts. However, in the presence of commercial TiO\(_2\) Degussa P25, under the same experimental conditions, only about 18% of levofloxacin degradation was achieved. The result is higher than that obtained by Li et al. (2011), who achieved only 55% of methylene blue degradation in the presence of BiVO\(_4\) nanoparticles after 300 min of visible light irradiation.

Furthermore, in order to quantitatively compare the photocatalytic performance of the as-synthesized BiVO\(_4\) photocatalyst, the rate of levofloxacin degradation was calculated and presented in Fig. 4b. The calculated rate constant \( k \) for the P25 and the as-synthesized BiVO\(_4\) photocatalyst are 2.52 \( \times 10^{-3} \) min\(^{-1}\) and 22.35 \( \times 10^{-3} \) min\(^{-1}\) respectively. The as-synthesized BiVO\(_4\) photocatalyst has a higher rate constant, which is almost 9 folds higher than that of commercial TiO\(_2\) Degussa P25. Moreover, from the high values of correlation coefficients \( R^2 \), it could be deduced that the degradation process follows pseudo-first-order kinetic model. The milestone recorded in this work has been compared to other works in the literature as shown in Table 2.
Mineralization studies

The extent of mineralization was determined with respect to decrease in total organic carbon content (TOC) in the levofloxacin solution. Fig 5 show that the as-synthesized BiVO₄ photocatalyst possesses higher mineralization than Degussa P25, which is due to higher absorption of visible light that led to formation of a large number of reactive species such as hydroxyl radicals. However, TOC removal rate was much lower than the degradation process under the same experimental condition. This may be due to formation of stable and recalcitrant intermediates in the mineralization process.

Reusability

The reusability studies for the as-synthesized BiVO₄ photocatalyst were conducted by collecting the used photocatalyst sample after photocatalytic reactions. The used photocatalyst was then dried at 60 ºC for 12 h. The dried photocatalyst was then used under the same conditions as described earlier. Fig. 6 shows the remarkable performance of the as-synthesized BiVO₄ photocatalyst, with little decrease in catalytic activity after five cycles. This gives a clear indication that the as-synthesized BiVO₄ photocatalyst is highly stable and may be used for other practical applications.
Fig. 6 Reusability of the as-synthesized BiVO₄ photocatalyst on the degradation of levofloxacin

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dosage (g/L)</th>
<th>[TC] (ppm)</th>
<th>Light source</th>
<th>Efficiency (%)</th>
<th>Time (min)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂CO₃/CeO₂/AgBr</td>
<td>0.5</td>
<td>10</td>
<td>300 W Xe lamp</td>
<td>87.63</td>
<td>40</td>
<td>(Wen et al., 2018)</td>
</tr>
<tr>
<td>Ag₂O/TiO₂ QDs</td>
<td>0.25</td>
<td>10</td>
<td>85 W CFL bulbs (4150 lumens)</td>
<td>81</td>
<td>90</td>
<td>(Kaur et al., 2017)</td>
</tr>
<tr>
<td>BiVO₄/CeVO₄</td>
<td>0.5</td>
<td>50</td>
<td>150 W Xe lamp</td>
<td>95.7</td>
<td>300</td>
<td>(Lu et al., 2019)</td>
</tr>
<tr>
<td>CdS/g-C₃N₄</td>
<td>0.4</td>
<td>5</td>
<td>455 nm light</td>
<td>64.42</td>
<td>210</td>
<td>(Rengaraj et al., 2019)</td>
</tr>
<tr>
<td>BiVO₄</td>
<td>0.25</td>
<td>20</td>
<td>Visible light (45 mW/cm²)</td>
<td>85</td>
<td>90</td>
<td>present study</td>
</tr>
</tbody>
</table>

Proposed mechanism of the photocatalysis

When a semiconductor photocatalyst such as BiVO₄ is illuminated by photon energy which is greater or equal to its band gap energy, it excites electron (e⁻) from its valence band (VB) to the conduction band (CB). Simultaneously, it causes the formation of an electron vacancy, a positive charge called hole (h⁺), in the valence band (VB). The energy differences between the valence band (VB) and the conduction band (CB) is known as band gap (Eg). The photo-generated positive holes react with water to produce hydroxyl radical (•OH), while the photo-generated electrons react with oxygen to produce superoxide radicals (O₂⁻). Both of these primary products (•OH, O₂⁻ and h⁺) are strong oxidizing species that attacks organic pollutants such as levofloxacin and degrade them to CO₂ and H₂O. The proposed mechanism of this process can be illustrated in equations 5 - 8.

CONCLUSION

BiVO₄ photocatalysts have been successfully synthesized using a facile chemical precipitation method. The as-synthesized photocatalyst was characterized using XRD, SEM and UV-vis DRS analyses. Its efficiency as a photocatalyst was evaluated using levofloxacin as a model pollutant under visible light irradiation. Compared to commercial photocatalyst P25 Degussa, the as-synthesized BiVO₄ photocatalysts demonstrated remarkable enhancement in the photocatalytic activity towards levofloxacin degradation. Such improved performance has been attributed to the higher absorption of visible light that led to formation of a large number of reactive species such as h⁺ and •OH. Reusability studies show that the as-synthesized BiVO₄ photocatalyst retained its high-level degradation efficiency even after 5 cycles.

RECOMMENDATION

It is recommended that analytical method such as LCMS should be conducted on the irradiated mixture of levofloxacin to know the actual end products after the degradation.
REFERENCES


Qiao, Z., Yan, T., Li, W., & Huang, B. (2017): In situ anion exchange synthesis of In₂S₃/In(OH)₃ heterostructures for efficient photocatalytic degradation of MO under solar light. New Journal of Chemistry, 41(8), 3134-3142.


