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$BiVO_4$-based photoanodes for the photoelectrocatalytic removal of trace organic pollutants from water: A mini review on recent developments

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This mini review explores the potential of visible light–driven bismuth vanadate ($BiVO_4$)-based photoanodes for removing trace organic pollutants from water. It highlights the advantages of using $BiVO_4$-based photoanodes over conventional UV-driven photoanodes in water treatment. The mechanism of reactive species generation through water oxidation is discussed. The review also highlights the role of sulfate and sulfite radicals in enhancing pollutant degradation. Furthermore, it evaluates how heterojunction formation improves the removal efficiency of $BiVO_4$-based photoanodes by reducing charge carrier recombination. Limited research on $BiVO_4$-based photoanodes for the simultaneous removal of multiple organic pollutants at low concentrations (<1 mg L^{-1}) from real wastewater is identified as a key knowledge gap. Addressing this gap could advance the application of $BiVO_4$-based photoanodes in photoelectrocatalytic-based advanced oxidation processes.

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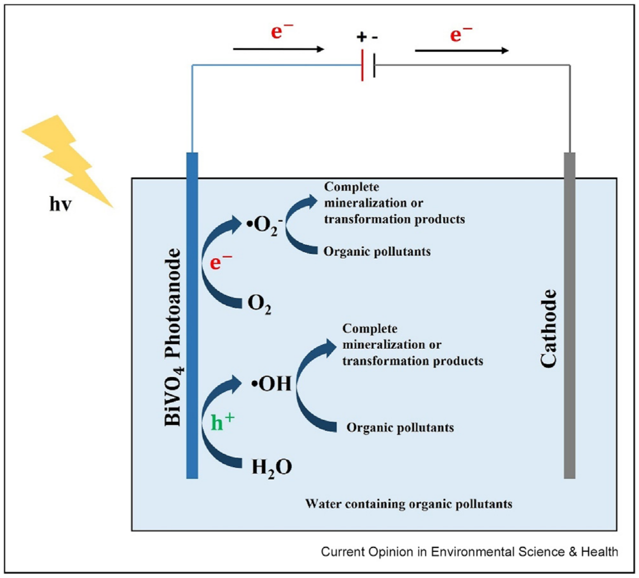
Introduction

Organic pollutants such as synthetic dyes, pharmaceuticals and pesticides contaminate water resources and pose serious risks to human health and aquatic ecosystem [1–3]. The concentrations of these organic pollutants vary by source and location, ranging from a few ng L^{-1} to several μg L^{-1} [4,5]. Conventional wastewater treatment technologies often fail to remove organic pollutants completely. As a result, these pollutants are released into the aquatic environment [6]. Advanced oxidation processes (AOPs) are gaining importance for the removal of organic pollutants [7]. AOPs generate hydroxyl radicals ($\cdot OH$) and superoxide radicals ($^{\cdot}O_2^-$) in water as the main reactive oxygen species (ROS), which degrade organic pollutants [8,9]. Among AOPs, photoelectrocatalytic (PEC)-based AOP has gained attention due to its enhanced charge separation under applied voltage, which improves the ROS generation and removal efficiency for organic pollutants [10–13].

Bismuth vanadate ($BiVO_4$) is a small band gap (∼2.4 eV) semiconducting photocatalyst, widely used in PEC AOPs for removing organic pollutants from aqueous solutions [14]. Figure 1 illustrates a typical PEC cell for the removal of organic pollutants using a $BiVO_4$ photoanode. Electrons and holes are generated in the $BiVO_4$ photoanode upon its interaction with the incoming photons. The photogenerated holes oxidize the water molecules to produce $\cdot OH$, whereas the photogenerated electrons reduce oxygen to produce $^{\cdot}O_2^-$ [15]. An external voltage is applied to the photoanode to minimize electron–hole recombination, thereby enhancing charge separation [16]. Unlike conventional photocatalysts such as titanium oxide (TiO_2) [17], zinc oxide (ZnO) [18], and tungsten oxide (WO_3) [19], which primarily absorb UV light ($\lambda < 400$ nm), $BiVO_4$ can absorb both UV and visible light ($\lambda \leq 520$ nm), improving solar energy utilization [14]. $BiVO_4$ has demonstrated superior photocatalytic efficiency for water oxidation compared with TiO_2, ZnO, and WO_3 [20]. This is attributed to its favorable conduction and valence band positions, which allow effective generation of reactive oxygen species (ROS) such as hydroxyl ($\cdot OH$) and superoxide ($\cdot O_2^-$) radicals.

Figure 1



Schematic of the photoelectrocatalytic removal of organic pollutants from water using a $BiVO_4$ photoanode. Solar photons (hv) interact with the photoanode, generating electron (e^-)–hole (h^+) pairs. These charge carriers facilitate the formation of hydroxyl and superoxide radicals, which oxidize the organic pollutants.

Additionally, $BiVO_4$ has a relatively positive valence band potential (∼2.5 V vs. standard hydrogen electrode (SHE)), making it effective for oxidative degradation of organic pollutants [20]. Compared with ZnO, which undergoes photo-corrosion in aqueous solutions [21], $BiVO_4$ is more stable under visible light [22]. Additionally, it can be used effectively under neutral to slightly acidic conditions (pH 5–6), making it suitable for real wastewater treatment applications [23]. This mini review provides an analysis of recent advancements in the application of $BiVO_4$-based photoanodes for the removal of organic pollutants, with a particular emphasis on pharmaceuticals. It highlights the role of heterojunction in enhancing $BiVO_4$ removal efficiency by improving charge separation. Additionally, this review identifies critical knowledge gaps, particularly the limited research on $BiVO_4$-based photoanodes for the simultaneous removal of multiple organic pollutants at low concentrations (<1 mg L^{-1}) in real wastewater. Finally, it offers recommendations to guide future research and advance the application of $BiVO_4$ in PEC-based water treatment.

Structural and optical properties of $BiVO_4$

$BiVO_4$ is a nontoxic, cost-effective n-type semiconductor with good chemical stability [14]. Its absorbance depends on its crystal structure, existing in three polymorphs: pucherite (orthorhombic), dreyerite (tetragonal zircon), and clinobisvanite (monoclinic scheelite or tetragonal scheelite) [24]. The monoclinic scheelite structure is favored for photoelectrocatalysis due to its lower band gap energy (about 2.4 eV) [25] and reduced recombination rate of photogenerated carriers compared with the other crystal structures [26]. These properties are linked to the unique local bonding environment in monoclinic scheelite $BiVO_4$, making it more effective for PEC applications [27,28].

Photoelectrocatalytic removal of organic pollutants using $BiVO_4$ photoanodes

Monoclinic scheelite $BiVO_4$ photoanodes have been effectively utilized in laboratory-scale research for the PEC removal of phenols, dyes, and pharmaceuticals. Fluorine-doped tin oxide (FTO) is mostly used as a substrate for the deposition of $BiVO_4$ [14]. Bennani et al. (2016) investigated the application of spray-coated FTO/$BiVO_4$ photoanodes for the PEC-based removal of phenol (20 mg L^{-1}) in demineralized water [29]. The fabricated photoanodes achieved a removal efficiency of 70 % with an applied potential of 1.0 V (vs Ag/AgCl) after 4 h reaction time. Under identical conditions, this efficiency was 14 % higher than that observed with TiO_2 photoanodes. The higher removal efficiency of $BiVO_4$ is attributed to the visible light absorption and improved charge separation compared with TiO_2. Bacha et al. (2019) utilized $BiVO_4$ photoanodes to remove methyl orange (10 mg L^{-1}) in demineralized water under visible light, generated with a 300 W xenon lamp [30]. The fabricated photoanode removed only 11 % of the methyl orange at an applied voltage of 2.0 V (vs Ag/AgCl) after 2 h. However, after adding 16 mM of Na_2SO_3 in the electrolyte, 97 % of methyl orange was removed after 2 h with the same photoanode at 2.0 V (vs Ag/AgCl). This increase was likely due to the generation of sulfite radicals ($SO_3^{\cdot-}$) through the interaction of sulphite anions (SO_3^{2-}) with the ·OH radicals at the $BiVO_4$ surface. Similarly, in another study, the removal efficiency of $BiVO_4$ photoanode for bisphenol A (10 mg L^{-1}) was enhanced by the addition of peroxymonosulfhate (PMS) in the electrolyte [31]. PMS acted as an electron acceptor for the photogenerated electrons in $BiVO_4$, facilitating the generation of ·OH radicals and enabling complete removal of bisphenol A at an applied voltage of 0.25 V (vs saturated calomel electrode (SCE)) within 2 h. Wang et al. (2020) investigated the use of $BiVO_4$ photoanode and polydopamine-modified carbon felt polydopamine-modified carbon felt (PDA/CF) cathode for the removal of ofloxacin (8 mg L^{-1}) [32]. They found that addition of 2 mM PMS in the electrolyte accelerates the removal reaction rate by generating sulfate radicals ($SO_4^{\cdot-}$), leading to complete ofloxacin removal within 2 h at 1.5 V (vs Ag/AgCl). Based on the results of electron spin resonance, ·OH radicals and $SO_4^{\cdot-}$ radicals were identified as the main oxidizing species responsible for the removal of ofloxacin. Cheng et al. (2019) demonstrated effective

Table 1

Summary of recent studies using $BiVO_4$ heterojunction photoanodes for the removal of organic pollutants.

Heterojunction photoanode	Configuration of PEC cell	Light intensity	Pollutant	Removal efficiency	Rate coefficient (k)	Ref
$BiVO_4/MnO_2$	Cathode: Pt sheet Applied potential: 1.5 V (vs Ag/AgCl)	100 W xenon lamp with $\lambda \geq 420$ nm	Ciprofloxacin (C_0 = 10 mg L^{-1})	76 %, 2 h	1.05×10^{-2} min^{-1}	[35]
$BiVO_4/Ag_2S$	Cathode: Pt sheet Applied potential: 1.2 V (vs Ag/AgCl)	100 W xenon lamp with $\lambda \geq 420$ nm	Ciprofloxacin (C_0 = 10 mg L^{-1}) Sulfamethoxazole (C_0 = 10 mg L^{-1})	80 %, 2 h 86 %, 2 h	1.37×10^{-2} min^{-1} 1.47×10^{-2} min^{-1}	[36]
$BiVO_4/WO_3$	Cathode: Pt plate Applied potential: 1.0 V (vs SCE)	300 W xenon lamp with $\lambda \geq 420$ nm and intensity of 1 mW cm^{-2}	Norfloxacin (C_0 = 10 mg L^{-1})	67 %, 3 h	2.68×10^{-3} min^{-1}	[37]
$BiVO_4$/g-C_3N_4	Cathode: Pt wire Applied potential: 1.23 V (vs Ag/AgCl)	300 W xenon lamp with light intensity of 100 mW cm^{-2}	Methyl orange (C_0 = 5 mg L^{-1})	90 %, 75 min	4.56×10^{-2} min^{-1}	[22]
$BiVO_4/WO_3$	Cathode: Pt foil Applied potential: 1.5 V (vs Ag/AgCl)	Solar simulator with light intensity of 100 mW cm^{-2}	Ibuprofen (C_0 = 100 mg L^{-1})	82 %, 150 min	Not available	[38]
TiO_2/RuO_2-BiVO_4	Cathode: Pt foil Applied potential: 2.0 V (vs SCE)	300 W xenon lamp with $\lambda \geq 420$ nm	Acetaminophen (C_0 = 332 mg L^{-1})	100 %, 3 h	3.38×10^{-2} min^{-1}	[39]
$BiVO_4$/NiS	Cathode: Pt wire Applied potential: 1.8 V (vs Ag/AgCl)	100 W xenon lamp	Rhodamine B (C_0 = 10 mg L^{-1}) Sulfamethoxazole (C_0 = 10 mg L^{-1})	73 %, 2 h 57 %, 2 h	0.108 min^{-1} 7.4×10^{-3} min^{-1}	[40]
$TiO_2/BiVO_4-Bi_2S_3$	Cathode: Pt sheet Applied potential: 1.8 V (vs Ag/AgCl)	Xenon lamp with light intensity of 100 mW cm^{-2}	Rhodamine B (C_0 = 10 mg L^{-1})	64.3 %, 150 min	6.13×10^{-3} min^{-1}	[41]
$CoFe_2O_4-BiVO_4$	Cathode: Pt mesh Applied potential: 0.6 V (vs Ag/AgCl)	300 W xenon lamp with $\lambda \geq 420$ nm	Tetracycline (C_0 = 20 mg L^{-1})	89 %, 1 h	3.7×10^{-2} min^{-1}	[42]
$BiVO_4/TiO_2$	Cathode: Pt wire Applied potential: 4 V (vs Ag/AgCl)	300 W xenon lamp with $\lambda \geq 420$ nm with light intensity of 200 mW cm^{-2}	Rhodamine B (C_0 = 10 mg L^{-1})	93.9 %, 5 h	Not available	[43]
$BiVO_4$/ZnO	Cathode: Pt foil Applied potential: 0.8 V (vs SCE)	300 W xenon lamp with $\lambda \geq 420$ nm	Tetracycline (C_0 = 20 mg L^{-1})	66.1 %, 2 h	1.94×10^{-3} min^{-1}	[44]
$BiVO_4/MoS_2$	Cathode: Pt wire Applied potential: 1.5 V (vs Ag/AgCl)	300 W xenon lamp with $\lambda \geq 435$ nm	Bisphenol A (C_0 = 10 mg L^{-1})	100 %, 75 min	5.12×10^{-2} min^{-1}	[45]
$BiVO_4$/Ag	Cathode: Pt foil Applied potential: 1.5 V (vs Ag/AgCl)	300 W xenon lamp with $\lambda > 420$ nm	β-naphthol (C_0 = 10 mg L^{-1})	80 %, 8 h	3.33×10^{-3} min^{-1}	[46]
$BiVO_4$/ZnO	Cathode: Pt wire Applied potential: 1.6 V (vs Ag/AgCl)	300 W xenon lamp with $\lambda \geq 420$ nm	Tetracycline (C_0 = 20 mg L^{-1})	95.4 %, 1 h	4.55×10^{-2} min^{-1}	[47]
$BiVO_4/\alpha$-Fe_2O_3	Cathode: Pt foil Applied potential: 2 V (vs Ag/AgCl)	350 W xenon lamp	Bisphenol A (C_0 = 20 mg L^{-1})	86.8 %, 2 h	Not available	[48]
$BiVO_4$/g-C_3N_4	Cathode: Pt wire Applied potential: 1 V (vs SCE)	Xenon lamp with $\lambda \geq 420$ nm	Diclofenac sodium (C_0 = 10 mg L^{-1})	30.1 %, 2 h	3.23×10^{-3} min^{-1}	[49]
$BiVO_4$/CuO	Cathode: Pt foil Applied potential: 4.0 V (vs Ag/AgCl)	44 W LED with $\lambda \geq 420$ nm	4-Nitrophenol (C_0 = 30 mg L^{-1})	50.2 %, 8 h	1.86×10^{-2} min^{-1}	[50]
$BiVO_4$/ZnO (with exfoliated graphite as substrate)	Reference electrode: Ag/AgCl Cathode: Pt sheet Applied current density: 10 mA cm^{-2}	100 W xenon lamp with $\lambda \geq 420$ nm	Rhodamine B (C_0 = 10 mg L^{-1})	91 %, 4 h	9.21×10^{-3} min^{-1}	[51]
$BiVO_4/Cu_2O$	Cathode: Pt foil Applied potential: 0.6 V (vs Ag/AgCl)	300 W xenon lamp	Ciprofloxacin (C_0 = 30 mg L^{-1})	60 %, 150 min	6.5×10^{-3} min^{-1}	[52]
$WO_3/BiVO_4$	Cathode: Pt wire Applied potential: 1.2 V (vs Ag/AgCl)	320 W xenon lamp	Sodium 2-napthalenesulfonate (S2NS) (C_0 = 50 mg L^{-1}) Benzyl alkyl dimethylammonium (BAC-C12) (C_0 = 50 mg L^{-1})	100 %, 150 min 100 %, 150 min	Not available	[53]
$BiVO_4/MoS_2-Co_3O_4$	Cathode: platinum plate Applied potential: 3.5 V	Xenon lamp with light intensity of 100 mW cm^{-2}	Bisphenol A (C_0 = 10 mg L^{-1})	80 %, 5 h	5.8×10^{-3} min^{-1}	[54]

$BiVO_4$, bismuth vanadate; PEC, photoelectrocatalytic.

tetracycline (TC) removal using a $BiVO_4$ photoanode paired with a dual hemin/Cu-carbon cloth cathode [33]. The photogenerated holes in $BiVO_4$ produced ·OH radicals and also directly oxidized the molecules of TC while the photogenerated electrons were transferred to the cathode for the production of H_2O_2. This combination of $BiVO_4$ photoanode and dual hemin/Cu-carbon cloth cathode removed 93.6 % of TC after 2 h reaction time with an applied voltage of 0.8 V (vs Ag/AgCl) to the photoanode.

$BiVO_4$-based heterojunction photoanodes

To improve charge separation, $BiVO_4$ is often combined with other photocatalysts to form a heterojunction. $BiVO_4$-based heterojunction photoanodes show higher removal efficiency for organic pollutants compared with pristine $BiVO_4$ photoanodes. Cao et al. (2018) investigated a $BiVO_4/Ag_3PO_4$ heterojunction photoanode for the PEC-based removal of norfloxacin (5 mg L^{-1}), achieving complete removal within 90 min at 0.5 V (vs SCE), compared with 61.4 % removal by pristine $BiVO_4$ photoanode [34]. The enhanced performance is attributed to the enhanced charge separation in the heterojunction photoanode, which increases ·OH radicals production, significantly improving the removal kinetics. Table 1 summarizes recent studies that utilized $BiVO_4$ heterojunction photoanodes for the removal of organic pollutants.

Conclusions and outlook

$BiVO_4$-based photoanodes have demonstrated comparable and even superior removal efficiency for a number of organic pollutants compared with UV-driven photoanodes such as TiO_2 (Table 1). In PEC based systems, ·OH radicals are the primary reactive species responsible for oxidizing organic pollutants. Several studies have also reported enhanced removal efficiency with the addition of PMS, attributed to the oxidation of organic pollutants by $SO_4^{\cdot-}$ generated through the visible light activation of PMS in the bulk solution. Similarly, heterojunction photoanodes have shown higher removal efficiencies than pristine $BiVO_4$ photoanodes due to improved charge separation. The studies reviewed predominantly targeted synthetic dyes and pharmaceutical compounds, using concentrations in demineralized water ranging from 5 to 50 mg L^{-1}.

There remains ample research potential in the field of PEC-driven removal of organic pollutants using $BiVO_4$ photoanodes. Further studies are particularly needed to explore the effectiveness of $BiVO_4$-based photoanodes for the removal of organic pollutants at concentrations below 1 mg L^{-1} as most organic pollutants detected in surface water or groundwater range from low ng L^{-1} levels to higher μg L^{-1} levels [55], which can impact the removal kinetics. Additionally, investigating the simultaneous removal of multiple organic pollutants in aqueous solutions is essential, given that pollutants of emerging concern typically occur in aquatic environments as mixtures rather than as isolated compounds [56,57]. Research should also focus on applying $BiVO_4$-based photoanodes to remove organic pollutants from real wastewater or effluent from industrial processes and wastewater treatment plants as this would provide valuable insights into the removal mechanism and the effect of the overall water composition on the removal efficiency. Moreover, employing process simulation tools such as computational fluid dynamics (CFD) modeling for $BiVO_4$-based PEC removal in full-scale reactors could be beneficial. Simulation results can be used for a techno-economic analysis, helping to evaluate the feasibility of reactor designs of scaled-up PEC reactors employing $BiVO_4$-based photoanodes.

In conclusion, $BiVO_4$-based photoanodes have demonstrated considerable potential in water treatment applications. Given the advancements achieved to date, it is expected that $BiVO_4$-based photoanodes will be increasingly used for full-scale water treatment applications in the future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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** of outstanding interest

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This article is particularly interesting as it presents $BiVO_4$/g-C_3N_4 Z-scheme photoanode that significantly enhances photocurrent density and methyl orange dye removal efficiency. The study addresses key limitations of $BiVO_4$ by achieving enhanced charge separation, light absorption, and long-term stability, making it a valuable contribution to sustainable water treatment.

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