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Citation (APA)

Ali, A. Z., Wu, Y., Doekhi-Bennani, Y., & van der Hoek, J. P. (2023). Photo-electrocatalytic based removal of acetaminophen: Application of visible light driven heterojunction based BiVO₄/BiOI photoanode. *Chemosphere*, 324, Article 138322. <https://doi.org/10.1016/j.chemosphere.2023.138322>

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Photo-electrocatalytic based removal of acetaminophen: Application of visible light driven heterojunction based BiVO₄/BiOI photoanode

Agha Zeeshan Ali^{a,*}, Yiqian Wu^a, Yasmina-Doekhi Bennani^b, Henri Spanjers^a, Jan Peter van der Hoek^{a,c}

^a Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, P.O. Box 5048, 2600, GA, Delft, the Netherlands

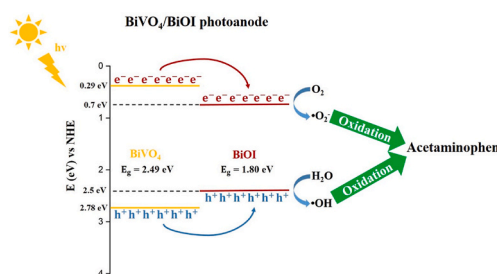
^b Nijhuis Water Technology B.V, Innovatieweg 4, 7007 CD, Doetinchem, the Netherlands

^c Waternet, Department of Research & Innovation, P.O. Box 94370, 1090, GJ, Amsterdam, the Netherlands

HIGHLIGHTS

- Electrode deposition process for the successful fabrication of photoanodes.
- Increase in absorbance area and quantum efficiency by combing BiVO₄ and BiOI.
- In-situ generation of hydroxyl and super-oxide radicals by BiVO₄/BiOI photoanode.
- 87% removal of acetaminophen (40 μg L⁻¹) by BiVO₄/BiOI photoanode.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: E. Brillas

Keywords:

Organic micro-pollutants
Advanced oxidation process
Photoelectrocatalysis
Heterojunction photoanodes
BiVO₄/BiOI
Acetaminophen

ABSTRACT

The presence of organic micro-pollutants (OMPs) in wastewater treatment effluents is becoming a major threat to the water safety for aquatic and human health. Photo-electrocatalytic based advanced oxidation process (AOP) is one of the emerging and effective techniques to degrade OMPs through oxidative mechanism. This study investigated the application of heterojunction based BiVO₄/BiOI photoanode for acetaminophen (40 μg L⁻¹) removal in demineralized water. Photoanodes were fabricated by electrodeposition of BiVO₄ and BiOI photocatalytic layers. Optical (UV-vis diffusive reflectance spectroscopy), structural (XRD, SEM, EDX) and optoelectronic (IPCE) characterization confirmed the successful formation of heterojunction for enhanced charge separation efficiency. The heterojunction photoanode showed incident photon to current conversion efficiency of 16% ($\lambda_{\text{max}} = 390 \text{ nm}$) at an external voltage of 1 V under AM 1.5 standard illumination. The application of the BiVO₄/BiOI photoanode in the removal of acetaminophen at 1 V (external bias) vs Ag/AgCl under simulated sunlight showed 87% removal efficiency within the first 120 min compared to 66% removal efficiency of the BiVO₄ photoanode. Similarly, combining BiVO₄ and BiOI exhibited 57% increase in first order removal rate coefficient compared to BiVO₄. The photoanodes also showed moderate stability and reusability by showing 26% decrease in overall degradation efficiency after three cycles of each 5 h experiment. The results obtained in this study can be considered as a stepping stone towards the effective removal of acetaminophen as an OMP present in wastewater.

* Corresponding author. Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, P.O. Box 5048, 2600, GA, Delft, the Netherlands.

E-mail address: a.aghzeeshan@tudelft.nl (A.Z. Ali).

<https://doi.org/10.1016/j.chemosphere.2023.138322>

Received 10 November 2022; Received in revised form 3 March 2023; Accepted 4 March 2023

Available online 6 March 2023

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1. Introduction

Water pollution is a major environmental concern due to various factors among which increase in industrial growth, population growth and water scarcity are the most important (Rogowska et al., 2020). Owing to the importance of water safety, The United Nations (UN) also included access to clean water and sanitation in its sustainable development goals list ("THE 17 GOALS | Sustainable Development," n.d.). Keeping the surface water bodies safe for use is imperative because major part of the drinking water supply comes from surface water resources (van der Hoek et al., 2014). The majority of the research efforts within wastewater treatment domain is focused on ensuring that the wastewater treatment plant's (WWTP) effluent is safe for aquatic and human life (Corominas et al., 2013). Apart from resource recovery from the wastewater (Puyol et al., 2017; Solon et al., 2019), using the treated wastewater for different practical purposes is also becoming increasingly important within the circular economy domain (Smol et al., 2020). Conventional treatment plants only remove carbon (C), nitrogen (N) and phosphorous (P) from the wastewater (Neczaj and Grosser, 2018). However, over the past several decades analysis of WWTP effluents has shown that some chemical compounds mainly belonging to the industrial and pharmaceutical compounds category (Petrie et al., 2015) are still present in the effluent within the range of 1–10 $\mu\text{g L}^{-1}$ (Ratola et al., 2012). The compounds that are present in the water resources in the ng L^{-1} to $\mu\text{g L}^{-1}$ range are called micro-pollutants (MPs), and MPs that are organic are called organic micro-pollutants (OMPs) (Golovko et al., 2020).

Advanced oxidation processes (AOPs) are becoming increasingly important for the complete removal of OMPs from industrial or municipal wastewater. Among various types of AOPs, photo-electrocatalytic (PEC) based AOP is gaining importance due to the use of solar energy to activate photocatalytic materials for the generation of reactive species. PEC based AOP involves the use of semiconducting anode materials for the in-situ production of oxidants that are mainly hydroxyl ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$). The in-situ oxidants unselectively oxidize the organic pollutants to remove them from the wastewater (Garcia-Segura and Brillas, 2017). Metal oxide based photocatalysts such as titanium dioxide (TiO_2) (Collivignarelli et al., 2021), tungsten trioxide (WO_3) (Liao et al., 2021), zinc oxide (ZnO) (Rajeswari and Venkatesh, 2021), zirconium dioxide (ZrO_2) (Sponza and Oztekin, 2016) and iron oxide (Fe_2O_3) (Aragaw et al., 2021) are widely reported in literature for the removal of pharmaceuticals and industrial dyes (1–10 mg L^{-1}) in aqueous solution. However, these photocatalysts have an intrinsic drawback that due to their large band gap energy (3.0–3.5 eV) they can only absorb photons in the UV range of solar irradiation. Bismuth vanadate (BiVO_4) in its monoclinic scheelite phase is a small band gap (~ 2.4 eV) visible light driven photocatalyst and, due to its stability and non-toxicity, BiVO_4 is used as anodic material for the PEC based removal of organic micro-pollutants in aqueous solution (Deshpande et al., 2020; Shao et al., 2020a). However, PEC activity of pristine BiVO_4 is hindered due to poor charge transport and high rate of recombination of photo-generated electron-hole pairs (Orimolade and Arotiba, 2020a). The PEC activity corresponds to the removal efficiency of the BiVO_4 photoanode for the removal of pollutants from aqueous solution. Combining monoclinic scheelite BiVO_4 with other photocatalysts to make a heterojunction is one of the effective strategies to improve the PEC activity of BiVO_4 (Orimolade and Arotiba, 2020a). Depending on the band gap alignment of the photocatalysts under consideration, the heterojunction between them can be of two types, either type I or type II (Orimolade and Arotiba, 2020b). Photogenerated holes and electrons in type I heterojunction are transferred to the electrode-electrolyte interface, whereas in type II heterojunction the photogenerated charge carriers are transferred in opposite directions thereby effectively enhancing the charge separation in the photoanode (Orimolade and Arotiba, 2020b) (illustrated in Fig. 1). Various heterojunction structures that are mostly type II such as $\text{WO}_3/\text{BiVO}_4$ (Du et al.,

2019, p. 3), CuO/BiVO_4 (Bai et al., 2018), CdS/BiVO_4 (Li et al., 2018), $\text{BiVO}_4/\text{Ag}_2\text{S}$ (Orimolade and Arotiba, 2020c) and $\text{BiVO}_4/\text{Ag}_3\text{PO}_4$ (Cao et al., 2018) are reported in literature that have shown enhanced PEC based removal of dyes and pharmaceutical compounds compared to pure BiVO_4 .

Bismuth oxyiodide (BiOI) is also a bismuth based small band gap (~ 1.9 eV) photocatalyst that can be used for visible-light applications. Combining BiVO_4 with BiOI is also possible as $\text{BiVO}_4/\text{BiOI}$ heterojunction based nanoparticles are used to remove dyes. The heterostructure based $\text{BiVO}_4/\text{BiOI}$ nanoparticles shows improved PEC activity compared to pristine BiVO_4 and BiOI due to enhanced charge separation efficiency (He et al., 2016; Ni et al., 2018). Only one application of $\text{BiVO}_4/\text{BiOI}$ photoanode is reported in literature for the degradation of pharmaceuticals (Orimolade et al., 2019a), however, the concentration of pharmaceuticals was 10 mg L^{-1} , which is much higher than actual concentration of OMPs present in the aquatic environment (Golovko et al., 2020). At lower concentrations ($< 100 \mu\text{g L}^{-1}$) the removal kinetics of organic micro-pollutants would be different as there will be chances of lack of diffusion of organic molecules from bulk solution to the surface of the photoanode. To the best of our knowledge and based on a literature review (Orimolade and Arotiba, 2020b), there is a lack of knowledge regarding the use of BiVO_4 and $\text{BiVO}_4/\text{BiOI}$ photoanode for the removal of organic micro-pollutants in the concentration range of $0\text{--}100 \mu\text{g L}^{-1}$.

Acetaminophen (ACT) belongs to the non-steroidal anti-inflammatory drugs (NSAIDs) category that can be purchased as over the counter (OTC) drug without any specific prescription (Sajid et al., 2022). Due to the excessive use of ACT for pain and fever reduction (Chowdhury et al., 2021), it is one of the most commonly found OMP in wastewater, surface water and drinking water (Phong Vo et al., 2019). Eco-toxic effects of ACT and its transformation products on aquatic and human life have been widely investigated and now ACT is recognized as an environmental and human health concern (López Zavala et al., 2020). Conventional WWTPs are unable to completely remove ACT from the influent and a concentration between 0 and $20 \mu\text{g L}^{-1}$ is still present in the WWTPs effluent in many European countries (Lee et al., 2020). Electrochemical AOP (eAOP) has been widely employed to remove ACT from secondary effluents of WWTPs and simulated wastewater within the range of 1–10 mg L^{-1} (Ouarda, 2020). However, there is a lack of information available on the removal kinetics of ACT at lower concentrations ($< 100 \mu\text{g L}^{-1}$) using photo-electrocatalysis (PEC).

The objective of this study was to successfully fabricate a visible light driven heterojunction $\text{BiVO}_4/\text{BiOI}$ photoanode and to employ it for ACT ($40 \mu\text{g L}^{-1}$) removal in demineralized water. Removal kinetics of ACT by using the $\text{BiVO}_4/\text{BiOI}$ photoanode was also compared with pristine BiVO_4 and BiOI photoanodes. BiVO_4 , BiOI and $\text{BiVO}_4/\text{BiOI}$ photoanodes were fabricated by electrodeposition. Fabricated photoanodes were characterized by using structural, morphological, optical and optoelectronic characterization techniques to analyse and confirm the formation of heterojunction between BiVO_4 and BiOI . Lastly, the fabricated photoanodes were used to remove ACT in demineralized water in a three electrode PEC set-up. Quenching experiments were also performed by using methanol and p-benzoquinone (p-BZQ) to evaluate the role of reactive species ($\bullet\text{OH}$ and $\bullet\text{O}_2^-$) in $\text{BiVO}_4/\text{BiOI}$ photoanode based ACT removal.

2. Materials and methods

Three different kinds of photoanodes (BiOI , BiVO_4 and $\text{BiVO}_4/\text{BiOI}$) were prepared in the first stage and their fabrication processes are described below.

2.1. Fabrication of BiOI photoanode

As previously reported, electrodeposition (Kim and Choi, 2014; Orimolade and Arotiba, 2020c) with minor adjustments was used to

deposit BiOI on fluorine doped tin oxide (FTO) glass (40 mm × 40 mm × 2.2 mm). To prepare the electrolyte for electrodeposition, 0.04 M bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was added to 50 mL of 0.4 M potassium iodide (KI) solution and the pH was adjusted to 1.5–1.6 by using 1 M HNO_3 . This solution was mixed with 20 mL of ethanol (100%) containing 0.23 M p-benzoquinone and sonicated afterwards for 10–15 min. To electrodeposit the BiOI layer on the FTO glass, a cathodic bias of -0.2 V was applied for 5 min to the working electrode in a three electrode electrochemical cell. FTO glass, Ag/AgCl (3.0 M KCl) electrode and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively. After 5 min the working electrode was taken out from the cell and was rinsed with de-ionized water. After drying, a bright red coloured BiOI photoanode (shown in [supplementary Fig. 2](#)) was stored for further use.

2.2. Preparation of BiVO_4 photoanode

A BiVO_4 photoanode was prepared by converting the BiOI layer to BiVO_4 . First the BiOI layer on the surface of FTO glass (40 mm × 40 mm × 2.2 mm) was electrodeposited in the same way as described in the above section (2.1). To convert the BiOI layer to BiVO_4 a 0.15–0.2 mL of Dimethyl Sulfoxide (DMSO) solution containing 0.2 M Vanadyl-Acetylacetonate was drop casted on the BiOI layer. Then, the electrode was placed in a furnace for annealing treatment at 450°C for 2 h (ramping rate at $5^\circ\text{C}/\text{min}$). After annealing treatment, the electrode was taken from the furnace and as a last step the electrode was soaked in 1.0 M NaOH for 15 min under gentle stirring to remove the excess vanadium oxide (V_2O_5). After removing excess V_2O_5 , the bright yellow coloured electrode (shown in [supplementary Fig. 2](#)) was kept in a dry place under normal atmosphere for further use.

2.3. Fabrication of $\text{BiVO}_4/\text{BiOI}$ heterojunction photoanode

To fabricate a heterojunction photoanode, first BiVO_4 photoanode was fabricated in the same way as described in section 2.2. To electrodeposit a BiOI layer on top of the BiVO_4 photoanode same procedure was followed as described in section 2.1. The only change was that the BiVO_4 photoanode replaced FTO as the working electrode in the three electrode electrochemical set-up. After the electrodeposition process, the $\text{BiVO}_4/\text{BiOI}$ photoanode was washed with deionized water and after drying the $\text{BiVO}_4/\text{BiOI}$ photoanode (shown in [supplementary Fig. 2](#)) was stored in a dry place under normal atmosphere for further use.

[Fig. 1](#) in the supplementary information explains why 5 min was selected as the deposition time for the fabrication of the BiVO_4 photoanode and for the deposition of BiOI on the BiVO_4 photoanode.

2.4. Structural and morphological characterization

Morphological and micro/nano-structure analysis of fabricated photoanodes was carried out by using field emission scanning electron microscopy (SEM) (FEI, Quanta F650) coupled with an Inca 250 SSD XMax20 detector for energy-dispersive X-ray spectrometer (EDS) analysis. The degree of crystallinity and purity of the photoanodes were determined with X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation within a range of $2\theta = 10^\circ$ – 130° , a step size of 0.040° 2θ , and a counting time of 2 s per step. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Thermo Fisher K-Alpha surface analysis machine (Thermo Fisher Scientific, USA).

2.5. Optical and opto-electronic characterization

Optical properties of fabricated photoanodes were studied between 300 and 700 nm (5 nm step size) by using diffusive reflectance UV–vis spectroscopy (The LAMBDA 1050+ UV/Vis/NIR spectrophotometer, UV Winlab software). Incident photon-to-electron conversion efficiency (IPCE) was also measured between 280 and 700 nm by using a customized incident photon to current conversion efficiency (IPCE) set-up under 1 sun illumination (AM 1.5 standard conditions). Each IPCE measurement was carried out by using the $\text{BiVO}_4/\text{BiOI}$, BiVO_4 and BiOI photoanode each time as working electrode at 1 V (external bias) and a platinum wire as the counter electrode. $40\ \mu\text{g L}^{-1}$ ACT dissolved in 0.1 M Na_2SO_4 solution was used as electrolyte for IPCE measurements. Linear sweep voltammetry (LSV) was carried out in a three electrode arrangement between -0.2 and 1.5 V (vs Ag/AgCl) at a scan rate of $100\ \text{mV s}^{-1}$ in 0.1 M Na_2SO_4 .

2.6. Photo-electrocatalytic (PEC) experiments

PEC based removal of ACT by using the prepared photoanodes was carried out by using Autolab potentiostat (PGSTAT128 N) in three electrode configuration set-up. A quartz reactor cell containing three electrodes and 167 mL of electrolyte solution was used for the PEC removal experiments. 0.1 M Na_2SO_4 containing $40\ \mu\text{g L}^{-1}$ ACT having a pH of 6.8 was used as electrolyte for the removal experiments and demineralized water was used for the preparation of the electrolyte. Fabricated photoanodes, Ag/AgCl (3.0 M KCl) electrode and graphite plate (40 × 40 mm) were used as working electrode, reference electrode and counter electrode, respectively. A constant voltage of 1 V vs Ag/AgCl was applied during the removal experiment to minimize the rate of recombination in the fabricated photoanodes. Solar simulator SUNTEST XXL + having three air cooled 1700 W Xenon lamps emitting 1 sun

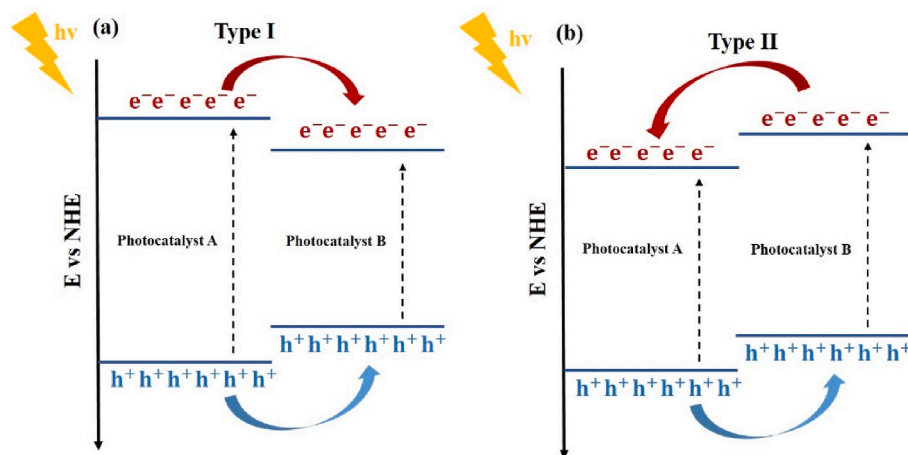


Fig. 1. Illustration showing the transfer of photogenerated holes and electrons in type I and type II heterojunction after the interaction of incoming solar photons with the BiVO_4 heterojunction photoanode.

illumination spectra was used as light source. The intensity of emitted light between 300 and 400 nm was calibrated to 60 W/m² and the distance between the light source and the photoanode was 13 cm. Each experiment ran for 5 h and samples were taken at an interval of 1 h for the analysis of ACT. Reusability experiments with BiVO₄/BiOI photoanode were performed by using same photoanode for three consecutive removal experiments of each 5 h experiment. Between successive experiments the photoanode was rinsed with demineralized water to remove any adsorbed acetaminophen on the photoanode.

2.6.1. Quenching experiments

Quenching experiments were carried out in a similar way as the removal experiments described in section 2.6, except the addition of quenching agents in the electrolyte. To quench the [•]OH reactive species 5 mM methanol was added in the electrolyte because methanol has a high reaction rate constant of $9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ with [•]OH (Liang and Su, 2009), whereas in a separate experiment 5 mM p-BZQ (Orimolade and Arotiba, 2020c) was added in the electrolyte to quench [•]O₂⁻. Each experiment ran for 5 h and samples were taken at an interval of 1 h for the quantification of ACT.

2.7. Analytical measurement of ACT

The concentration of ACT in the samples was measured by using liquid chromatography combined with tandem triple-quadrupole mass spectrometry (LC-MS). Acquity UPLC BEH C18 column from Waters was used in LC-MS to measure ACT in the samples. All Samples were first filtered with 0.2 μm glass fibre filters (GF-75, ADVANTEC®, Japan) and then 495 μL of filtered sample solution and 5 μL of internal standard (ACT-ring D4) calibration solution were added to the LC-MS sample vials. After mixing, the quantification of the target compound (ACT) in the samples was accomplished by the LC-MS device. Based on the concentration values of ACT, removal efficiency of each photoanode was calculated by using the following equation:

$$\text{Removal efficiency (\%)} = \left(1 - \frac{C_0}{C_t}\right) \times 100$$

where C₀ = Initial concentration at time t = 0 and C_t = Concentration at any time

3. Results and discussion

3.1. Structure and morphology of photoanodes

Fig. 2 shows the X-ray diffractograms of BiVO₄, BiOI and BiVO₄/BiOI photoanodes. In the case of BiVO₄, the characteristic peaks at 18.8°, 19.1°, 29.03°, 30.64°, 34.63°, 35.32°, 39.95°, 42.5°, 46.83°, 47.39°, 51.54°, 59.7° and 60.08° corresponded to monoclinic scheelite phase of BiVO₄ (JCPDS no. 75–1866). These characteristic peaks were in accordance with previous studies (Orimolade and Arotiba, 2020c; Orimolade et al., 2019a) indexed as (110), (011), (121), (040), (200), (002), (211), (015), (240), (042), (161), (321) and (123), respectively (Liu et al., 2018). Main peaks of BiOI at 30.01°, 32.19°, 45.89°, 51.95° and 55.65° are previously reported in literature (Xiao et al., 2018) and were indexed as (102), (110), (200), (114) and (212), respectively (Tang et al., 2019). The XRD pattern of BiVO₄/BiOI photoanode contains the characteristic peaks of both monoclinic scheelite BiVO₄ and BiOI (Ni et al., 2018), which confirms the successful deposition of BiOI on top of the BiVO₄ layer.

The scanning electron microscopy (SEM) images in Fig. 3 show the surface morphology of pristine BiVO₄ and heterojunction BiVO₄/BiOI photoanode. Fig. 3a shows homogenous distribution of BiVO₄ particles over FTO substrate after electrodeposition. The fabrication process proved to be effective in producing BiVO₄ particles of similar shape and size. Fig. 3b shows the magnified image of BiVO₄ particles that were

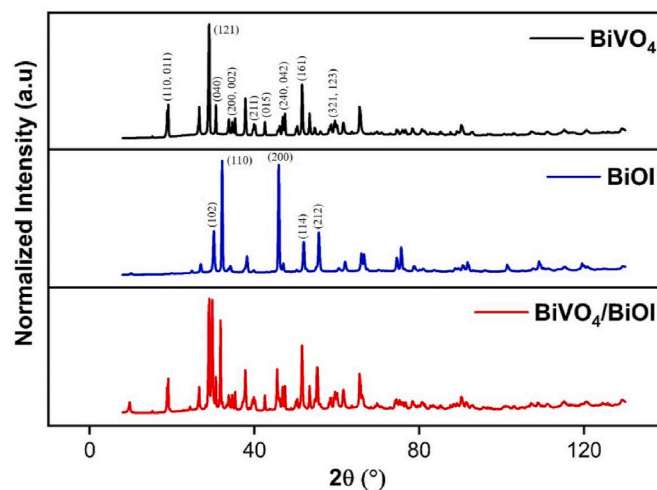
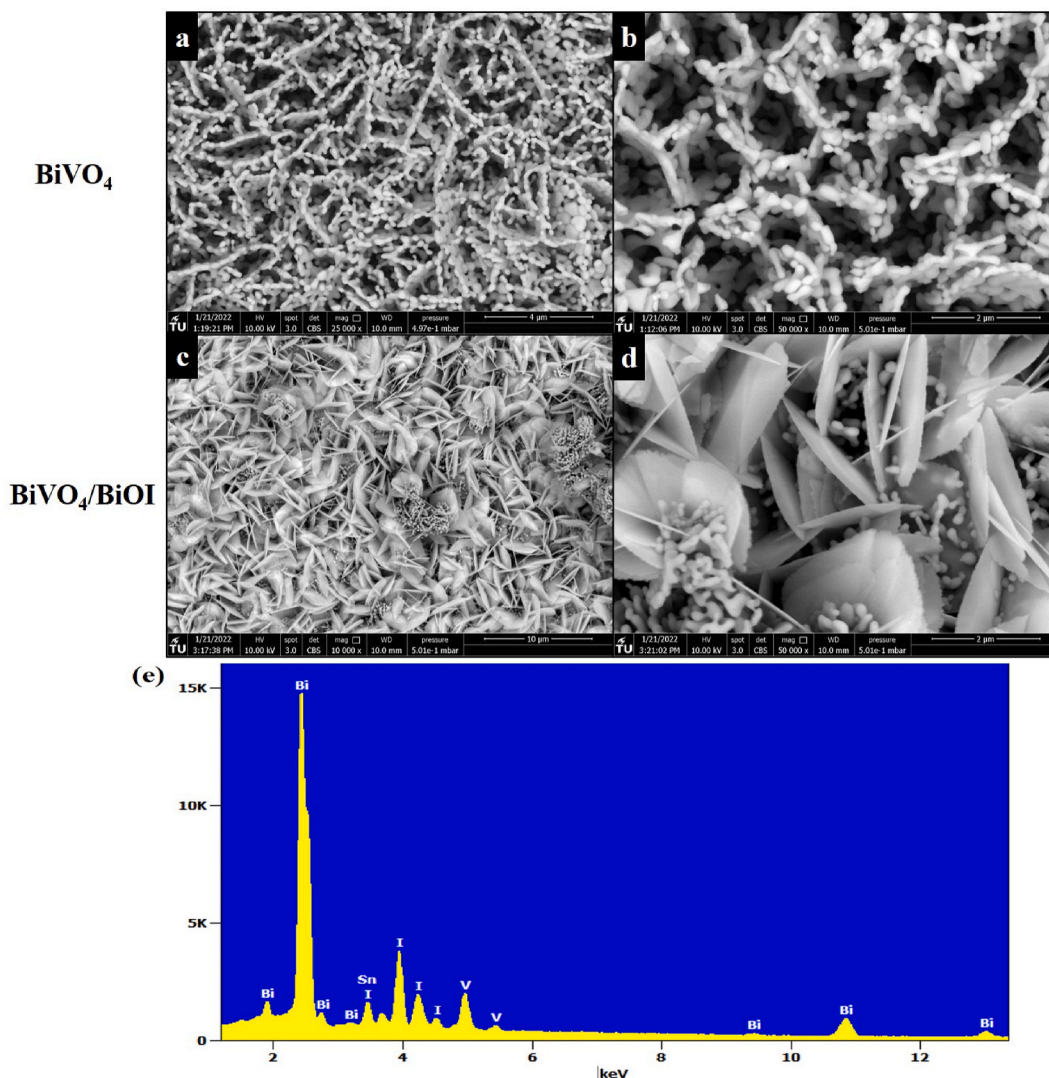


Fig. 2. XRD patterns of BiVO₄, BiOI and BiVO₄/BiOI photoanodes showing indexed characteristic peaks.

inter-connected to form a branched network. This branched network could facilitate an effective charge transfer at the interface of heterojunction. Fig. 3c shows the surface morphology of the BiVO₄/BiOI photoanode, which exhibited a homogeneous deposition of needle-like BiOI particles on top of the BiVO₄ layer. The magnified image in Fig. 3d shows the interaction of needle-like BiOI particles with the branched BiVO₄ particles. The interaction shows that there was an interfacial contact between the photocatalytic layers that will hold the potential to enhance the charge separation in the photoanode (McDonald and Choi, 2012). The energy dispersive X-Ray (EDX) spectrum shown in 3 (e) gives the compositional analysis of the heterojunction photoanode, and it consisted of only Bi, I, O and V. The element tin (Sn) in the EDX spectra came from the fluorine doped tin oxide (FTO) substrate. The EDX result also confirmed the purity of the deposited photocatalytic layers without any major impurity element present.

X-Ray photoelectron spectroscopy (XPS) survey results are shown in supplementary Fig. 3. The survey confirmed that only Bi, V, O, I, and C were present in the photoanodes and showed distinct peaks at their respective binding energies. The survey of BiVO₄/BiOI in particular confirmed the co-existence of Bi, V, O, I and C, which indicated the formation of a heterojunction. Carbon (C) is considered as impurity element and came from the atmosphere during the measurement. The de-convoluted high resolution spectra of elements (Bi, V, I, O) present in the photoanodes are also shown in Fig. 4. Starting with the Bi, two asymmetric peaks with different binding energies corresponded to two different spin orbit splitting states (4f_{5/2} & 4f_{7/2}) of Bi4f. The peaks at 162.85, 157.48 eV in BiVO₄ and 163.98, 158.58 eV in BiOI were related to Bi4f_{5/2} and Bi4f_{7/2} respectively (Meng et al., 2020; Ni et al., 2018, p. 4). These characteristic peaks of Bi4f also suggest that Bi was present in the form of Bi³⁺ in the crystal lattice. The peak positions of Bi4f_{5/2} and Bi4f_{7/2} in BiVO₄/BiOI photoanode were at 163.58 and 158.28 eV, respectively. The slight increase in binding energies of Bi4f in BiVO₄/BiOI photoanode compared to pristine BiVO₄ could be due to a loss of surface bound oxygen and hydroxyl groups, which decreased the electron concentration around Bi (Ni et al., 2018, p. 4). Vanadium was also present in two different spin orbital states as V2p_{1/2} and V2p_{3/2} in both BiVO₄ and BiVO₄/BiOI photoanode. Two distinct peaks at 528.28 and 515.08 eV corresponded to V2p_{1/2} and V2p_{3/2} in BiVO₄, whereas the peaks at 529.08 and 515.98 eV were related to V2p_{1/2} and V2p_{3/2} in BiVO₄/BiOI photoanode. The peak positions of V2p_{1/2} and V2p_{3/2} suggest that V was present as V⁵⁺ in both photoanodes (Zhang et al., 2019; Fang et al., 2017). Two relatively sharp peaks at 629.98 and 618.48 eV are attributed to I3d_{3/2} and I3d_{5/2} in BiOI electrode. The peaks at 629.68 and 618.18 eV corresponded to I3d_{3/2} and I3d_{5/2}, respectively, in the



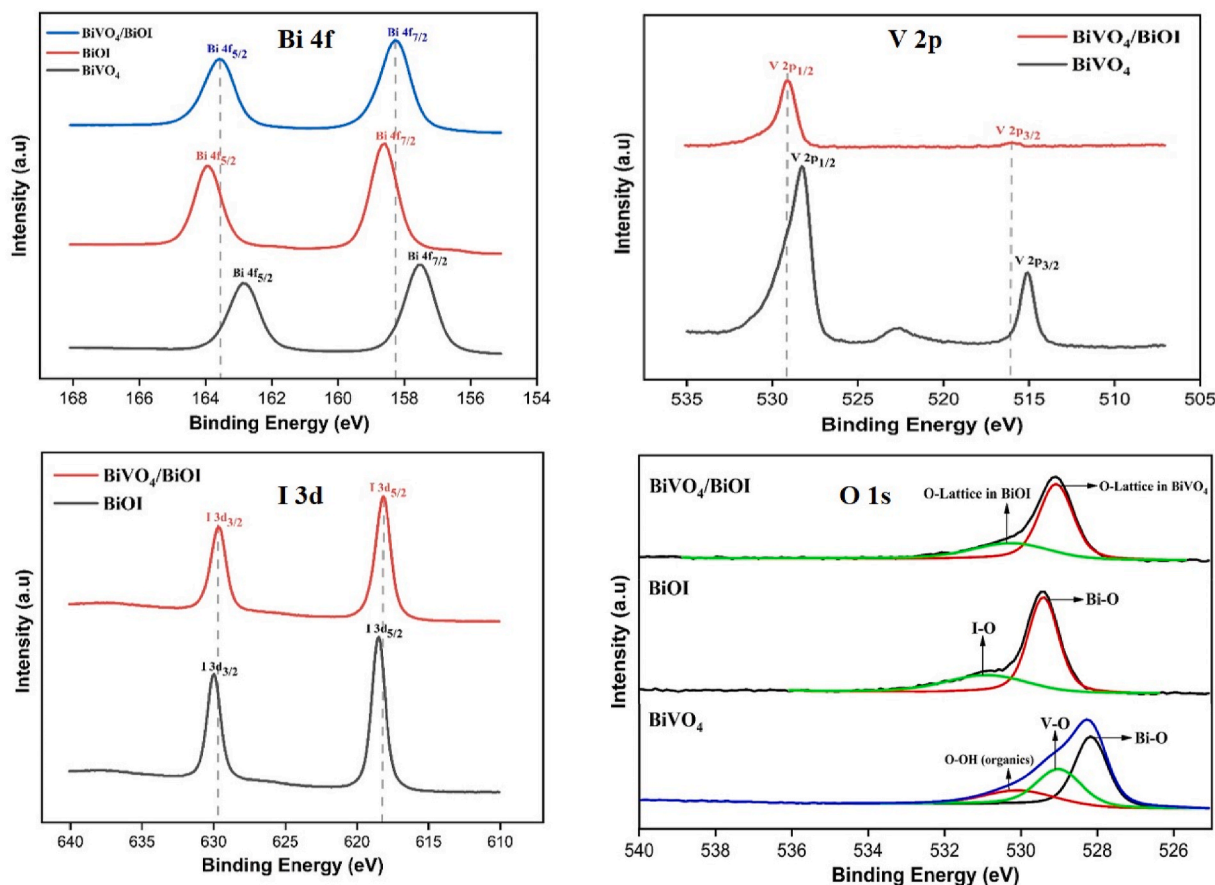


Fig. 4. De-convoluted and high resolution elemental XPS spectra of Bi4f, V2p, I3d and O1s showing different orbital states, bonding environment and their respective binding energies.

as BiVO_4 is 1 (Ju et al., 2016). Therefore, a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) was made as shown in [supplementary Fig. 4](#) to estimate the band gap energy, which was 2.49 eV. Similarly, BiOI is an indirect optical transition semiconductor whose n value is 4 (Xiang et al., 2016). After substituting the value of $n = 4$ in the Tauc equation a plot between $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) is made from which a band gap energy of 1.80 eV was obtained. The calculated values of band gap energies for BiVO_4 and BiOI photoanodes were very close to previously reported values in the literature (Xiang et al., 2016; Orimolade et al., 2019a). UV-vis absorbance results clearly showed that the absorbance region of $\text{BiVO}_4/\text{BiOI}$ photoanode was broader compared to BiVO_4 and BiOI, which confirmed the successful formation of a heterojunction.

Calculated band gap energies (E_g) were used to calculate the valence band (E_{VB}) and conduction band (E_{CB}) potentials of BiVO_4 and BiOI. Following equations were used to calculate E_{VB} and E_{CB} (Orimolade et al., 2019a, p. 4).

$$E_{CB} = X - E_C - 0.5E_g \quad (2)$$

$$E_{VB} = E_g + E_{CB} \quad (3)$$

wherein X is the geometric mean of the absolute electronegativities of all the constituent atoms present in the photocatalyst. The value of X for BiVO_4 is 6.04 eV, whereas for BiOI it is 6.10 eV (Pearson, 1988). E_C corresponds to the energy of free electrons with respect to hydrogen scale (NHE) and its value is 4.50 eV. E_g corresponds to the band gap energies of the respective photoanodes that were calculated using Tauc plots. By substituting the values of X , E_C and E_g in the above equations, the band edge potentials of BiVO_4 and BiOI were calculated. For BiOI the values of E_{CB} and E_{VB} were 0.7 and 2.5 eV, respectively, whereas for BiVO_4 the values of E_{CB} and E_{VB} were 0.29 and 2.78 eV, respectively.

These band edge potential values show that the heterojunction that was formed between BiVO_4 and BiOI was of type I. In type I heterojunction both photogenerated charge carriers are transferred to the electrode-electrolyte interface (Orimolade and Arotiba, 2020b) as shown in [Fig. 5b](#). One intrinsic drawback of type I heterojunction is that there is a high chance of recombination if the photogenerated charge carriers are not consumed at the electrode electrolyte interface (Orimolade, 2020b). Application of a positive bias (applied potential >0) in type I heterojunction enhances the charge separation efficiency by creating an electric field at the heterojunction that pulls apart electrons and holes (Orimolade and Arotiba, 2020a; Li et al., 2022). Furthermore, in PEC based water treatment processes, the photogenerated holes and electrons are used to produce $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals which oxidize the organic pollutants (Orimolade and Arotiba, 2020c). Therefore, chances of recombination are reduced if photogenerated holes and electrons are consumed for the generation of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$.

Linear sweep voltammetry (LSV) was carried out to study the effect of applying external voltage on the photocurrent generated by the photoanodes. In [Fig. 5c](#), as expected the photocurrent generated by $\text{BiVO}_4/\text{BiOI}$ photoanode in the presence of simulated solar light was higher compared to pristine BiVO_4 and BiOI. In illuminated conditions, the increase in the application of external voltage yielded a positive impact on the photo-current of all three types of photoanodes, confirming that the application of external bias reduced the rate of recombination. 1.0 V was chosen as the optimum potential to be applied for the PEC removal of ACT because at this potential sufficient current was generated. Increase in photocurrent of $\text{BiVO}_4/\text{BiOI}$ photoanode implied that more charges (electrons and holes) were available at the electrode-electrolyte interface for the generation of reactive oxygen

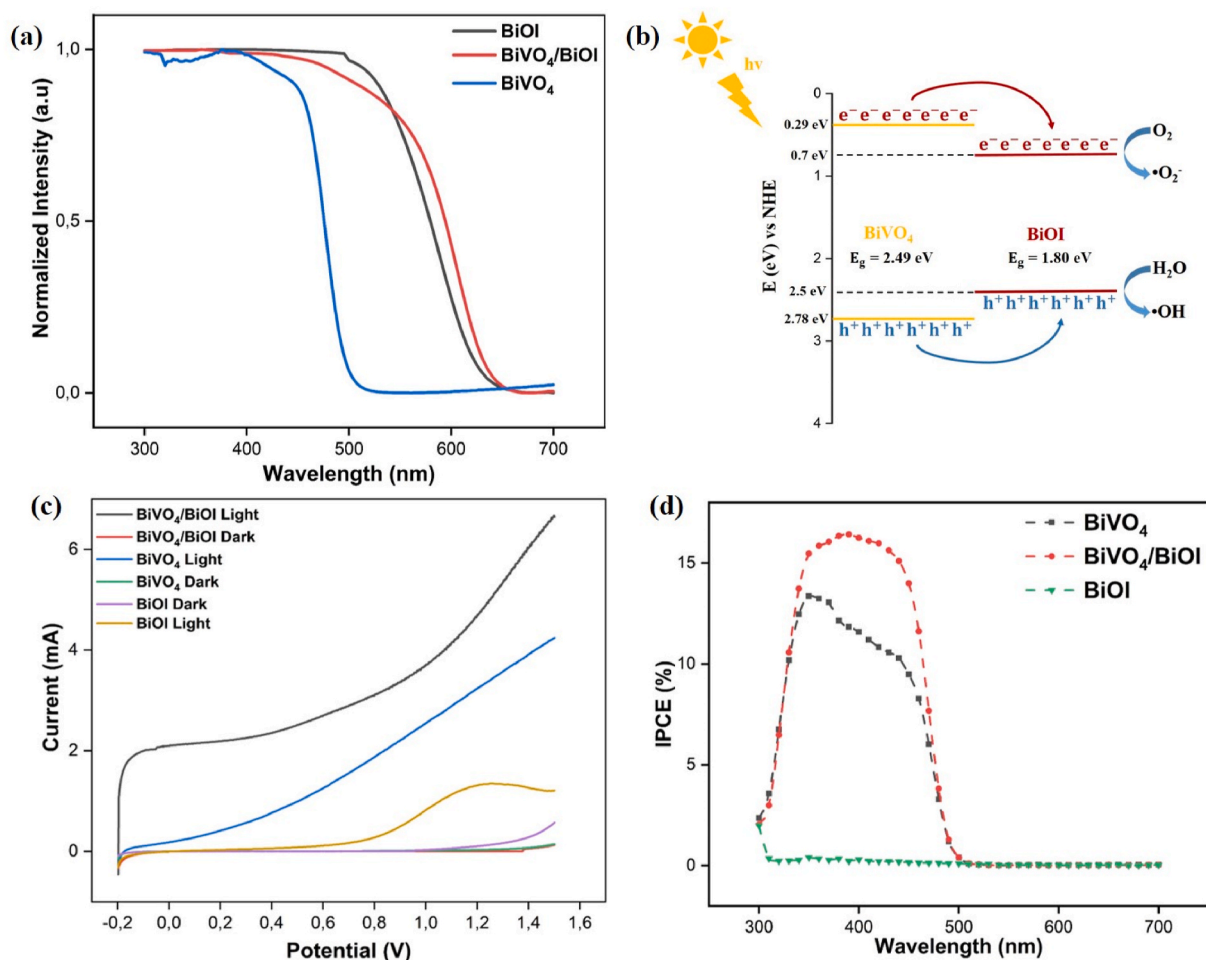


Fig. 5. (a) UV–Visible diffusive reflectance spectra of BiVO₄, BiOI and BiVO₄/BiOI photoanodes showing the absorbance range (b) Illustration of photogenerated holes and electrons for the generation of •OH and •O₂⁻ radicals after the interaction of solar photons with BiVO₄/BiOI photoanode (c) LSV curves for BiVO₄, BiOI and BiVO₄/BiOI photoanodes under dark and illuminated conditions performed from -0.2 to 1.5 V at 100 mV s⁻¹ scan rate (d) IPCE plots for BiVO₄, BiOI and BiVO₄/BiOI photoanodes under 1 sun illumination at 1 V external bias vs platinum wire as counter electrode.

species (ROS). As a result, the formation of heterojunction will increase the removal kinetics of ACT in demineralized water because of the increased in-situ generation of •OH and •O₂⁻. There is negligible current in the absence of light (dark), which means that applying an external voltage to the photoanodes in the absence of light will be of no use for the removal of ACT.

Incident photon to current conversion efficiency (IPCE) measurements were performed to study the quantum efficiency of fabricated photoanodes. Quantum efficiency measures the amount of electrons generated in response to the incident photons absorbed by the photoanode. Fig. 5d shows the IPCE plots of BiOI, BiVO₄ and BiVO₄/BiOI photoanodes. Fig. 5d clearly shows that BiVO₄ and heterojunction photoanode exhibits high incident photon to current conversion efficiency in UV–visible range. In case of BiVO₄, the maximum IPCE yield was 13% and it occurred at 350 nm (λ_{\max}), whereas after the formation of heterojunction the maximum IPCE yield increased to 16% at λ_{\max} = 390 nm. Pristine BiOI photoanode showed negligible IPCE yield which corresponded to its intrinsic high rate of recombination. Overall, the IPCE result illustrates that the formation of heterojunction not only increased the incident photon to current conversion efficiency by 23% but it also shifted the λ_{\max} further in the visible region. The IPCE measurement also gives the value of short circuit photo-current (J_{sc}), which corresponds to the maximum current that can be drawn from the photoanode (Gong et al., 2016). The BiVO₄ photoanode yielded a J_{sc} of 4.88 A m⁻², whereas BiVO₄/BiOI photoanode yielded a J_{sc} of 7.05 A/m². This

increase in IPCE and J_{sc} values as compared to BiVO₄ and BiOI was attributed to the interface of BiVO₄ and BiOI photocatalysts that increased the charge separation efficiency and thus reduced the rate of recombination in the heterojunction photoanode.

3.3. Photoelectrocatalytic removal of ACT

Fig. 6a shows the normalized decrease in concentration of ACT in demineralized water by using BiVO₄, BiOI and BiVO₄/BiOI photoanodes at an applied external voltage of 1 V vs Ag/AgCl (reference electrode). Direct irradiation with simulated sunlight from the solar simulator (photolysis) of the ACT solution had limited effect as it only removed 7% ACT in 5 h. PEC based removal of ACT by using BiOI photoanode showed 24% removal in 5 h. Fig. 6a shows that formation of heterojunction had a positive impact on the ACT removal. Although both BiVO₄ and BiVO₄/BiOI removed 100% ACT after 5 h, the evolution of the removal efficiency is different. Fig. 6b provides more detailed insight on the removal efficiency of ACT on hourly basis. Fig. 6b shows that BiVO₄/BiOI photoanode removed more than half of the ACT within the first hour, which was a 22% increase in removal efficiency compared to BiVO₄. This increasing trend in the removal efficiency continued till 2 h and after that the removal efficiency of both photoanodes were similar. It can be observed in Fig. 6b that the removal efficiency increased with time, however, its rate of increment decreased with time. This was explained by the decrease in ACT concentration in the bulk solution, therefore, the

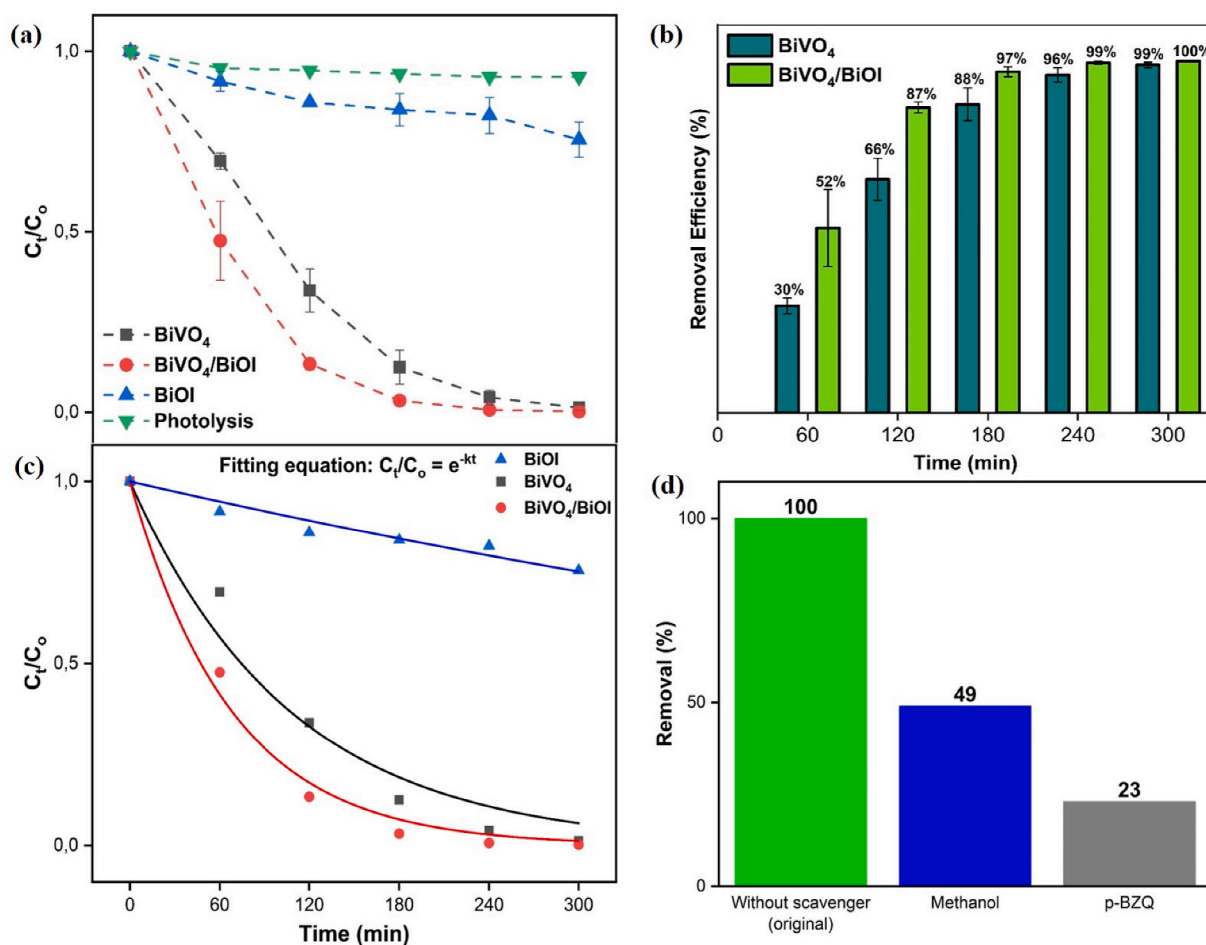


Fig. 6. (a) Normalized decrease in concentration of ACT during 5 h of removal experiment by using the fabricated photoanodes at an external bias of 1 V vs Ag/AgCl (b) Comparison of removal efficiency of BiVO₄ and BiVO₄/BiOI photoanode on hourly basis (c) Determination of first order rate coefficients of BiVO₄, BiOI and BiVO₄/BiOI photoanodes during 5 h of removal experiments (d) Removal efficiency of BiVO₄/BiOI photoanode in the presence of quenching agent. 5 mM methanol was used to quench $\cdot\text{OH}$ radicals and 5 mM p-BZQ was used to quench $\cdot\text{O}_2^-$ radicals.

reaction became partially diffusion controlled in which the diffusion of ACT molecules from bulk towards the surface of the photoanode became slower. The diffusion of ACT molecules to the surface is important because the oxidation reaction takes place within the vicinity of photoanode-electrolyte interface due to the short lifetime of ROS ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals) (Attri et al., 2015). According to previous studies related to ACT degradation suggest that three initial oxidation/hydroxylation reactions compete with each other (Vogna et al., 2002; Moctezuma et al., 2012). In these reactions the reactive species ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals) attack the aromatic ring of ACT to form ortho-, para- or meta-hydroxylation products of ACT (Vogna et al., 2002). Nuclear magnetic resonance (NMR) studies have shown that the meta-position is relatively favourable for further degradation of ACT (Moctezuma et al., 2012), however, the complete mechanism of ACT degradation cannot be proposed in this study because the intermediates/transformation products of ACT were not analysed.

Kinetic plots for BiVO₄, BiOI and BiVO₄/BiOI are shown in Fig. 6c. Because the normalized removal followed a classical first order reaction, first order rate equation ($C_t/C_0 = e^{-k/t}$) was used to determine the rate coefficients of BiVO₄, BiOI and BiVO₄/BiOI photoanodes. As expected, the rate coefficient of BiVO₄/BiOI photoanode (shown in Table 1) compared to BiVO₄ is 57% higher. The overall superior performance of BiVO₄/BiOI in removing ACT from demineralized water is attributed to the formation of heterojunction that facilitated the charge separation efficiency. Similarly, the applied external voltage of 1 V (vs Ag/AgCl) further decreased the rate of recombination by diverting the electrons

from the conduction band to the external electrical circuit.

The removal rate coefficient of the BiVO₄/BiOI photoanode given in Table 1 is similar or higher than the rate coefficients reported in literature that applied BiVO₄ based photoanodes for the removal of different pharmaceuticals such as phenol (20 mg L⁻¹; $k = 0.5 \times 10^{-2} \text{ min}^{-1}$) (Bennani et al., 2016), bisphenol A (10 mg L⁻¹; $k = 4.1 \times 10^{-2} \text{ min}^{-1}$) (Shao et al., 2020b), norfloxacin (10 mg L⁻¹; $k = 0.268 \times 10^{-2} \text{ min}^{-1}$) (Du et al., 2019, p. 3), tetracycline hydrochloride (10 mg L⁻¹; $k = 0.51 \times 10^{-2} \text{ min}^{-1}$) (Lu et al., 2019) and dyes such as methyl orange (10 mg L⁻¹; $k = 2.9 \times 10^{-2} \text{ min}^{-1}$) (Bacha et al., 2019) and rhodamine B (10 mg L⁻¹; $k = 0.92 \times 10^{-2} \text{ min}^{-1}$) (Orimolade et al., 2019b). Although, these studies report first order removal kinetics and the pollutant concentrations vary between 8 and 20 mg L⁻¹, the reported rate coefficients are not drastically higher than those of the BiVO₄/BiOI photoanode given in Table 1. In terms of applied external potential (electrical energy input) most studies used between 1 and 2 V vs Ag/AgCl as an external bias for an average reaction time of around 2.5 h with approximately 80%

Table 1

First order rate coefficients of BiOI, BiVO₄ and BiVO₄/BiOI photoanodes after 5 h of illumination.

Photoanode	Rate coefficient (min ⁻¹)	R ²
BiOI	9.50×10^{-4}	0.928
BiVO ₄	9.32×10^{-3}	0.967
BiVO ₄ /BiOI	1.46×10^{-2}	0.928

removal of organic compounds from aqueous solution (Bennani et al., 2016; Bacha et al., 2019; Orimolade et al., 2020; Orimolade and Arotiba, 2020c; Wang et al., 2020). In this study PEC based ACT removal showed faster removal kinetics than in most of the studies reported in literature with a similar electrical energy input.

Quenching studies are normally performed to gain information about the main oxidants involved in the removal reaction of organic pollutants (Orimolade and Arotiba, 2020c). According to previous studies (Orimolade and Arotiba, 2020c), hydroxyl radicals ($\cdot\text{OH}$) and super oxide radicals ($\cdot\text{O}_2^-$) are the two main oxidising species responsible for the removal of organic micro-pollutants. Quenching experiments were carried out for $\text{BiVO}_4/\text{BiOI}$ photoanode by using methanol and p-benzoquinone (p-BZQ) to quench $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, respectively, in the reaction solution of ACT. The results of the quenching experiments after 5 h of illumination are shown in Fig. 6d. The figure shows that the removal efficiency of $\text{BiVO}_4/\text{BiOI}$ photoanode in the presence of both quenching agents was lower than without quenching agents, which confirmed the effect of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals on the removal of ACT.

Removal in the presence of methanol was higher than in the presence of p-BZQ, which indicates that the $\cdot\text{O}_2^-$ was the main reactive specie in our research, because the $\text{BiVO}_4/\text{BiOI}$ photoanode only removed 23% ACT in the presence of p-BZQ. Overall, the results of the quenching study suggest that both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ were responsible for the ACT removal as the removal efficiency also decreased in the presence of methanol. This joint attack of both reactive species was due to the formation of type I heterojunction as mentioned in section 3.2, where both reactive species ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) were generated within the vicinity of photoanode surface. The finding of the quenching study is in accordance with the literature where researchers have reported different photocatalysts for the in-situ oxidation of organic compounds and dyes through $\cdot\text{O}_2^-$ as the main oxidant (Li et al., 2011; Byzyski et al., 2018). The results of reusability experiments are shown in the supplementary information. Fig. 5 in the supplementary information shows the removal efficiency of a $\text{BiVO}_4/\text{BiOI}$ photoanode that was used for 3 consecutive removal experiments of each 5 h. The removal efficiency after the third run dropped down from 100% to 74%, meaning a decrease of 26% after 15 h of using the same photoanode. This drop in efficiency could be because of the adsorption of ACT molecules within the surface pores of $\text{BiVO}_4/\text{BiOI}$ photoanode that reduced the available surface area for the ROS generation.

In summary, the formation of heterojunction enhanced the kinetics of the ACT removal as shown in Fig. 6c and this enhancement was attributed to type I heterojunction that generated both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals at the photoanode-electrolyte interface. The generated $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals unselectively attacked the molecules of ACT to remove them from the electrolyte.

4. Conclusions

Successful fabrication of BiVO_4 , BiOI and $\text{BiVO}_4/\text{BiOI}$ photoanodes was achieved by using electrodeposition. Fabricated photoanodes were characterized by using structural, morphological, optical and optoelectronic characterization techniques. Successful and effective formation of $\text{BiVO}_4/\text{BiOI}$ heterojunction was confirmed with diffusive reflectance UV-Vis spectroscopy and IPCE characterization. Band edge potential calculations showed that a type I heterojunction was formed that enhanced the kinetics of ACT removal in demineralized water. BiOI , BiVO_4 and $\text{BiVO}_4/\text{BiOI}$ photoanodes showed removal efficiency of 24, 99 and 100%, respectively. Although the removal efficiency of BiVO_4 and $\text{BiVO}_4/\text{BiOI}$ after 5 h were almost the same, the first order rate coefficient of $\text{BiVO}_4/\text{BiOI}$ photoanode showed a 57% higher value as compared to BiVO_4 photoanode. Furthermore, the quenching study demonstrated that $\cdot\text{O}_2^-$ radicals were the main reactive species in the removal of ACT. In conclusion, our research demonstrated the successful formation of $\text{BiVO}_4/\text{BiOI}$ heterojunction photoanode that enhanced the

removal kinetics of ACT ($40 \mu\text{g L}^{-1}$) in demineralized water compared to BiVO_4 and BiOI photoanodes.

Author contributions statement

Agha Zeeshan Ali: Conceptualization, Methodology, Validation, Formal Analysis, Writing – original draft, Writing – review & editing, Visualization, Project administration, **Yiqian Wu:** Investigation, Validation, Data curation, **Yasmina-Doekhi Bennani:** Supervision, Writing – review & editing, **Henri Spanjers:** Supervision, Writing – review & editing, Funding acquisition, **Jan Peter van der Hoek:** Supervision, Writing – review & editing, Funding acquisition.

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.

Data availability

Data will be made available on request.

Acknowledgement

This research study was part of InnovEOX project that has received funding from the European Union's EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No 861369.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.138322>.

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