Degradation of a mixture of pharmaceuticals through photoelectrochemical oxidation

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1. Introduction

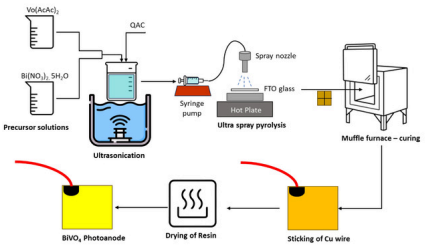
- Advanced oxidation (AOP)-based treatments have been widely employed, as they have the potential to remove organic micro pollutants (OMPs), from secondary-treated effluent.
- Photoelectrochemical oxidation (PEC) has garnered significant attention due to its combined advantages of photodegradation and electrochemical oxidation.
- However, challenges remain in addressing their photocurrent conversion efficiency, catalytic activity, and stability. These limitations can potentially be overcome through strategic surface modifications.

Objectives

- To enhance the photoelectrochemical activity of $BiVO_4$-based photoanodes for the degradation of pharmaceutical mixtures in secondary-treated wastewater. This enhancement is achieved by surface modification of the photoanodes using quaternary ammonium-based compounds (QACs), such as DADMAC C18.

2. Methodology

Figure 1: Fabrication of photoanode for PEC degradation study



3. Results & Discussion

Figure 2: X-ray diffraction (XRD) analysis of photoanodes

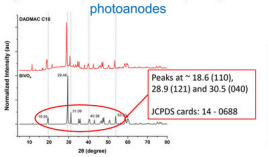


Figure 3: Scanning electron microscope (SEM) images

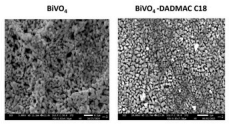


Table 1: List of pharmaceuticals used in this experiment (10 µg/L)

Pharmaceuticals	Application	Pharmaceuticals	Application	Pharmaceuticals	Application	Pharmaceuticals	Application
Carbamazepine	Anticonvulsant	Sulfamethoxazole	Antibiotic	Ketoprofen	NSAID	Caffeine	Stimulant
Diclofenac	NSAID	Propranolol	β-blocker	Metformin	Antidiabetic	Theophylline	Bronchodilator
Hydrochlorothiazide	Diuretic	Sotalol	β-blocker	Clofibric acid	Lipidlowering	Acetaminophen	Analgesic
Metoprolol	Beta-blocker	Trimethoprim	Antibiotic	Sulfadimethoxine	Antibiotic	Gabapentin	Anticonvulsant

Figure 4: Linear sweep voltammetry (LSV) of selected of photoanodes

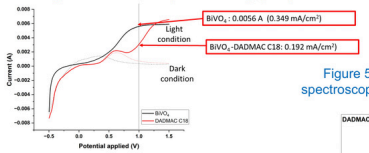


Figure 5: X-ray photoelectron spectroscopy (XPS) - Area under curve for O1S

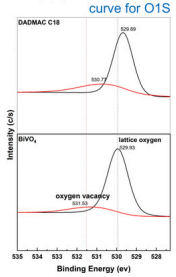


Figure 6: Scanning electron microscope (SEM) images of selected of photoanodes

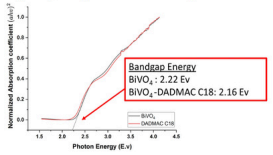
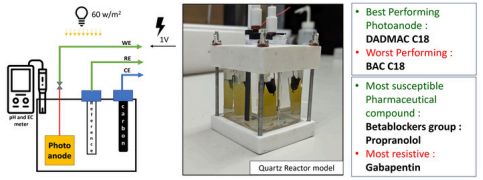
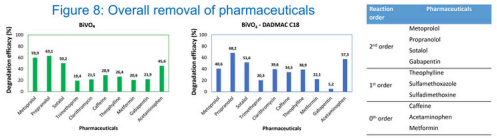


Figure 7: PEC oxidation reactor setup



- Best Performing Photoanode : **DADMAC C18**
- Worst Performing : **BAC C18**
- Most susceptible Pharmaceutical compound : **Betablockers group : Propranolol**
- Most resistive : **Gabapentin**

Figure 8: Overall removal of pharmaceuticals



Reaction order	Pharmaceuticals
2nd order	Metoprolol
	Propranolol
	Sotalol
	Gabapentin
1st order	Theophylline
	Sulfamethoxazole
	Sulfadimethoxine
0th order	Caffeine
	Acetaminophen
	Metformin

- XRD results (Figure 2) confirm monoclinic structure of $BiVO_4$.
- SEM analysis (Figure 3) confirms successful QAC incorporation while retaining of $BiVO_4$ original structure.
- LSV results shows (Figure 4) photo current generation under simulated light condition.
- XPS analysis (Figure 5) shows more oxygen vacancy for DADMAC C18.
- Electrodes absorb solar radiation under visible range (Figure 6).

- After analyzing the results, the DADMAC C18 variant exhibited a high removal for metoprolol (40.59%), propranolol (68.15%), sotalol (51.59%), and acetaminophen (57.28%).
- Among the compounds, propranolol exhibited the highest removal efficacy across all variants, with a peak removal of 68.15% (DADMAC C18) and an average removal of 62.5% with a deviation of only ± 7.3%.
- DADMAC C18 demonstrated a consistent degradation profile, ensuring uniform breakdown of pharmaceutical compounds over the entire 120-minute reaction period.

4. Conclusions and Future Work

- QAC-modified $BiVO_4$ was successfully synthesized; structural and chemical analysis validated its purity, stability, and readiness for PEC degradation applications. QAC based photoanodes also showed more oxygen vacancies.
- DADMAC C18-modified $BiVO_4$ performed best, though only slightly better than unmodified $BiVO_4$. Beta-blockers degraded easily, while gabapentin showed strong resistance.

Future Work: Pesticide and PFAS removal in the PEC system.

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Organic micropollutants such as pharmaceuticals pose significant environmental and public health risks. These contaminants not only contribute to the spread of antibiotic resistance but also disrupt aquatic ecosystems. Advanced oxidation processes are known to effectively degrade pharmaceuticals, and among these, photoelectrocatalysis (PEC) offers a promising method for removing contaminants present at trace levels (µg/L to ng/L). The focus of the presented study was to assess the influence of five quaternary ammonium compounds (QACs) on $BiVO_4$ photoanodes, modifying the structural properties and enhancing photoelectrocatalytic performance. The QAC-modified $BiVO_4$ photoanode variants were characterized using X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, UV-Vis spectroscopy, and linear sweep voltammetry. PEC degradation experiments were conducted using effluent, collected after secondary treatment, at a wastewater treatment plant, spiked with 10 selected pharmaceuticals at an initial concentration of 10 µg/L. The removal efficacy of the modified $BiVO_4$ photoanodes was evaluated under simulated solar irradiation. Among the tested variants, the photoanode modified with the alkyl trimethyl ammonium compound ATMAC C18 modified exhibited the most rapid degradation, with several pharmaceuticals removed within the first 15 minutes. However, dialkyl dimethyl ammonium compound DADMAC C18 modified photoanode was identified as the best-performing variant, with sulfamethoxazole emerging as the critical compound due to its longest half-life.

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