Photocatalytic degradation of Ofloxacin using Bare $BiVO_4$

A Dissertation

Submitted in the partial fulfilment of the Degree

Of

Master of Science (Chemistry)

By

Ishita

(302202016)

Under the guidance of

Dr. Raj Kumar Das

(Assistant Professor)

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Department of Chemistry and Biochemistry

Thapar Institute of Engineering and Technology

Patiala-147004, Punjab

DECLARATION

I, hereby declare that the dissertation entitled **"Photocatalytic degradation of Ofloxacin using Bare $BiVO_4$"** is a record of my own work carried out under the supervision of **Dr. Raj Kumar Das** from **Jan-July, 2024** being submitted in the partial fulfilment of the requirements for the award of the degree of **Master of Science in Chemistry to the Department of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala.** Furthermore, no other university has received any of this dissertation's work for the award of another degree or certification.

Signature of candidate

Ishita

(302202016)

Place: Patiala

Date: 26-07-2024

CERTIFICATE

This is to certify that the dissertation entitled **"Photocatalytic degradation of Ofloxacin using Bare $BiVO_4$"** being submitted by **Ishita** to the **Department of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala** in partial fulfilment of the requirements for the award of the degree of **Master of Science in Chemistry**, is an authentic record of the work carried out by the candidate under my/our guidance and supervision. She has fulfilled the requirements for the submission of this dissertation, which to my knowledge has reached the requisite standard.

The results embodied in the dissertation have not been submitted in part or whole to any other University or Institute for the award of any other degree or diploma.

Date: 26-07-2024

Place: Patiala

Signature

Dr. Raj Kumar Das

(Assistant Professor)

Department of Chemistry and Biochemistry

Thapar Institute of Engineering and Technology

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Signature of Candidate

Date: 26-07-2024

Ishita

Place: Patiala

ABSTRACT

Presently, the most pressing issue is meeting the need for clean and pure water. Several difficulties have come up that impede the availability of this essential resource. In view of foregoing problem, various techniques such as adsorption, coagulation, photocatalytic degradation, and biological methods were executed for treating the toxic pollutants from wastewater. Photocatalytic degradation is enormously effective advanced oxidation process used for the dismissal of noxious pollutants. Considering it, the photocatalyst $BiVO_4$ was prepared from hydrothermal method, which then employed for the degradation of ofloxacin. Ofloxacin is fluoroquinolone antibiotic, popular in practices of anti-infective therapy and used to address various bacterial ailment The photocatalyst have been characterised by XRD, FESEM, DRS, DLS and ZETA. The FESEM reveals that $BiVO_4$ having an irregular worm-like shape and an average particle size of 240 nm. The photocatalyst shows its maximum degradation efficiency of 72 % in 120 min in neutral medium when irradiated with visible light. Degradation studies in acidic and basic medium has similarly been noted. The reactive species participated in the photocatalytic process were superoxide and hydroxyl radicals. As a results, $BiVO_4$ has a potential of a photocatalyst for effectively degradation of ofloxacin attribute to its high stability and environment friendly synthesis.

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LIST OF ABBREVIATIONS

BV = Bismuth Vanadate ($BiVO_4$)

OFL = Ofloxacin

DRS = UV-Vis Diffused Reflectance Spectroscopy

DLS = Dynamic Light Scattering

XRD = X-Ray Diffraction Technique

FESEM = Field Emission Scanning Electron Microscope

V.B = Valence Band

C.B = Conduction Band

UV = ultraviolet

Vis = Visible

pH = potential of Hydrogen

m-s = monoclinic scheelite

t-s = tetragonal scheelite

t-z = tetragonal zircon

LIST OF SYMBOLS

M = molar

g = gram

ml = millilitre

mg = milligrams

min = minute

hr = hour

% = percentage

°C = degree Celsius

a.u. = arbitrary constant

A° = angstrom

k = rate constant

rpm = revolutions per minute

eV = electron-Volt

nm = nanometre

CHAPTER 1

1.1 Introduction and Literature review

Water is the most valuable component for all life on earth. The accessibility of fresh water is the foremost concern for existence of humans and animals because of growing global population and their high standard living raised the water consumption faster[1]. The use of freshwater has experienced a yearly increase of 1% since 1980's[2]. Water reservoirs are continuously polluted by human activities. Human actions like sewage discharge into rivers, crude agriculture practices and industrial waste dumping into the waterbodies produce largest number of drugs and dyes contaminants which causes hazardous health problems such as diarrhea, cancer, eyes and skin allergies which may lead to some permanent injuries[3]. A challenge in attaining water security is that wastewater treatment satisfies the required quality expectations. To attain this, the unwanted contaminants must be removed from wastewater. During the pre-treatment techniques, synthetic dyes and pharmaceutical drugs are commonly found pollutants in wastewater. Ofloxacin is the famous pharmaceutical antibacterial drugs used to treat bacterial infections. It is found in aquatic surroundings which may seriously threating to living organisms by inducing antibiotic resistance in bacteria. It may affect the neural system and increases the heart rhythm issues[4]. Thus, it is important to find an efficient and economical approach for the removal of fluoroquinolone antibiotics[5]. Various techniques consisting physical methods- sedimentation and filtration, chemical methods including adsorption, coagulation and flocculation, biological methods containing activated sludge process and advanced techniques compressing advanced oxidation processes (AOP)[6]. Advanced oxidation processes (AOP) are considered as highly competitive technology in the treatment of wastewater toxic products. It comprises reactions which generate active free radicals such as hydroxyl ($^{\cdot}OH$), Hydrogen ($H^{\cdot}$), hydroperoxyl ($HO_2^{\cdot}$) and superoxide ($^{\cdot}O_2^{-}$) that respond to the conversion of organic and inorganic compounds into harmless simple products (CO_2 and H_2O)[7,8] . Of all the methods, photocatalytic degradation technology has gained credit pursuant to its versatility and high efficiency to degrade pollutants. This process having an array of benefits such as (i) low cost, (ii) mineralisation, and (iii) zero waste production, etc[9]. In essence, visible-light sensitive photocatalytic cycle comprises mainly three steps- Initially, illumination drives electron transition from the valence band (VB) to the conduction band (CB), creating equal number of vacant sites (holes); thereafter, excited electrons and created holes move towards the surface. In third step, they react with the electron donor and acceptor, respectively that had been absorbed. But in second step, there is a possibility that the recombination of holes and electrons may take place resulting lowering the efficiency of degradation. To prevent this electron-hole pairs recombination, the approach of loading co-catalyst such as noble metals (Pt[10], Ag[11]), non-noble metals (Ni[12], Cu[13]), metal oxides and sulphides and carbon-based material (g-C_3N_4[14], rGO[15]), etc on the surface of semiconductor has been applied. Co-catalyst improves the charge separation by introducing heterojunction between semiconductor and co-catalyst provides an internal electric field. Furthermore, this co-catalyst can make the process more energetically favourable by lowering the overpotential of redox reactions. It also increases the selectivity, stability and durability of the photocatalyst[16].

Bimetallic bismuth oxide for instance Bi_2WO_6 [17], $BiFeO_3$ [18] and $Bi_2Ti_2O_7$ [19] have been regarded as effective photocatalyst[20]. Bismuth vanadate ($BiVO_4$) considered as green photocatalyst because of its non-toxic, heat resistance and physicochemical stable nature[21]. It also shows ferro-elasticity, ionic-conductivity and O_2 evolution property under the visible light irradiation[20]. $BiVO_4$ exist mainly in three crystal forms- tetragonal with zircon structure (t-z), tetragonal with scheelite structure (t-s), and monoclinic with scheelite structure (m-s) with band gap of 2.90, 2.34 and 2.40 eV respectively, as reported[20]. $BiVO_4$ (m-s) obtained by high temperature processes show highest performance of photocatalytic degradation among all the stated structures, following the transition occur from valence band (VB) composed of Bi 6s orbital or hybrid orbital of Bi 6s and O 2p to the CB of V 3d orbitals[20].

The current research will focus on the fabrication of $BiVO_4$ photocatalyst. The photoreaction has been evaluated with the visible light degradation of ofloxacin as well as understanding the photocatalytic study.

1.2 Objectives

- Synthesis and characterizations of Bare $BiVO_4$.
- To study the photocatalytic degradation, pH study and kinetics of Ofloxacin antibiotic.

CHAPTER 2

2.1 Materials and Methods

Apparatus - Beaker, Measuring cylinder, Petri Plates, Dropper and Spatula, Glass rod, Test tubes, Falcon tubes and vials, Eppendorf, Magnetic beads, Magnetic Stirrer, Centrifuge machine, pH meter, visible light chamber, Cuvettes, UV-Visible Spectrophotometer.

Chemicals - Bismuth nitrate pentahydrate 98%, pellets of sodium hydroxide 97%, Ammonium metavanadate 99% were procured from Loba Chemie, India. Nitric acid was brought from Thermo fischer scientific, India. (DI) Deionised water was acquired from Milli-Q, Millipore ultrafiltration system used throughout the experiment. Ofloxacin tablets (OFLOX - 200) manufactured by Cipla were purchased from medical store.

Synthesis of $BiVO_4$ - For the synthesis of $BiVO_4$, hydrothermal method was used. Firstly, solution A and B were prepared by dissolving 0.9701 g [Bi $(NO_3).5H_2O$] in 20 ml (2M) HNO_3 and 0.2340 g NH_4VO_3 into 30 ml NaOH (2M) respectively, under magnetic stirrer. In the next step, solution B was added to solution A dropwise on continuous stirring to form suspension. Using HNO_3, pH was adjusted to neutral followed by 1 hr stirring then transferred to 100 ml Teflon lined autoclave for 4 hr at 180 °C for crystallization process. After centrifugation and drying at 60°C, yellow coloured powder BV was obtained[22].

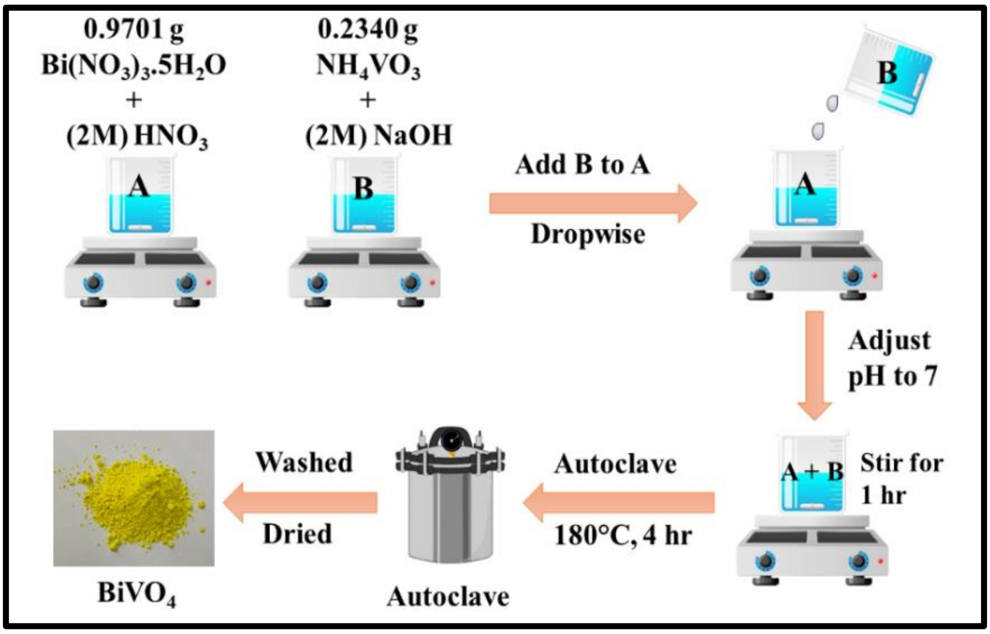

Fig 1: Representation of synthesis of BV.

2.2 Characterization Techqniues

The crystal structure, composition and morphology of $BiVO_4$ synthesised from hydrothermal method were examined using characterisations that described below:

X-ray Diffraction technique (XRD): XRD provides the information about chemical composition, properties and crystal structure of the synthesised material. The measurements were executed using Xpert pro-CuKα radiation at λ=1.54 Å in the range from 10 ° to 65 ° at a scanning rate of 10 ° min^{-1}. XRD analysis give details about lattice parameters, crystallite size and phase & quantitative identification.

Field Emission Scanning Electron Microscopy (FE-SEM): Surface morphology structure of photocatalyst was analyzed through FESEM using Carl Zeiss sigma 500. For this technique, 2mg BV was dispersed in DI water and sonicated for 45 min after that dropped cast it on the copper tape and dried at 60°C.

UV-Vis Diffused Reflectance Spectroscopy (DRS): DRS is a non-destructive technique analyses opaque samples. It also determines the surface properties and band gap of semiconductors. This technique was performed using UV-visible spectrophotometer (Shimadzu UV-2600).

Dynamic Light Scattering (DLS) and Zeta Potential: The surface charge of $BiVO_4$ and its particle size were determined using zeta potential analyzer (ZEN 3600, Malvern, U.K.) by dissolving 2 mg BV in 10 ml DI water and sonicating it for 30 min. Dynamic light scattering technique is used to measure the hydrodynamic particle size of photocatalyst.

Photocatalytic activity: Photocatalytic activity was explored by the degradation of ofloxacin under the visible light irradiation. Initially, dissolved 2.5 mg of photocatalyst in 5 ml ofloxacin (20 ppm). Before illumination, the suspension was stirred for 15 min in dark to achieve adsorption-desorption equilibrium. The solution mixture was then illuminated with visible light (Wipro Garnet B22-50 W LED bulb) for fixed time intervals. After centrifugation, the concentration of pollutants was monitored using Shimadzu UV-2600 UV-Visible spectrophotometer. The degradation efficiency was formulated by using equation **(1)**

$$\%\, Degradation = \frac{[C_0 - C_t]}{C_0} \times 100 \qquad \textbf{(1)}$$

where C_0 signifies the initial concentration of pollutants and C_t indicates the concentration after time 't'.

CHAPTER 3

3.1 Results and Discussions:

3.1.1 Structure and Morphology:

XRD (X-Ray Diffraction)

The diffraction pattern of BV is shown in **Fig 2**, it states that the sharp and distinct peaks indicated the crystallinity of the product. The fabricated BV is analogues to monoclinic scheelite structure with the existence of peaks through corresponding planes at 15.14° (020)[23], 18.62° (110), 18.95° (011), 28.87° (-121), 30.62° (040), 34.54° (200), 35.30° (002), 39.88° (211), 42.50° (051), 46.10° (231), 47.19° (240), 50.35° (202), 53.29° (161), 58.41° (321), and 59.29° (123) [24]. The peaks at 2θ = 24.41° (200) and 30.67° (211) confirm the tetragonal zircon type phase structure of BV[25]. The peak at 30.67° (211) of tetragonal zircon is merged with the peak of monoclinic phase's peak which is correspond to (040) plane. The diffraction peaks were categorized correspondence to ICDD card 14-0688 and ICDD card 14-0133, respectively for monoclinic and tetragonal phase. The well matching of the peaks with the reported data confirmed that the samples have no impurities.

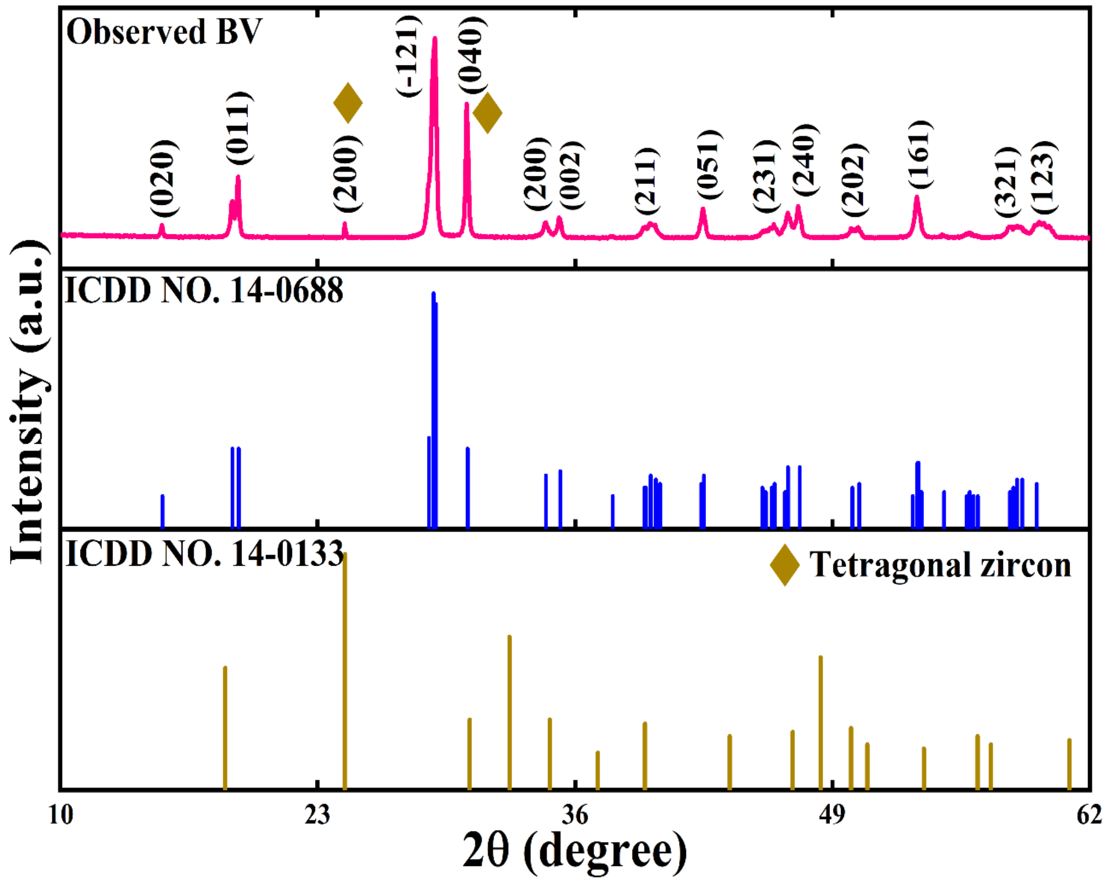

Fig 2: XRD spectrum of $BiVO_4$.

FESEM (Field Emission Scanning Electron Microscopy)

The morphologies of the synthesized sample were analyzed by using field emission scanning electron microscopy (FESEM). The SEM images in **Fig. 3a** depicts the generation of irregular worm-like particles[26] of BV with an average particle size around 240 nm in **Fig. 3b**.

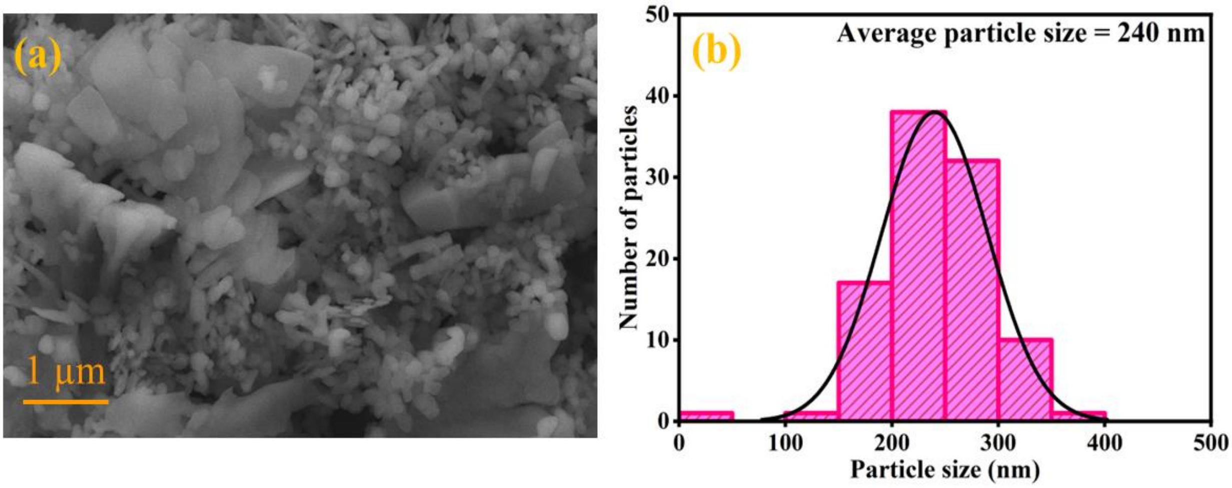

Fig 3: FESEM images of BV.

3.1.2 Optical properties:

DRS (UV-Vis Diffused Reflectance Spectroscopy)

The optical properties of BV were characterized using the UV-Vis DRS technique that reveals the band gap of the material which was calculated using a Tauc plot. The absorption edge was lying at 536 nm in **Fig 4a** which is in good agreement with the reported result[27]. In **Fig 4b** the measured band gap of BV was 2.38 eV[28].

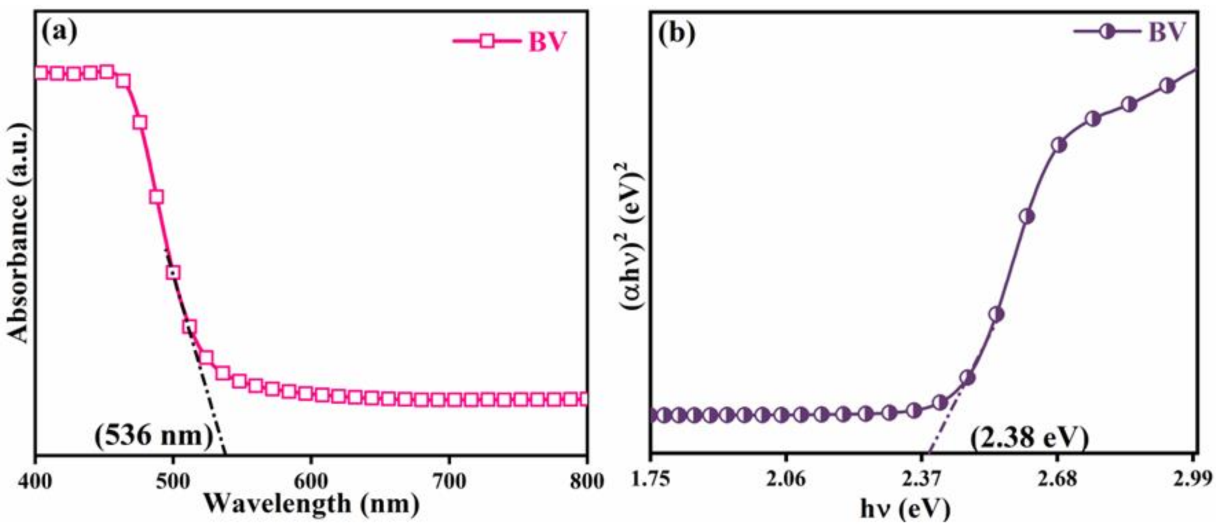

Fig 4: (a) UV-Vis diffuse reflectance spectra (b) tauc plot.

DLS (Hydrodynamic Size) and Zeta

The hydrodynamic particle size of synthesized sample was 905.9 nm in **Fig 5a**, it was evaluated using the Dynamic light scattering technique. The charge on the surface of photocatalyst was determined by Zeta potential which comes out to be -22 eV **Fig 5b.**

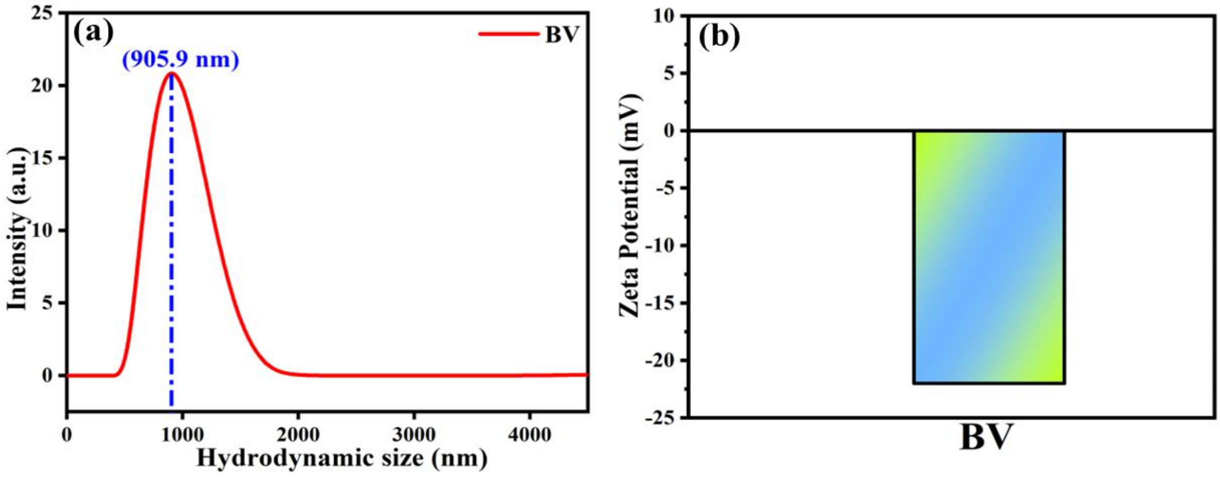

Fig 5: (a) Hydrodynamic size (b) zeta Potential of synthesized material.

3.1.3 <u>Photocatalytic Degradation</u>

To examine the productiveness of photocatalyst in abatement of OFL includes optimization of catalyst's amount **(Fig 6a)**, this optimized amount of catalyst (2.5 mg) was dissolved in 5 ml of OFL (20 ppm) solution. Initially, the suspension was given with 15 min dark to attain the adsorption-desorption equilibrium then irradiated to the visible light for 120 min shown in **Fig 6 (b and c)**. Consequently, the pollutant was degraded up-to 72% calculated by using equation **(1).**

In the determination of rate constant (k), equation **(2)** was followed

$$ln\left(\frac{C}{C_0}\right) = -kt \quad \textbf{(2)}$$

where, C is concentration at time 't' and C_0 is concentration at time = 0.

The kinetic study of photocatalytic degradation of OFL is shown in **Fig 7** at pH = 7 which adheres to pseudo first order kinetics with a rate constant 0.00958 min^{-1}.

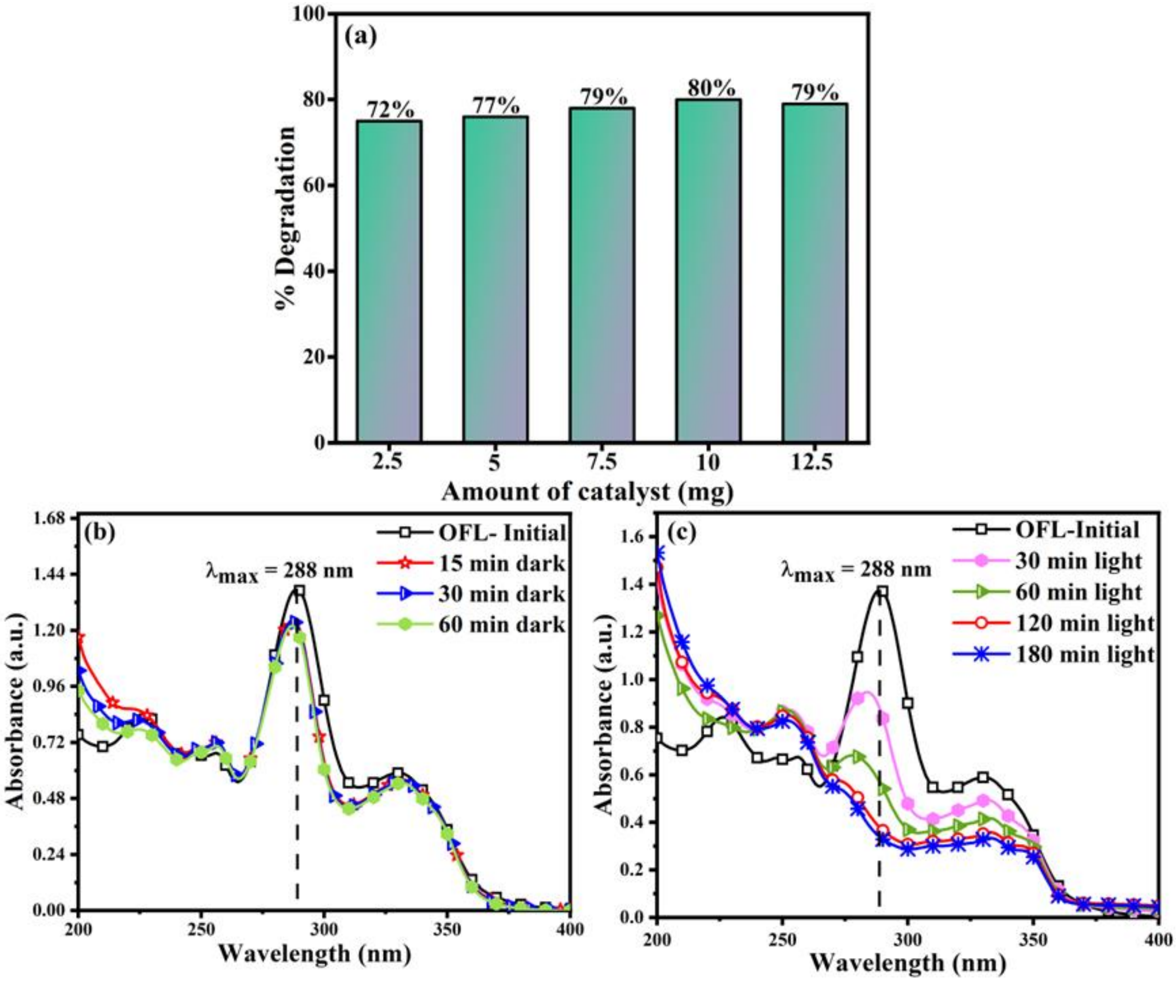

Fig 6: (a) Showing optimal catalyst amount, (b) absorption process in dark conditions, and (c) photocatalytic degradation at different time period.

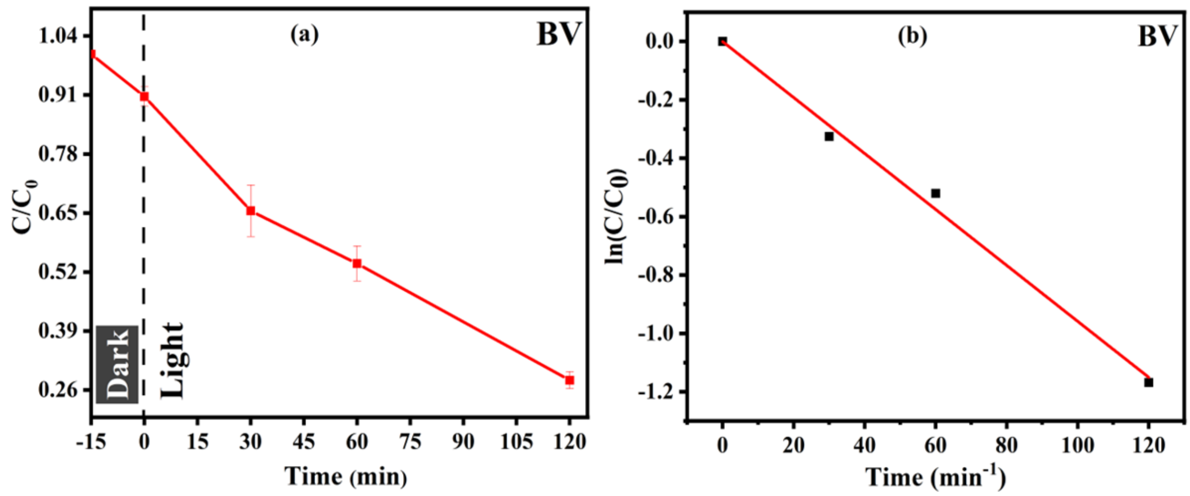

Fig 7: (a) Kinetics of OFL with time, (b) degradation with ln (C/C_0) at different time.

Effect of pH on degradation

The photocatalytic efficacy is largely dependents on the pH of the solution. Variations in pH can influence the surface charge of catalyst, adsorption of intended compound and possibly change the degradation efficiency[29]. The pH effect on photocatalytic degradation of OFL was examined using pH values including 4 and 10. The acidic and basic medium were maintained using 0.1 M HCl and 0.1 M NaOH, respectively. The degradation efficiency in acidic, neutral and basic medium is almost the same but kinetic of reaction followed second order predominantly at pH 4 and 10 as shown in **Fig 8 (a, b)**. The rate constant values at pH 4 and 10 was 0.00114 M^{-1} s^{-1} and 0.00137 M^{-1} s^{-1}, respectively was depicted in **Fig 9**.

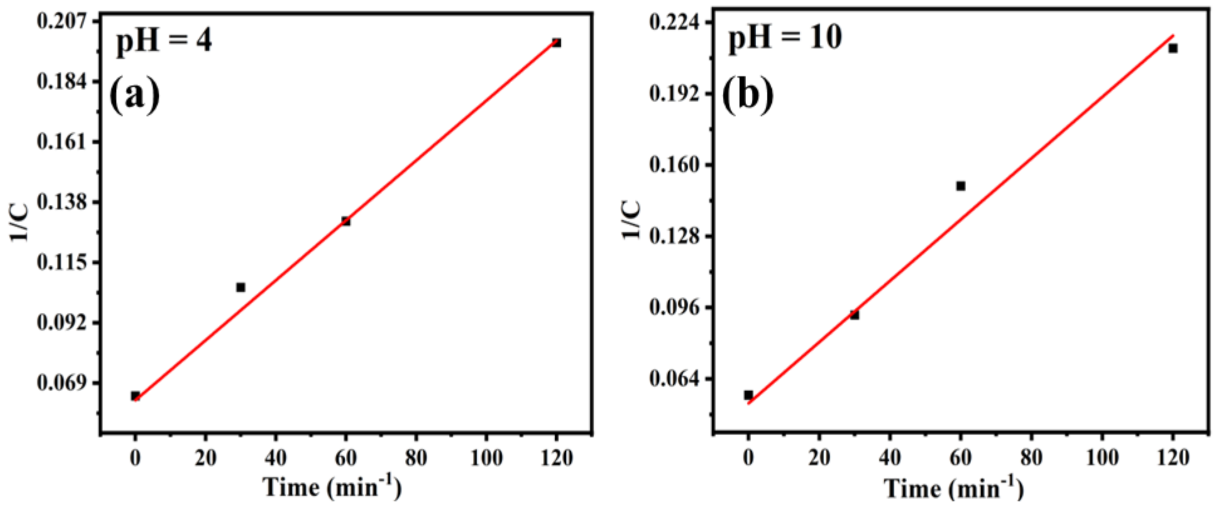

Fig 8: Kinetic study in (a) acidic and (b) basic medium respectively.

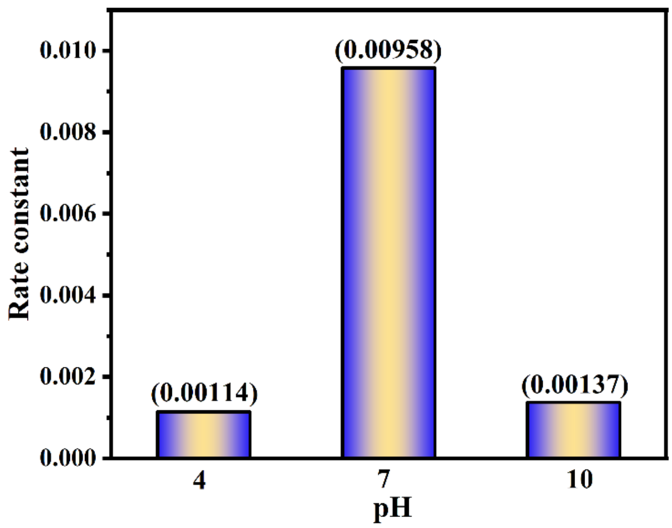

Fig 9: Bar plot of rate constant values at different pH respectively.

3.1.4 Mechanistic studies

Proposed photocatalytic mechanism

$$BiVO_4 + h\nu \longrightarrow BiVO_4\,(e^-_{CB} + h^+_{VB})$$

$$O_2 + e^- \longrightarrow {}^{\cdot}O_2^-$$

$$H_2O + h^+ \longrightarrow {}^{\cdot}OH + H^+$$

$$OH^- + h^+ \longrightarrow {}^{\cdot}OH$$

$$\text{Pollutant} \xrightarrow{{}^{\cdot}O_2^-\ /\ {}^{\cdot}OH} \text{Degraded products}$$

According to significant findings, the $BiVO_4$ plausible photocatalytic mechanism is presented in **Fig 10**. Number of photons were absorbed by $BiVO_4$ semiconductor when irradiated to visible light which results in the excitation of electrons from valence band to conduction band owing to generation of electron-hole pairs. Eventually, there is a possibility of recombination of electrons and holes resulting reducing the degradation process. The generated electrons reduce the molecular oxygen (O_2) to produce superoxide radicals (${}^{\cdot}O_2^-$) and the retaining holes in valence band of $BiVO_4$ can oxidize hydroxide ions (OH^-) to hydroxyl radicals (${}^{\cdot}OH$) produced by water molecules. Subsequently, this redox interactions between reactive species degrade the pollutant[30].

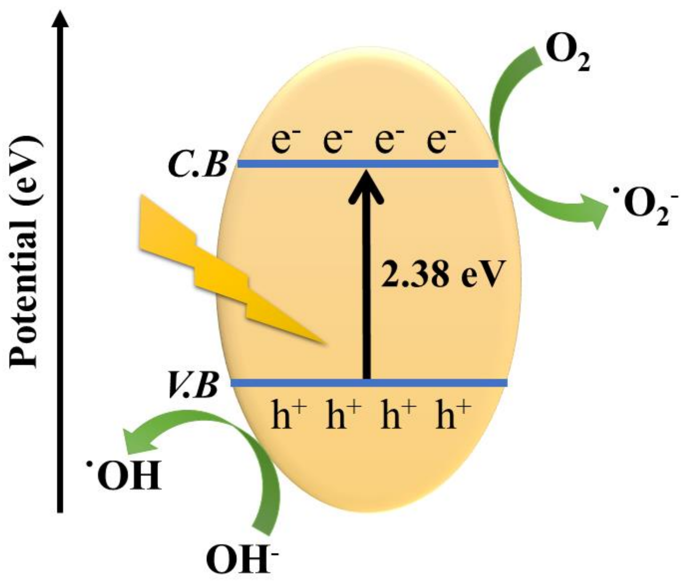

Fig 10: Photocatalytic degradation mechanism of OFL by BV.

Scavenger study

The scavenger experiment was performed in order to examine the effect of reactive species. The degradation efficiency was reduced to 65%, 53% and 45%, from 72% when monitored using hole scavengers like iPA, methanol and NH_4SCN respectively in **Fig 11**, which helps in the evasion of hydroxyl radical production by holes during the oxidation process of water molecules.

The argon gas purging drops the degradation efficiency to 4% preventing the production of superoxide radical by removing the oxygen from reaction mixture[31,32]. Hence these findings proved that degradation of pollutant is promoted majorly by superoxide and minorly by holes, hydroxyl radicals.

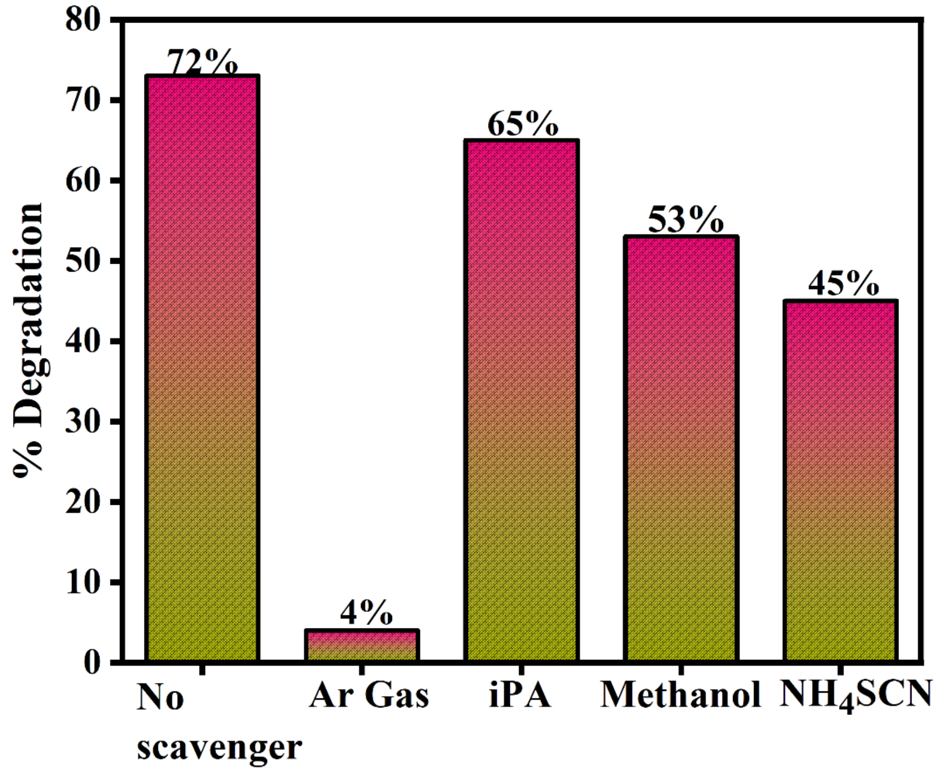

Fig 11: Variance of photocatalytic activity upon addition of different scavengers.

Reusability

In an attempt to ensure the stability of photocatalyst, reusability experiment was performed in four cycles with the same photocatalytic conditions. After the reaction practices, the photocatalyst was extracted from the reaction solution and with the same conditions it was employed again in the subsequently reactions. Remarkably, there is only a 10% decrease in the photocatalytic proficiency **Fig 12** equated to the initial which may be due to loss of amount during centrifugation or drying[33][33].

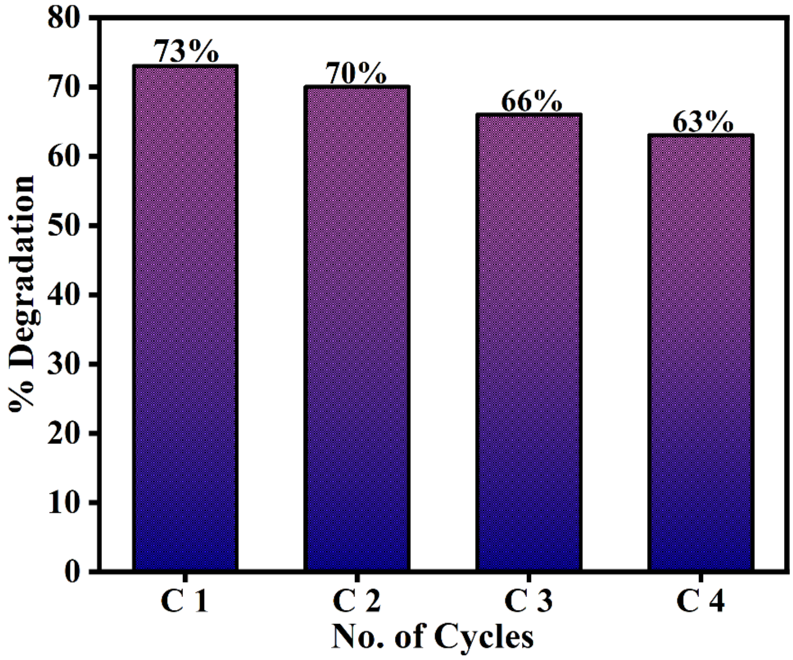

Fig 12: The stability of photocatalyst $BiVO_4$ for degradation of OFL in visible light for four pursuing cycles.

CHAPTER 4

4.1 Conclusion

The present study focuses on the successful fabrication of $BiVO_4$ photocatalyst stimulated by visible light and addresses its performance in declining the Ofloxacin antibiotic. The $BiVO_4$ was synthesised using hydrothermal method and various technique were used to characterised it. The irregular worm shaped $BiVO_4$ compresses both monoclinic scheelite and tetragonal zircon phase structures with an average particle size 240 nm. The band gap of the material was 2.38 eV examined through Tauc plot. The photocatalyst was used to study the pH effects on degradation efficiency which exhibits second order kinetics at both pH=4 and pH=10 but pseudo first order at neutral. The optimized 2.5 mg of photocatalyst effectively degrades ofloxacin by 72% in the exposure of visible light for 120 min. With the aid of proposed mechanism, it is believed that superoxide and hydroxyl radical act as reactive species for deteriorating the complex compounds into simpler products. In conclusion, the high stability, low cost and non-toxic nature of $BiVO_4$ serves as a prospective photocatalyst in the treatment of pharmaceutical drugs in wastewater.

4.2 References

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4	Selective hydrolysis of whey proteins using a flow-through monolithic by Mao-2018	1	Publication
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Raj Kumar Das
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