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## Research Article

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# **Pre-Magnetized Water Hyacinth Biochar-Supported Bismuth Oxybromide Nanocomposite for Solar Photocatalytic Degradation of Paracetamol**

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## Abstract

Paracetamol (PC) is one of the most frequently detected emerging contaminants in wastewater due to its extensive consumption, persistence, and incomplete removal by conventional treatment processes. In this study, pre-magnetized water hyacinth (WH) biochar-supported bismuth oxybromide nanocomposite (MBC<sub>Pre</sub>BiOBr) was synthesized and evaluated for the solar photocatalytic degradation of paracetamol in aqueous solution and greywater. WH feedstock was magnetised and then magnetic biochar (MBC<sub>Pre</sub>) was formed using microwave assisted pyrolysis (800 W, 20 min). MBC<sub>Pre</sub> was then loaded with BiOBr in the ratio 1:1. SEM analysis revealed overall porous framework remained intact maintaining the structural stability. Successful incorporation of Fe, Bi and Br was observed from EDS analysis. Uniform deposition was confirmed by elemental mapping. The presence of O–H stretching and aliphatic C–H groups were indicated by FTIR analysis. The BET study revealed specific surface area, total pore volume, and average pore diameter to be 16.783 m<sup>2</sup>/g, 0.086 cm<sup>3</sup>/g, and 20.507 nm, respectively. The Tauc plot analysis yielded a band gap energy of ~ 2.17 eV, indicating that the MBC<sub>Pre</sub>BiOBr can be readily activated under visible-light irradiation. Operating parameters optimization revealed at 1 mg/L of initial PC concentration complete degradation was observed with 1 g/L of MBC<sub>Pre</sub>BiOBr at neutral pH for 30 min treatment time under sunlight. The inhibitory effect of the cations and anions followed the order Al<sup>3+</sup> > Ca<sup>2+</sup> > Fe<sup>3+</sup> for cations and NO<sub>3</sub><sup>-</sup> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> ≈ HCO<sub>3</sub><sup>-</sup> respectively. MBC<sub>Pre</sub>BiOBr achieved 83.33% PC degradation, 73.65% TOC removal, and simultaneous removal of nitrate (63.92%), sulphate (40.43%), and phosphate (25.33%) from greywater, demonstrating its effectiveness for treating complex greywater matrices. Moreover, reusability study showed <10% reduction in PC degradation after fourth cycle in greywater. The regulating mechanism was adsorption accompanied by photocatalytic degradation.

**Keywords:** Solar Photocatalysis; Biochar; Pre-magnetization; Water hyacinth; BiOBr; Paracetamol

## Abbreviations:

AOPs: Advanced Oxidation Processes

BC: Biochar

BET: Brunauer-Emmett-Teller

BiOBr: Bismuth Oxybromide

DTG: Derivative Thermogravimetry

e<sup>-</sup>: Electrons

ECs: Emerging Contaminants

EDS: Energy Dispersive X-ray Spectroscopy

FTIR: Fourier transform infrared

$h^+$ : Holes

HPLC: High-Performance Liquid Chromatography

MAP: Microwave-Assisted Pyrolysis

MBC<sub>Pre</sub>: Pre-Magnetised water hyacinth Biochar

MBC<sub>Pre</sub>BiOBr: Pre-Magnetised water hyacinth Biochar-supported Bismuth Oxybromide

PC: Paracetamol

ROS: Reactive Oxygen Species

SEM: Scanning Electron Microscope

TES: Trace Element Solution

TGA: Thermogravimetric Analysis

TOC: Total Organic Carbons

$\bullet O_2^-$ : Superoxide radical

$\bullet OH$ : Hydroxyl radical

## 1. Introduction

The continuous discharge of emerging contaminants (ECs) into aquatic environments has become a major global environmental concern due to their persistence, widespread occurrence, and potential adverse effects on ecosystems and human health. Emerging contaminants comprise a diverse group of substances, including pharmaceuticals, personal care products, endocrine-disrupting compounds, pesticides, and industrial chemicals, which are frequently detected in water bodies but are not completely removed by conventional wastewater treatment processes. Among these pollutants, pharmaceutical compounds have attracted significant attention owing to their extensive consumption and continuous introduction into the environment through domestic, hospital, and industrial wastewater streams [1].

Paracetamol (PC) (acetaminophen) is one of the most widely consumed pharmaceutical drugs worldwide and is extensively used as an analgesic and antipyretic agent. Owing to its widespread consumption, significant quantities of PC and its metabolites are excreted after use and subsequently enter domestic wastewater and greywater streams through activities such as bathing, handwashing, and laundry. Additional sources include pharmaceutical manufacturing effluents, hospital discharges, and the improper disposal of unused medications. Greywater, which constitutes a major fraction of household wastewater, can therefore serve as an important pathway for the release of PC into the environment, particularly in regions where greywater is reused or discharged with minimal treatment. Reported concentrations of PC in greywater exhibit considerable variation across different studies. [2] reported an average concentration of  $256.1 \pm 875.3$   $\mu\text{g/L}$ , with a maximum concentration of  $1131.4$   $\mu\text{g/L}$ , indicating substantial variability among the collected samples. A comparable concentration of  $1130$   $\mu\text{g/L}$  was reported by [3]. In contrast, [4] detected PC at a much lower average concentration of  $4.94$   $\mu\text{g/L}$ , with values ranging from  $0.12$  to  $16.28$   $\mu\text{g/L}$ . [5] reported an average concentration of  $16.70 \pm 34.61$   $\mu\text{g/L}$ , with concentrations varying between  $0.150$  and  $126.120$   $\mu\text{g/L}$ , reflecting significant spatial and temporal variations in greywater composition. Similarly, [6] detected PC at a concentration of  $17.66$   $\mu\text{g/L}$ . Collectively, these studies demonstrate that PC is commonly present in greywater over a broad concentration range, from trace levels to approximately  $1.13$   $\text{mg/L}$ , depending on the source and characteristics of the greywater.

Emerging contaminants are often found in greywater, treated effluents, surface water, and groundwater due to the constraints of conventional wastewater treatment systems. Low degradation rates, ineffective removal of lower concentrations, the creation of hazardous byproducts, sensitivity to surrounding changes like pH and temperature, and the production of sludge that needs extra processing and disposal are some of these drawbacks [7]. Although typically present at low concentrations, the continuous discharge of PC into aquatic environments can pose ecological risks, including toxicity to aquatic organisms, disruption of biological processes, and the formation of potentially harmful transformation products. Consequently, the effective removal of PC from wastewater has become an important focus of environmental research [8].

These restrictions can be circumvented by advanced oxidation processes (AOPs), which present a viable way to treat wastewater that contains ECs. Reactive oxygen species (ROS), which are produced by AOPs, break down pollutants into non-toxic byproducts [9]. One of the most efficient AOPs is photocatalysis, which uses metal oxide-based semiconductors to capture photo energy and produce radicals [10]. Meanwhile, traditional photocatalysts for instance  $\text{TiO}_2$ ,  $\text{CdS}$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ , etc. confront constraints, including broad band gaps that limit their activation by solar radiation and high  $e^- h^+$  recombination rates, which hamper radical production and disturb photocatalytic degradation [11]. Bismuth oxyhalides ( $\text{BiOX}$ ;  $X = \text{Cl, Br, or I}$ ) are highly promising photocatalytic materials owing to their distinctive features. Their layered crystal structure facilitates efficient charge separation and visible-light utilization, while also imparting excellent chemical stability [12].

By providing a larger surface area, finely powdered photocatalysts can increase the formation of ROS and improve their interaction with pollutants in wastewater. However, it is difficult to separate them from the treated effluent after treatment due to their small particle size. In order to get over this restriction, photocatalysts can be supported or immobilized on appropriate carrier materials, making recovery and reuse simpler. For this aim, a variety of support materials have been investigated, including silica, activated carbon, charcoal, alumina, ceramics, and glass fibres [13]. Biochar (BC)-supported photocatalysts can enhance pollutant degradation by providing a highly porous structure with increased surface area and abundant active sites. In addition, biochar can act as an electron reservoir, facilitating charge separation and transfer while potentially reducing the effective band gap of the photocatalyst ([14]; [15]; [16]; [17]. Consequently, using BC as a

photocatalyst support can increase charge transfer and active-site availability, improving overall photocatalytic performance.

Various feedstocks, including rice husk, kitchen waste, food waste, bamboo, straw, pine pollen, reed straw, and industrial wood flour, have been utilized for BC production, which has subsequently been employed as a support material for BiOBr photocatalysts ([18] [19] [20] [21] [22]; [23] [24] [25]). Compared to other feedstocks, water hyacinth (WH) (*Eichhornia crassipes*) BC had a larger pore diameter and specific surface area; thus, BC from WH feedstock can help in wastewater treatment and alleviate the environmental nuisance it creates [26]. However, all WH BC are synthesized using traditional pyrolysis as per the literature. Microwave-assisted pyrolysis (MAP) is a novel conversion approach for waste-to-value added products. In contrast to traditional pyrolysis, which depends on direct or external heating, MAP employs microwave irradiation to heat the substance. This culminates in a unique and more effective thermal based conversion process ([27]; [28]).

The current study focused on the production of BC from WH via MAP, followed by magnetization and incorporation of BiOBr to develop a magnetically recoverable MBC<sub>Pre</sub>BiOBr nanocomposite. The photocatalytic performance of MBC<sub>Pre</sub>BiOBr for the solar-driven degradation of PC was evaluated by examining the effects of key operational parameters. Furthermore, the reusability of the photocatalyst was assessed, and a plausible photocatalytic degradation mechanism was proposed.

## **2. Materials and Methodology**

### **2.1. Materials required**

WH was collected from the Kuakhai River, Odisha, India (20° 18' 38.2032", 85° 52' 14.5452"). Analytical-grade bismuth(III) nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), cetrimonium bromide (CTAB), ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ethylene glycol, and PC were procured from Sigma-Aldrich, India. Deionized water was utilized throughout the experiments for solution preparation and washing purposes.

### **2.2. Synthesis of MBC<sub>Pre</sub>BiOBr**

The schematic illustration of the MBC<sub>Pre</sub>BiOBr synthesis procedure is presented in Fig. 1. The collected WH biomass was thoroughly washed, sun-dried for 24 h, and ground to achieve a uniform particle size of  $\leq 5$  mm. Magnetization was carried out by adding the WH biomass to an iron precursor solution containing  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  at a 1:2

mass ratio. Subsequently, 3 M NaOH was added dropwise under continuous stirring until the solution reached a pH of 10. The pre-magnetized biochar (MBC<sub>Pre</sub>) was then produced through MAP at an input power of 800 W under an N<sub>2</sub> flow rate of 0.2 L/min for 20 min. The resulting black precipitate was accumulated, thoroughly rinsed, and dried at 100 °C for 24 h. BiOBr was synthesized by dissolving 1 mmol each of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and CTAB in 50 mL of ethylene glycol. The prepared BiOBr and MBC were subsequently combined at a 1:1 ratio, ultrasonicated for 20 min, subjected to autoclaving for 2 h, and further oven dried at 80 °C for 24 h to obtain the MBC<sub>Pre</sub>BiOBr nanocomposite.

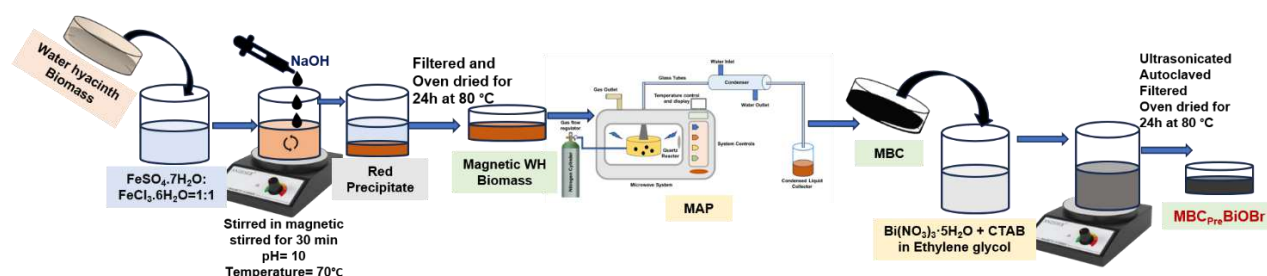


**Fig. 1** Schematic illustration of MBC<sub>Pre</sub>BiOBr synthesis procedure

### 2.3. MBC<sub>Pre</sub>BiOBr characterization studies

Thermogravimetric analysis (TGA) was performed on the precursor biomass to investigate its thermal degradation behaviour and to determine the optimum pyrolysis temperature for BC production. The morphology of the synthesized photocatalyst was characterized using scanning electron microscopy (SEM) (MERLIN Compact System). The elemental composition was determined by energy-dispersive X-ray spectroscopy (EDS) (51XMX 1004, Oxford Instruments). Surface functional groups were identified through Fourier transform infrared (FTIR) spectroscopy (Alpha-T, Bruker). The textural properties of the synthesized materials, including specific surface area, pore volume, and average pore diameter, were evaluated using Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption analysis. The optical properties and band gap energy of the synthesized photocatalyst were investigated using a UV–Vis diffuse reflectance spectroscopy (DRS) (JASCO V-770). Additionally, the point of zero charge (pH<sub>pzc</sub>) of the photocatalyst was determined by the pH drift method using a pH meter and an orbital shaker [14].

### 2.4. Analytical methods

High-Performance Liquid Chromatography (HPLC) (Thermo Scientific Dionex Ultimate 3000 Series) at the wavelength of 240 nm and mobile phase (Water:Methanol= 70:30) was applied to chromatographically analyse both the initial and final PC concentrations at a

retention time of 1.87 min. The degradation efficiency of PC was evaluated using equation (1).

$$\text{PC Degradation Efficiency (\%)} = \frac{PC_0 - PC_e}{PC_0} \times 100 \quad (1)$$

Where,  $PC_0$  and  $PC_e$  are the insipient and residual concentrations of PC.

The efficiency of PC mineralization was assessed through Total Organic Carbon (TOC) analysis using a TOC-L analyzer (Shimadzu). The percentage of TOC removal was determined using equation (2).

$$\text{TOC removal (\%)} = \frac{TOC_0 - TOC_e}{TOC_0} \times 100 \quad (2)$$

Where,  $TOC_0$  and  $TOC_e$  are the insipient and residual concentrations of TOC after solar photocatalytic degradation.

The incident sunlight intensity was monitored with a digital lux meter (LX-101A, HTC Instruments). Ion chromatography (IC) (Thermo Scientific Dionex Aquion) was used to determine the concentrations of sulphate ( $SO_4^{2-}$ ), nitrate ( $NO_3^-$ ), and phosphate ( $PO_4^{3-}$ ) in the greywater samples.

## 2.5. Solar photocatalytic degradation experiments of $MBC_{Pre}BiOBr$

Solar photocatalytic degradation experiments were carried out in batch mode to evaluate the photocatalytic performance of the synthesized  $MBC_{Pre}BiOBr$  nanocomposite toward the removal of PC from aqueous solution. All experiments were performed under natural sunlight, with the solar intensity varying between 70,000 and 100,000 lux, as measured using a digital lux meter. an initial PC concentration of 1 mg/L was selected for the present study, as it closely represents the highest concentrations reported in greywater. The use of 1 mg/L provides an environmentally relevant concentration for evaluating the photocatalytic performance of the developed catalyst while ensuring reliable analytical detection and kinetic assessment. Moreover, selecting a concentration comparable to the upper range of reported environmental levels enables the assessment of the photocatalyst under realistic yet challenging greywater contamination conditions ([2]; [3]; [4]; [5]; [6]).

## 2.6. Effect of inorganic ions

the influence of common inorganic ions on the photocatalytic degradation of PC was investigated, since, real wastewater contains various dissolved inorganic species along with pharmaceutical contaminants. To evaluate their effects, 1 mM concentrations of selected

anions and cations were individually introduced into the PC solution. The effects of cations were assessed using  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Fe}^{3+}$  ions, introduced in the form of  $\text{AlCl}_3$ ,  $\text{CaCl}_2$ , and  $\text{FeCl}_3$ , respectively. Similarly, the anions examined included sulphate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), bicarbonate ( $\text{HCO}_3^-$ ), nitrate ( $\text{NO}_3^-$ ), and hydrogen phosphate ( $\text{HPO}_4^{2-}$ ), supplied as  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaHCO}_3$ ,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{HPO}_4$ , respectively.

## **2.7. Degradation study in synthetic greywater**

The synthetic greywater used for the degradation study was prepared by first making a 20-times concentrated stock solution. The stock solution was formulated with sucrose, soluble starch, urea, ammonium chloride, potassium dihydrogen phosphate, toothpaste, dishwashing gel, and bathing gel at concentrations of 0.16 g/L, 0.09 g/L, 0.05 g/L, 0.05 g/L, 0.05 g/L, 0.01 g/L, 0.1 mL/L, and 0.044 mL/L, respectively. To provide essential micronutrients for microbial activity, a trace element solution (TES) consisting of zinc sulphate, ferrous sulphate, cobalt chloride, manganese sulphate, and sodium molybdate dissolved in distilled water was prepared, and 1 mL TES was added per litre of greywater. The stock solution was mixed using a magnetic stirrer at 1000 rpm and heated to 70 °C for 30 min to ensure complete dissolution and homogenization. Finally, the concentrated stock solution was diluted twenty-fold with tap water to obtain synthetic greywater with characteristics similar to domestic greywater [29]. This synthetic greywater was subsequently used as the influent for degradation of PC.

## **3. Results and Discussion**

### **3.1. Characterization studies of $\text{MBC}_{\text{PreBiOBr}}$**

TGA–DTG analysis of magnetized WH biomass in Fig. 2 revealed a multistage thermal degradation pattern. An initial weight loss below 150°C was attributed to the removal of physically adsorbed moisture. The major devolatilization process occurred between 250 and 370°C, exhibiting a maximum DTG peak at approximately 320°C, corresponding to the decomposition of hemicellulose and cellulose fractions. A broad degradation region extending from 370 to 650°C was associated with the gradual breakdown of lignin and the formation of aromatic carbon structures. Beyond 650°C, the TG curve reached a plateau with a residual mass of approximately 39 wt.%, indicating the formation of thermally stable BC and the contribution of magnetic iron oxide species. Based on the thermal behaviour, a pyrolysis temperature of 500°C was selected for BC preparation as it ensures complete

devolatilization while preserving adequate carbon yield and surface functionality suitable for photocatalytic applications.

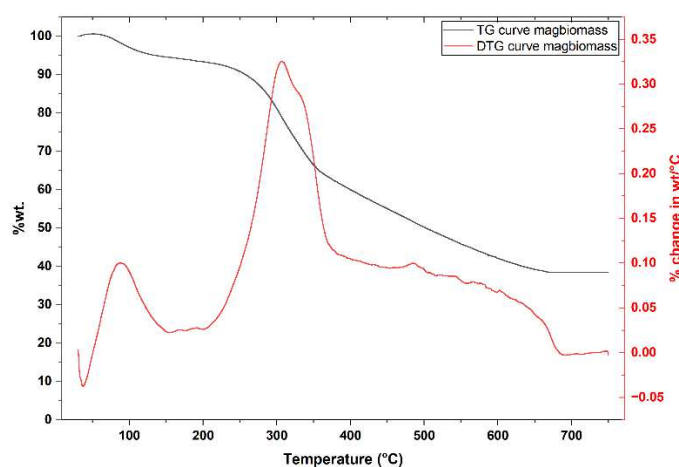


**Fig. 2** TGA-DTG curves of magnetized WH biomass

SEM analysis revealed substantial morphological changes during the preparation of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  photocatalyst. As observed in Fig. 3(a), pre-magnetized WH biomass exhibited a compact and heterogeneous surface with dispersed granular magnetic particles and limited porosity. Following pyrolysis,  $\text{MBC}_{\text{Pre}}$  developed a highly porous structure characterized by interconnected cavities and channels generated through the removal of volatile organic components (Fig. 3(b)). The increased surface roughness and pore development provided abundant anchoring sites for photocatalyst deposition. In Fig. 3(c), numerous fine particles were observed on the BC surface, indicating successful immobilization of the  $\text{MBC}_{\text{Pre}}\text{BiOBr}$ . Although partial pore filling occurred, the overall porous framework remained intact, suggesting that BC maintained its structural integrity during composite synthesis.

The pre-magnetized biomass primarily consisted of C (34.04 wt%), O (41.33 wt%), and Fe (24.51 wt%), confirming the successful incorporation of iron species onto the lignocellulosic matrix (Fig. 3(d)). Following pyrolysis, the carbon content increased to 53.69 wt% while the oxygen content decreased to 20.92 wt% (Fig. 3(e)), indicating effective carbonization and the removal of oxygen-containing volatile constituents. The Fe content remained nearly unchanged, demonstrating the thermal stability of the magnetic phase. After BiOBr deposition, characteristic Bi (4.39 wt%) and Br (1.69 wt%) signals appeared in the spectrum, confirming the successful formation of the  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  composite. The simultaneous presence of Fe, Bi, and Br indicates that

both the magnetic component and photocatalytic phase were successfully integrated within the  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  structure. These findings corroborate the SEM observations, which revealed the deposition of BiOBr particles on the porous BC surface.

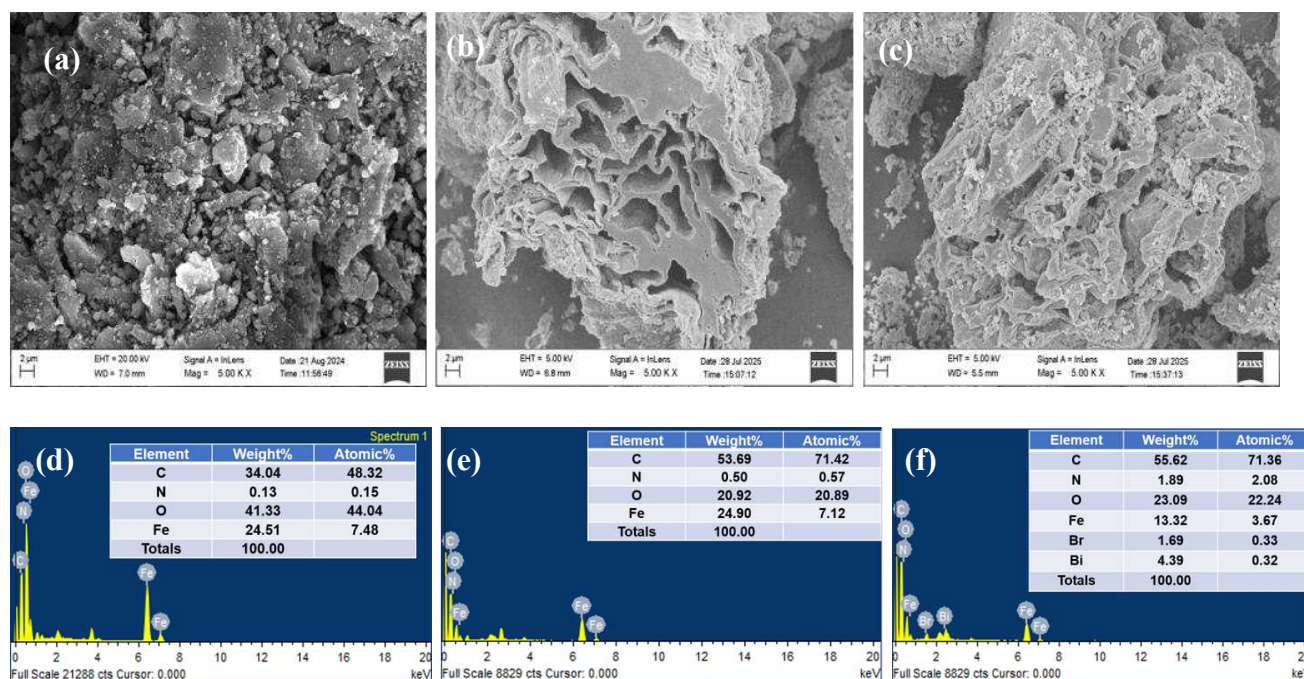


**Fig. 3** FESEM images of (a) Magnetic WH Biomass (b)  $\text{MBC}_{\text{Pre}}$  (c)  $\text{MBC}_{\text{Pre}}\text{BiOBr}$ ; EDS spectra of (d) Magnetic WH Biomass (e)  $\text{MBC}_{\text{Pre}}$  (f)  $\text{MBC}_{\text{Pre}}\text{BiOBr}$

Magnetized WH biomass exhibited homogeneous distributions of C, O, and Fe, confirming successful incorporation of iron species onto the lignocellulosic matrix (Fig. 4(a)). After pyrolysis as shown in Fig. 4(b), the resulting  $\text{MBC}_{\text{Pre}}$  retained uniformly dispersed Fe together with C, O, and trace N. Following BiOBr deposition, Bi and Br signals appeared and were uniformly distributed throughout the composite alongside Fe, C, and O as observed in Fig. 4(c). The overlapping distributions of Bi and Br confirm the successful formation and immobilization of BiOBr on  $\text{MBC}_{\text{Pre}}$ , while the persistence of Fe demonstrates retention of magnetic functionality.

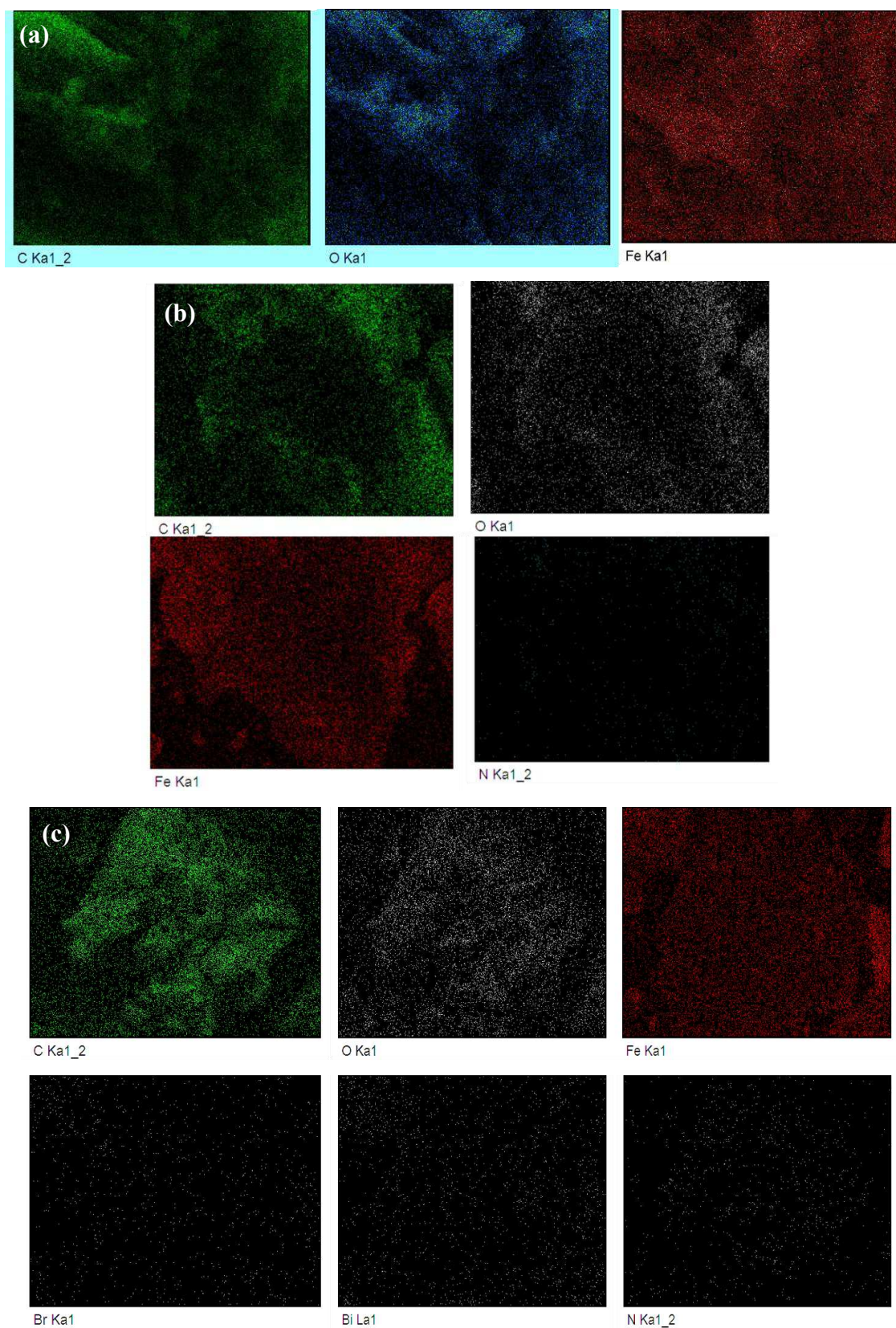


**Fig. 4** Elemental Mapping of (a) Magnetic WH Biomass (b) MBC<sub>Pre</sub> (c) MBC<sub>Pre</sub>BiOBr

As observed from the FTIR spectra shown in Fig. 5, both samples exhibited a broad absorption band in the range of 3700–3200 cm<sup>-1</sup>, corresponding to O–H stretching

vibrations of hydroxyl groups, and oxygen-containing surface functionalities. The higher intensity of this band in  $\text{MBC}_{\text{Pre}}$  indicates the abundance of oxygenated groups on the BC surface. In  $\text{MBC}_{\text{Pre}}\text{BiOBr}$ , the O–H band intensity decreased significantly, suggesting the involvement of these functional groups in the immobilization of BiOBr particles and the formation of strong interfacial interactions. Characteristic absorption bands located around 2920 and 2850  $\text{cm}^{-1}$  were assigned to asymmetric and symmetric stretching vibrations of aliphatic C–H groups. The persistence of these bands after  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  synthesis confirms the retention of the carbonaceous framework. The observed changes in the hydroxyl and aliphatic functional groups demonstrate that oxygen-containing surface functionalities serve as anchoring sites for BiOBr growth, facilitating the formation of a stable and well-integrated  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  composite.

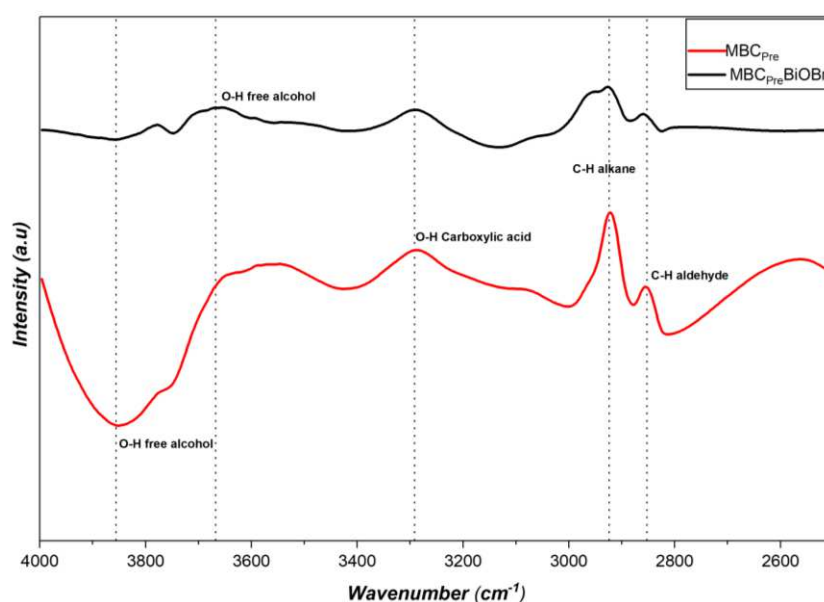


**Fig. 5** FTIR spectra of  $\text{MBC}_{\text{Pre}}$ , and  $\text{MBC}_{\text{Pre}}\text{BiOBr}$

$\text{N}_2$  adsorption-desorption isotherm of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  as depicted in Fig. 6(a) exhibited a typical Type IV isotherm with an H3 hysteresis loop, indicating the predominance of mesoporous structures within the composite. BET specific surface area, total pore volume, and average pore diameter were determined to be 16.783  $\text{m}^2/\text{g}$ , 0.086  $\text{cm}^3/\text{g}$ , and 20.507 nm, respectively. The average pore diameter falls within the mesoporous range, confirming the existence of pores favourable for molecular diffusion and photocatalytic reactions (Fig. 6(b)). The H3 hysteresis loop suggests the presence of slit-shaped pores generated by the layered BiOBr structure and the porous  $\text{MBC}_{\text{Pre}}$  matrix. Although the surface area is moderate, the retained pore volume and

mesoporous architecture indicate that the composite maintains an accessible porous network after BiOBr deposition. The mesoporous structure is expected to enhance PC adsorption, facilitate mass transfer, and improve the accessibility of photocatalytic active sites, thereby contributing to the overall photocatalytic performance of the composite.

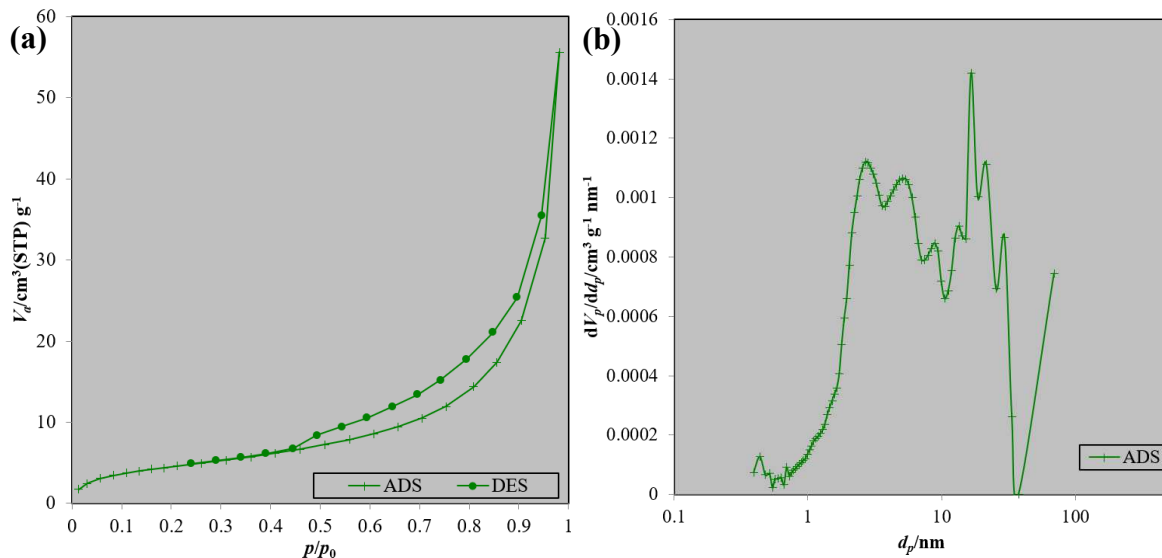


**Fig. 6 (a)** BET Adsorption/Desorption isotherm **(b)** Pore size distribution plot of MBC<sub>Pre</sub>BiOBr

UV–Vis diffuse reflectance spectrum of MBC<sub>Pre</sub>BiOBr in Fig. 7(a) revealed significant light absorption throughout the UV and visible regions, demonstrating its suitability as a solar-responsive photocatalyst. Tauc plot (Fig. 7(b)) analysis yielded a band gap energy of approximately 2.168 eV, indicating that the photocatalyst can be readily activated under visible-light irradiation. The reduced band gap may be attributed to the formation of interfacial interactions between BiOBr (~2.8 eV) [30], and the carbonaceous matrix, which introduce additional energy states and facilitate charge transfer. Such modifications enable easier excitation of electrons and improve the utilization of the visible portion of the solar spectrum. Consequently, MBC<sub>Pre</sub>BiOBr exhibits enhanced photoresponsiveness.

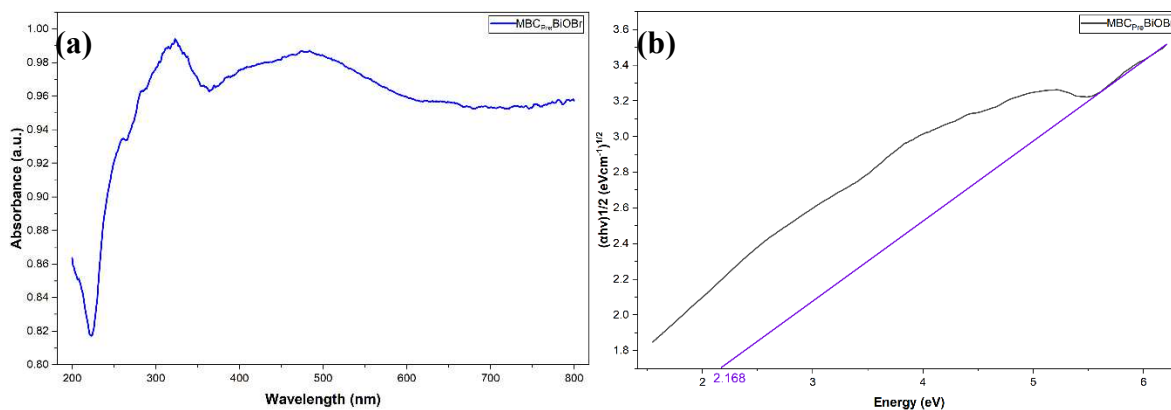


**Fig. 7 (a)** UV–Vis diffuse reflectance spectrum **(b)** Tauc plot of MBC<sub>Pre</sub>BiOBr

The  $pH_{pzc}$  was found to be approximately 4.9 as observed in Fig. 8. At solution pH values below 4.9, the composite surface becomes positively charged due to protonation of surface hydroxyl groups, whereas deprotonation above pH 4.9 results in a negatively charged surface. The relatively low  $pH_{pzc}$  can be attributed to the presence of oxygen-containing functional groups inherited from the BC matrix and surface hydroxyl species associated with BiOBr. This surface charge behaviour plays an important role in PC adsorption and photocatalytic degradation.

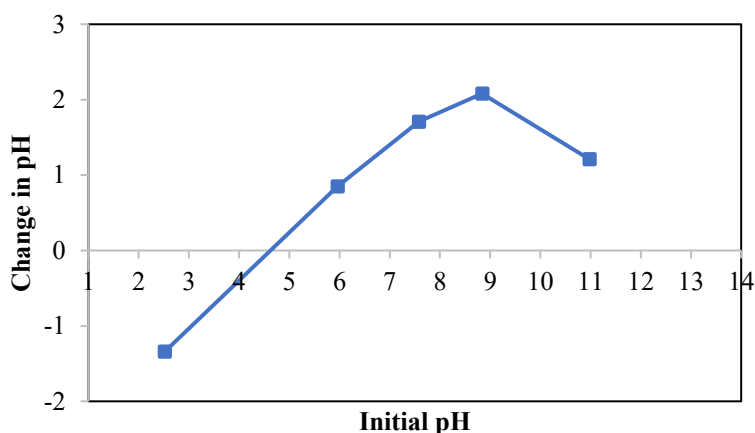


**Fig. 8** Change in pH vs Initial pH of MBC<sub>Pre</sub>BiOBr

### 3.2. Solar Photocatalytic Degradation of PC using MBC<sub>Pre</sub>BiOBr

As observed in Fig. 9 The degradation efficiency increased progressively with irradiation time, reaching complete removal of PC within 30 min under direct sunlight with intensity around 90000 to 100000 lux. Simultaneously, the TOC removal efficiency increased from 10% at 5 min to 94% at 30 min. Throughout the reaction, the degradation efficiency remained higher than the TOC removal efficiency, indicating the formation of intermediate

organic species during photocatalytic oxidation. The rapid disappearance of PC during the initial stages was followed by gradual oxidation of the generated intermediates into smaller molecules and ultimately  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The high TOC removal achieved at 30 min demonstrates that  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  possesses excellent mineralization capability rather than merely transforming PC into secondary products. The enhanced performance can be attributed to the synergistic effects of PC adsorption by the mesoporous  $\text{MBC}_{\text{Pre}}$ , efficient sunlight-driven charge generation by BiOBr, and improved charge separation at the  $\text{MBC}_{\text{Pre}}-\text{BiOBr}$  interface

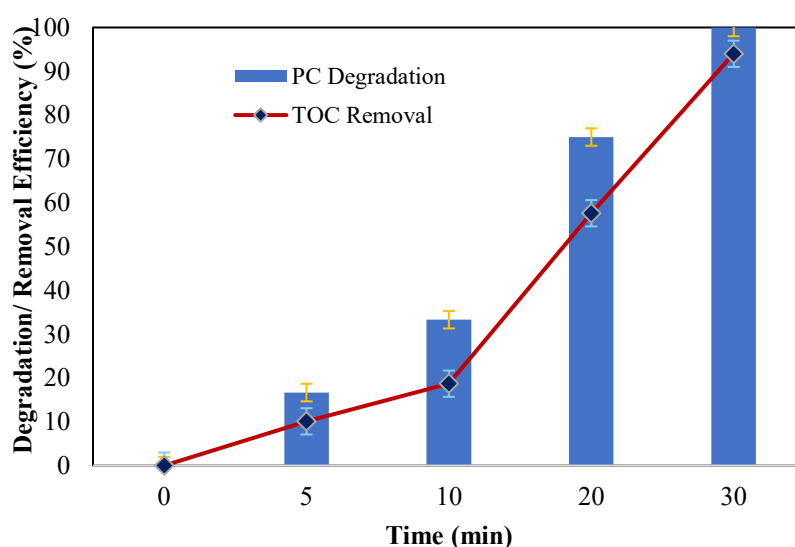


**Fig. 9** Solar photocatalytic degradation of PC using  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  at various interval

### 3.3. Effect of operating parameters on PC degradation

#### 3.3.1. Effect of pH

In Fig. 10(a), the degradation efficiency (54.17%) and TOC removal (21.14%) were the lowest due to the highly acidic (pH 3) environment, which suppresses the generation of ROS and reduces the interaction between PC molecules and the photocatalyst surface. At pH 5, the degradation efficiency increased to 66.67% and TOC removal to 44.27%, indicating improved radical formation and enhanced photocatalytic activity. The optimum performance was achieved at pH 7, where complete degradation of PC (100%) and maximum TOC removal (94.74%) were observed, owing to the favorable surface charge conditions and efficient generation of reactive species responsible for pollutant oxidation and mineralization. At pH 9, although degradation remained high (95.80%), TOC removal decreased to 83.18%, suggesting the formation and persistence of intermediate organic compounds during mineralization. Further increasing the pH to 11 reduced degradation

efficiency to 87.50% and TOC removal to 67.40%, likely due to the scavenging of photogenerated holes and changes in photocatalyst surface properties under strongly alkaline conditions, which hindered the overall photocatalytic process.

### 3.3.2. Effect of $\text{MBC}_{\text{Pre}}\text{BiOBr}$ dosage

The effect of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  dosage on the solar photocatalytic degradation of PC and TOC removal was investigated in the range of 0.25–1.0 g/L as shown in Fig. 10(b). At a dosage of 0.25 g/L, the degradation efficiency and TOC removal were 58.33% and 26.39%, respectively, due to the limited availability of active sites and lower generation of ROS. Increasing the dosage to 0.5 g/L significantly enhanced the degradation efficiency to 83.33% and TOC removal to 62.14%, indicating improved adsorption of PC molecules and greater production of oxidative radicals. The highest performance was achieved at 1.0 g/L, where complete degradation of PC (100%) and substantial TOC removal (92.64%) were obtained. The enhanced performance at higher catalyst loading can be attributed to the increased number of active sites, which promote efficient light absorption and ROS generation.

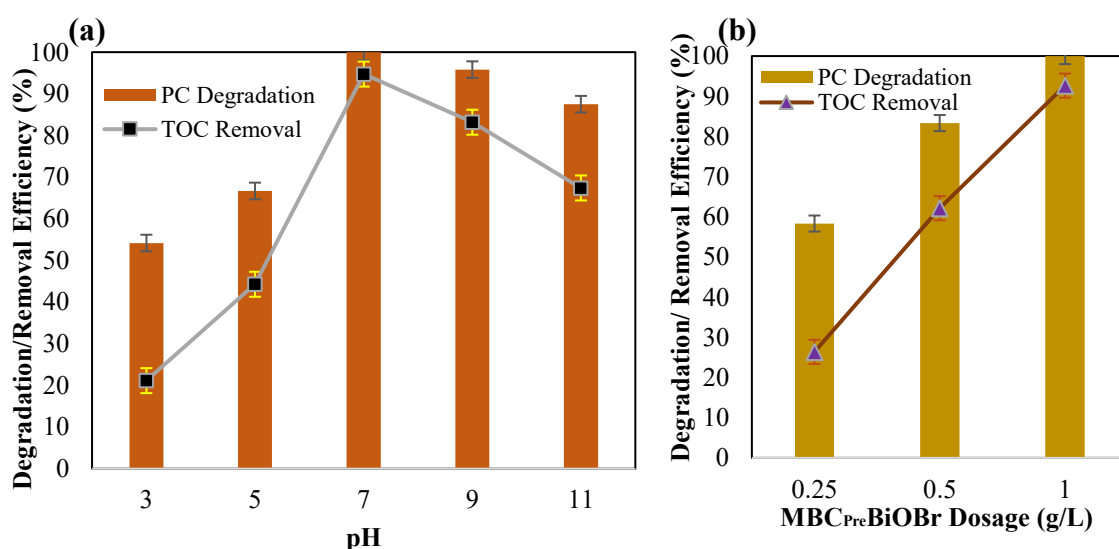


**Fig. 10** Effect of (a) pH, and (b)  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  dosage on degradation of PC and removal of TOC

### 3.4. Effect of inorganic ions on solar photocatalytic degradation and mineralisation of PC

The presence of cations inhibited the photocatalytic degradation of PC and TOC removal by  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  as depicted in Fig. 11(a).  $\text{Al}^{3+}$  showed the highest inhibition, reducing degradation efficiency to 21.17%, likely due to the precipitation of aluminium species on

the photocatalyst surface, which blocks active sites.  $\text{Ca}^{2+}$  caused moderate inhibition (67.67% degradation) by competing for adsorption sites and reducing pollutant-catalyst interactions.  $\text{Fe}^{3+}$  exhibited the least inhibition (87.00% degradation) but can react with photogenerated electrons to form  $\text{Fe}^{2+}$ , thereby suppressing hydroxyl radical ( $\bullet\text{OH}$ ) generation and reducing photocatalytic activity. Overall, the inhibitory effect followed the order  $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Fe}^{3+}$ .

Similarly, the presence of anions inhibited the photocatalytic degradation of PC and TOC removal by  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  as depicted in Fig. 11(b).  $\text{Cl}^-$  and  $\text{HCO}_3^-$  exhibited minimal inhibition, maintaining degradation efficiencies of 95.83% and 96.46%, respectively. However, bicarbonate can react with  $\bullet\text{OH}$  to form less reactive carbonate radicals, thereby reducing mineralization efficiency.  $\text{SO}_4^{2-}$  caused a slight reduction in degradation efficiency (93.33%) due to competition with PC molecules for active sites on the photocatalyst surface.  $\text{H}_2\text{PO}_4^-$  showed a stronger inhibitory effect, decreasing degradation efficiency to 83.33%, likely because phosphate ions adsorb strongly onto the photocatalyst surface and block active sites. The highest inhibition was observed in the presence of  $\text{NO}_3^-$ , which reduced degradation efficiency to 66.67% and TOC removal to 41.37%. This may be attributed to nitrate ions scavenging photogenerated electrons and reactive radicals, thereby suppressing the photocatalytic process. Overall, the inhibitory effect of the anions followed the order  $\text{NO}_3^- > \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-} > \text{Cl}^- \approx \text{HCO}_3^-$ .

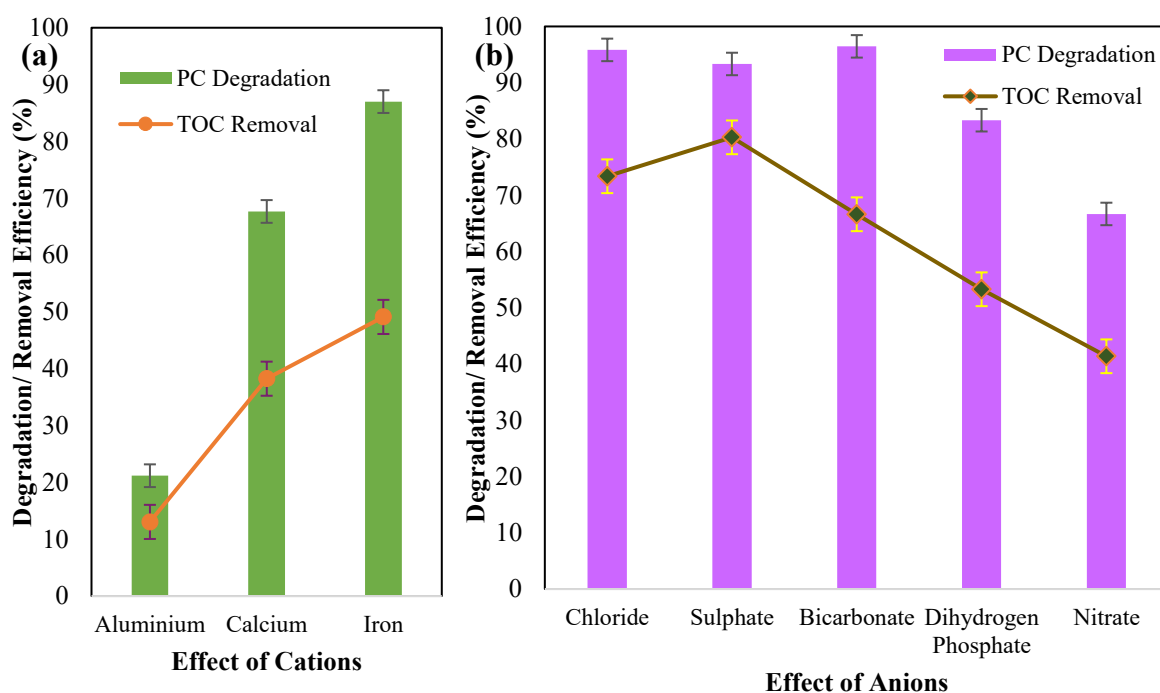


**Fig. 11** Effect of presence of (a) cations and (b) anions on photocatalytic degradation and mineralisation of PC

### 3.5. Degradation/Removal of PC and Coexisting Contaminants from Synthetic Greywater

The applicability of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  for treating synthetic greywater was assessed by monitoring the removal of PC, TOC, and selected inorganic ions under solar irradiation as shown in Fig. 12.  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  achieved 83.33% degradation of PC, confirming its effectiveness in degrading pharmaceutical contaminants in a complex water matrix. A TOC removal of 73.65% further demonstrated significant mineralization of PC and its transformation products. Among the inorganic constituents, nitrate showed the highest removal efficiency (63.92%), followed by sulphate (40.43%) and phosphate (25.33%). The simultaneous reduction of organic and inorganic contaminants highlights the potential of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  as an effective photocatalyst for greywater treatment under direct sunlight.

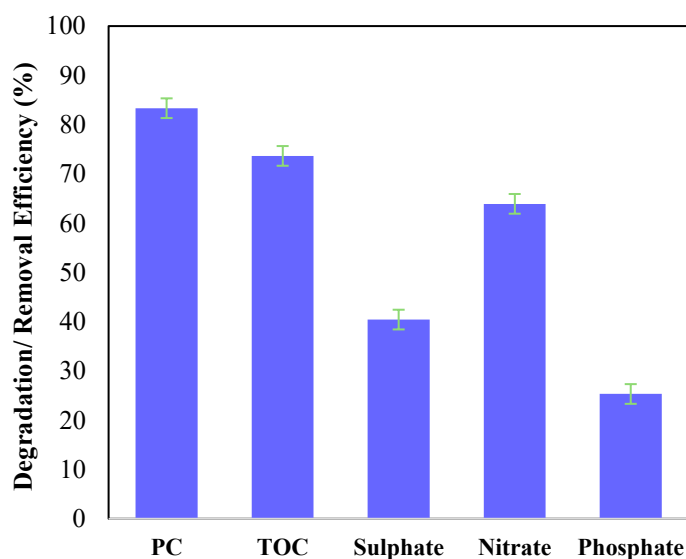


**Fig. 12** Performance of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$  for synthetic greywater treatment under solar irradiation

### 3.6. Reusability study

$\text{MBC}_{\text{Pre}}\text{BiOBr}$  maintained consistent photocatalytic performance over four sequential cycles, with less than a 10% decline in PC degradation efficiency and TOC removal by the fourth cycle (Fig. 13). This indicates the exceptional stability and reusability of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$ , demonstrating its potential for practical applications. The slight decrease in performance may be attributed to the accumulation of degradation byproducts on the

MBC<sub>Pre</sub>BiOBr surface, resulting in partial blockage or saturation of the available active sites.

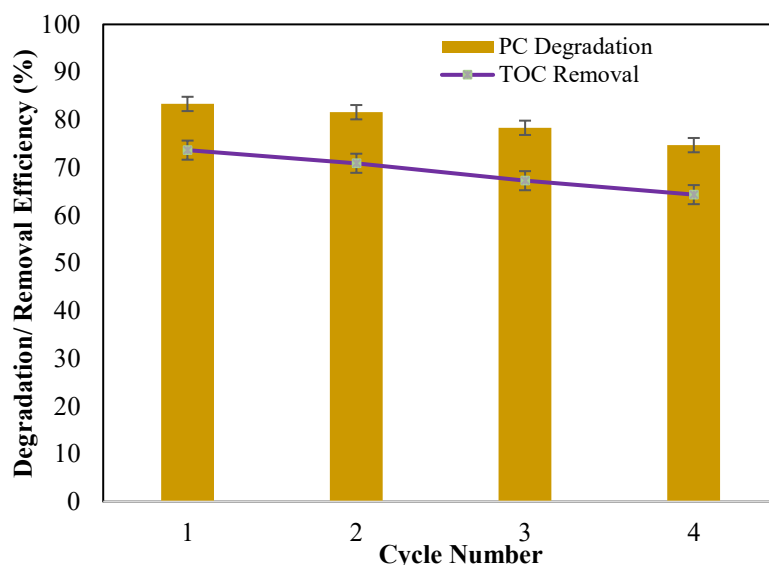


**Fig. 13** Reusability study of MBC<sub>Pre</sub>BiOBr to degrade PC and remove TOC

### 3.7. Plausible Degradation Mechanism of PC by MBC<sub>Pre</sub>BiOBr

The solution pH significantly influences the adsorption and photocatalytic degradation of PC by MBC<sub>Pre</sub>BiOBr due to the combined effects of the photocatalyst surface charge ( $\text{pH}_{\text{zpc}} = 4.9$ ) and the ionization state of PC ( $\text{pK}_a = 9.3$  [31]). At pH 3 ( $\text{pH} < \text{pH}_{\text{zpc}}$ ), the photocatalyst surface is positively charged, while PC remains predominantly neutral. Excess  $\text{H}^+$  ions compete with PC for the available active sites, resulting in poor adsorption (4.17%) and limited degradation (54.17%). When the pH increases to 5 and 7 ( $\text{pH}_{\text{zpc}} < \text{pH} < \text{pK}_a$ ), the catalyst surface becomes negatively charged whereas PC remains in its neutral molecular form, promoting adsorption through hydrogen bonding,  $\pi$ - $\pi$  interactions with the BC matrix, and van der Waals forces. The increased adsorption enhances the availability of PC at the catalyst surface, where photogenerated electrons ( $\text{e}^-$ ) and holes ( $\text{h}^+$ ) react with dissolved  $\text{O}_2$  and  $\text{H}_2\text{O}/\text{OH}^-$  to generate superoxide ( $\bullet\text{O}_2^-$ ) and hydroxyl ( $\bullet\text{OH}$ ) radicals. These ROS attack PC, ultimately leading to mineralization into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and other intermediates. Consequently, maximum degradation (100%) and TOC removal (94.74%) are achieved at pH 7. Under alkaline conditions ( $\text{pH} > 9.3$ ), PC is deprotonated to its anionic form while the catalyst surface remains negatively charged, resulting in electrostatic repulsion that decreases adsorption (20.83% at pH 9 and 8.33% at pH 11) [32]. This reduced adsorption, together with less efficient surface reactions, lowers the degradation efficiency and mineralization. Overall, neutral pH provides the

optimum balance between adsorption and ROS generation, making photocatalytic degradation the dominant mechanism for PC treatment.

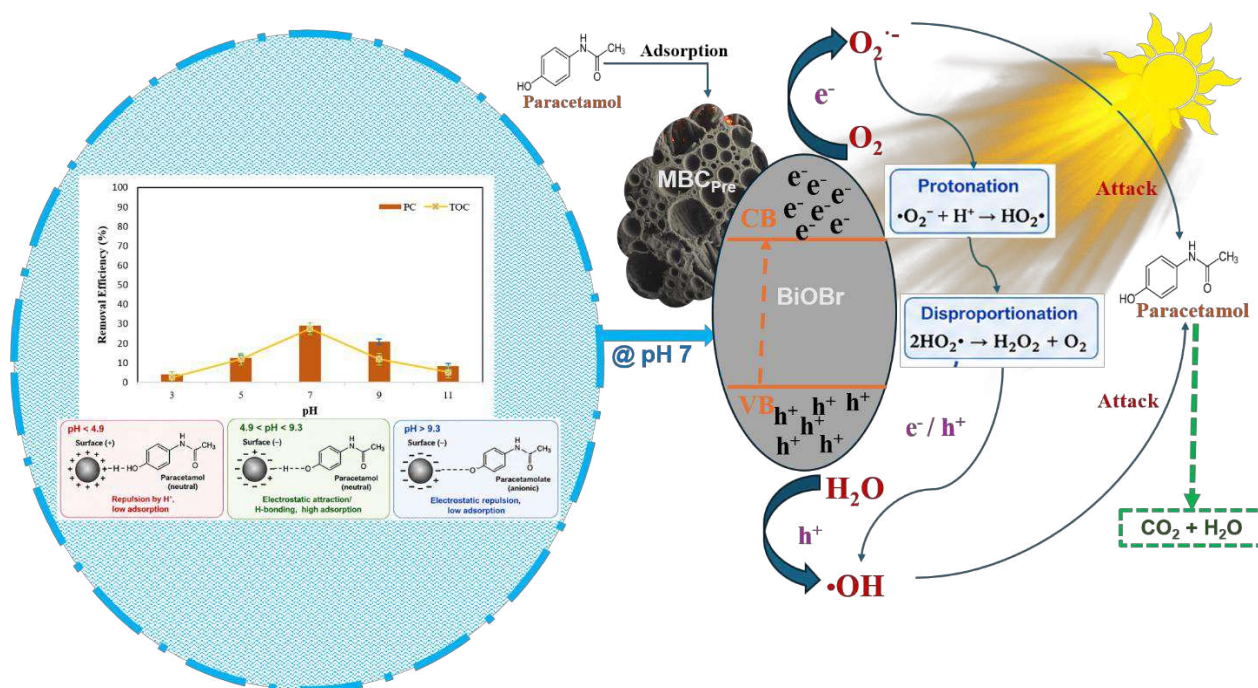


**Fig. 14** Plausible mechanism for solar photocatalytic degradation of PC over the MBC<sub>Pre</sub>BiOBr nanocomposite

#### 4. Conclusion

Solar-responsive pre-magnetized water hyacinth biochar-supported bismuth oxybromide nanocomposite (MBC<sub>Pre</sub>BiOBr) was successfully synthesized via microwave-assisted pyrolysis for the efficient removal of paracetamol from aqueous solution and greywater. The incorporation of BiOBr onto the porous magnetic biochar improved visible-light absorption (band gap of 2.17 eV) and provided abundant active sites for photocatalytic reactions. Under the optimum operating conditions, complete degradation of paracetamol was achieved within 30 min under sunlight, while the photocatalyst also exhibited excellent mineralization efficiency and satisfactory tolerance towards common coexisting ions. The pH-dependent study revealed that neutral conditions favoured adsorption and enhanced ROS generation, confirming that adsorption followed by photocatalytic oxidation is the dominant removal mechanism. Furthermore, the photocatalyst effectively treated greywater by simultaneously degrading PC and reducing organic and inorganic contaminants, while maintaining appreciable reusability after repeated cycles. The

utilization of invasive water hyacinth as a biochar precursor, coupled with the magnetic recoverability and solar-driven photocatalytic performance of  $\text{MBC}_{\text{Pre}}\text{BiOBr}$ , highlights its potential as an environmentally friendly and cost-effective material for decentralized greywater treatment and the removal of emerging pharmaceutical contaminants.

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### **Ethical Approval**

Not applicable

### **Clinical Trial Registration**

Not applicable, as this study does not involve clinical trial participants or interventions.

### **Plant Guidelines**

The water hyacinth (*Eichhornia crassipes*) plant material used in this study was collected from a naturally occurring/wild population. The collection was carried out in accordance with applicable local and national guidelines and regulations governing the collection and use of plant materials. The collection did not involve any protected or endangered plant species. No specific permissions or licences were required for the collection of the plant material used in this study.

### **Consent to Participate**

Not applicable

### **Consent to Publish**

Not applicable

### **Statements & Declarations**

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### **Competing Interests**

The authors declare no competing financial or non-financial interests related to this study.

### **Data Availability Statement**

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

### **Author Contributions**

Upasana Priyadarshini: Conceptualization, Methodology, Data curation, Experiments, Validation, Formal analysis, Writing – original draft. Remya Neelancherry: Supervision, Writing – review & editing.