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Mahmoud Samy

Mansoura University

Mohamed Gar Alalm

Mansoura University

Ribh S. abodlal

Alexandria University

Ali El-Dissouky

Alexandria University

Mohamed N. Khalil

National Research, Centre

Ehab R El-Helow

Alexandria University

Tarek Khalil

Alexandria University

Ahmed Tawfik (✉ prof.tawfik.nrc@gmail.com)

National Research, Centre

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A novel *Corchorus olitorius*-derived biochar/Bi₁₂O₁₇Cl₂ photocatalyst for decontamination of antibiotic wastewater containing tetracycline under natural visible light

Mahmoud Samy¹, Mohamed Gar Alalm¹, Ribh S. abodlal², Ali El-Dissouky², Mohamed N. Khalil³, Ehab R El-Helow⁴, Tarek El-Sayed Khalil², Ahmed Tawfik^{3©}

¹Department of Public Works Engineering, Faculty of Engineering, Mansoura University, Mansoura 35516, Egypt

²Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

³Water Pollution Research Department, National Research, Centre, P.O. Box 12622, Giza, Egypt

⁴Department of Botany and Microbiology, Faculty of Science, Alexandria University,

The 1st, 3rd and 8th author is equally contributed

Herein, a novel composite of *Corchorus olitorius*-derived biochar and Bi₁₂O₁₇Cl₂ was fabricated and utilized for the degradation of tetracycline (TC) in a solar photo-oxidation reactor. The morphology, chemical composition, and interaction between the composite components were studied using various analyses. The biochar showed a TC removal of 52.7% and COD mineralization of 59.6% using 150 mg/L of the biochar at a pH of 4.7±0.5, initial TC concentration of 163 mg/L, and initial COD of 1244 mg/L. The degradation efficiency of TC increased to 63% and the mineralization ratio to 64.7% using 150 mg/L of bare Bi₁₂O₁₇Cl₂ at a pH of 4.7±0.5, initial TC concentration of 178 mg/L, and COD of 1034 mg/L. In the case of

© Corresponding author : Ahmed Tawfik (prof.tawfik.nrc@gmail.com)

biochar/Bi₁₂O₁₇Cl₂ composite, the degradation efficiency of TC and COD mineralization ratio improved to 85.8% and 77.7% due to the potential of biochar to accept electrons which retarded the recombination of electrons and holes. The synthesized composite exhibited high stability over four succeeding cycles. According to the generated intermediates, TC could be degraded to caprylic acid and pentanedioic acid via the frequent attack by the reactive species. The prepared composite is a promising photocatalyst and can be applied in large-scale systems due to its high degradation and mineralization performance in a short time besides its low cost and stability.

The wide use of pharmaceuticals (e.g., antibiotics) for suppressing bacterial growth in humans and animals results in the uncontrolled release of antibiotics into the aquatic ecosystem ^{1,2}. Tetracycline (TC), an antibiotic, is continuously used in anti-infective treatment due to its low-cost and broad effectiveness towards various types of bacteria ³. The increase of TC residues in aquatic life causes the development of tetracycline-resistant bacteria that can lead to the deterioration of human health ⁴. Traditional treatment processes (e.g., biological treatment, adsorption, membrane filtration) cannot efficiently remove tetracycline due to its poor biodegradability and stability as well as the traditional technologies are expensive and produce secondary pollutants ⁵. Thus, it is fateful to control the release of antibiotics (e.g., tetracycline) to water streams via the development of an efficient and low-cost treatment technology.

Recently, advanced oxidation processes (AOPs) have exhibited excellent performance towards the degradation of refractory pollutants (e.g., antibiotics) ⁶. However, some AOPs (e.g., Fenton, ozonation) are costly and generate secondary contaminants which obstruct the full-scale application ⁷⁻⁹. Photocatalysis process, one of the AOPs, is featured by its inexpensiveness, green

and sustainable nature and effective degradation and mineralization performance towards bio-resistant pollutants via the generated reactive oxygen species (ROS) which qualify this technique to be implemented on a larger scale ^{10,11}. Nonetheless, the conventional photocatalysts such as TiO₂ and ZnO have some flaws such as the wide bandgap and rapid reunite of charge carriers which inhibit the efficient degradation of bio-resistant pollutants and the utilization of large portion of solar intensity ^{12,13}. Therefore, it is imperative to design an efficient photocatalyst with a narrow bandgap and reduced recombination rate which contributes to the efficient degradation of pollutants and enhances the practical implementation of photocatalysis process.

Bismuth oxychloride (Bi₁₂O₁₇Cl₂) photocatalyst has gained remarkable attention due to its ability to be utilized in photocatalysis process under visible light irradiation as well as its stability, excellent oxidation potential and non-toxicity ^{14,15}. However, the degradation performance by Bi₁₂O₁₇Cl₂ is modest because of the inefficient separation of electrons and holes ¹⁶. To overcome the aforementioned issue, researchers have fabricated Bi₁₂O₁₇Cl₂-based heterojunction photocatalysts to suppress the concourse between charge carriers such as AgI/Bi₁₂O₁₇Cl₂ ¹⁷, BiOBr/Bi₁₂O₁₇Cl₂ ¹⁸ and Bi₁₂O₁₇Cl₂/β-Bi₂O₃ ¹⁹. However, the preparation of these heterojunction photocatalysts increases the cost of treatment and the consumption of toxic chemicals.

Herein, dry stalks of *Corchorus olitorius* were compiled from the waste of food industry facility in Egypt and converted to a biochar via the pyrolysis in a muffle furnace under free-oxygen conditions followed by the preparation of a novel biochar/Bi₁₂O₁₇Cl₂ heterojunction. The employment of a composite of Bi₁₂O₁₇Cl₂ and carbonaceous material has not been extensively studied, as only a few studies reported the preparation of carbonaceous materials/Bi₁₂O₁₇Cl₂

heterojunctions. Zhou et al. (2018) synthesized a composite of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and carbon-doped carbon nitride for the degradation of tetracycline and the degradation rate in the case of case of the composite was higher than that of bare $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ by 2.9 times ¹⁴. The preparation of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite can participate in improving the photodegradation performance due to the potential of biochar to act as an electron acceptor which inhibits the recombination between the charge carriers ²⁰. Further, introducing biochar can improve the adsorption capacity of the composite due to the expected high surface area and porosity of the biochar ²¹. Additionally, the treatment cost can be reasonable in the case of using the biochar instead of the above-mentioned materials in $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ -based heterojunction photocatalysts due to the availability of *Corchorus olitorius* produced from the food industry. On the other hand, converting *Corchorus olitorius* wastes to biochar contributes to solving the problems associated with their management and decreases the dependance on landfills. The disposal of wastes into landfills results in the contamination of soil, groundwater and air ²². Thus, the utilization of biochar in photocatalysis process not only enhances the degradation performance, but also reduces the environmental hazards related to the improper management of solid waste.

In this study, a novel composite of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and *Corchorus olitorius*-derived biochar was fabricated and employed in photocatalysis process for the degradation of tetracycline. The degradation of tetracycline using $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, the synthesized biochar and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite was carried out under different doses to determine the optimum doses. Further, the recyclability performance of the composite and the degradation mechanism were studied. Additionally, the generated intermediates were recognized, and the degradation pathways were suggested.

Materials and methods

Materials and chemical

Sodium hydroxide (NaOH, 97%) was procured from Fisher chemical, Ltd. Absolut ethanol (C₂H₆O, 100%) and bismuth chloride (BiCl₃, 97%) were obtained from Emplura, Ltd and Alpha Chemika, respectively. Fresh *Corchorus olitorius* stalks were harvested from the wastes of food industry facility in Giza, Egypt. Real industrial effluents were compiled from a pharmaceutical industrial facility in Giza, Egypt. The collected wastewater was left for 24 h to provide the time for suspended solids to settle, then samples were decanted. The characteristics of the wastewater are provided in Table 1.

Table 1 Characteristics of real pharmaceutical wastewater.

Parameter	Min.	Max.	Average	STDEV
pH value	4.3	5.1	4.7	0.5
COD _t (mg/L)	1034	1244	1139	122.7
COD _s (mg/L)	934	988	961	67.8
COD _p (mg/L)	100	256	178	10.7
Tetracycline (mg/L)	163	178	170.5	15.7

Preparation of *Corchorus olitorius*-derived biochar and biochar/Bi₁₂O₁₇Cl₂ composite

Dry stalks of *Corchorus olitorius* were harvested from the wastes of food industry facility located in Giza, Egypt. The preparation of biochar from *Corchorus olitorius* started by drying the stalks at room temperature for 24 h, followed by grinding the stalks to a fine powder and washing with distilled water to remove any impurities. Subsequently, the powder was dried in an oven at 60 °C, followed by sieving using a 425 µm mesh sieve and pyrolyzing the powder for 2 h at 600 °C in a muffle furnace in the absence of oxygen. After cooling the biochar at room temperature, the prepared biochar was activated by adding 50 g of the biochar in 1000 mL of orthophosphoric

acid (H_3PO_4 , 0.3 M) and stirring for 30 min at 100 °C, followed by washing with distilled water until pH reaches neutral. Afterwards, the particles were dried in an oven at 100 °C for 30 min before being pyrolyzed in a muffle furnace at 550 °C for 30 min.

$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst was freshly prepared according to the method previously reported by Ma et al. (2021)²³. 1.62 g of bismuth chloride was dissolved in 20 mL of absolute ethanol. The mixture was stirred for 30 min, then 20 mL of 1.2 M NaOH was added to the solution in a drop-wise manner. The mixture was further stirred for 3.0 h and the solid powder was formed and filtered to harvest the catalyst. The obtained $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst powder was dried at a temperature of 60°C for 6.0 h under vacuum conditions.

To prepare the biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite, 0.951 g of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and 3.0 mg of the prepared biochar were added to 20 mL of absolute ethanol. The mixture was then stirred for 1.0 h at a temperature of 60 °C. Subsequently, the catalyst particles were filtered and dried in an oven at a temperature of 60 °C for 6.0 h under vacuum.

Experimental details

The experiments were executed in a solar photo-oxidation reactor with parabolic light collectors. The details of the reactor are described by Text S1 & Fig.S1). Firstly, the adsorption performance of the prepared biochar was investigated over 6 h using 100 mg/L of the biochar. Then, the effect of biochar dose was studied by varying the biochar dose from 50 to 200 mg/L under the optimum contact time. Additionally, the photocatalytic performance of bare $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite was explored over 6 h using 100 mg/L of both materials. Then, the effect of catalyst dose of the two materials was studied by varying the dose from 50 to 175 mg/L under the optimized time. Additionally, the reusability of the composite was tested via

the usage of the same catalyst dose under five repetitive cycles. The catalyst particles were gathered after each run, then dried at room temperature for 24 h prior the following run.

Analytical methods

The Fourier transfer infrared spectroscopy (FT-IR) data were measured on a Perkin-Elmer FT-IR Spectrophotometer (FT-IR 1650) to specify the functional groups of the synthesized materials.

The spectra were recorded in the range of $400 - 4000\text{ cm}^{-1}$. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were performed to study the morphology and chemical composition of the prepared materials using a JEOL-SEM operating at an accelerating voltage of 20.00 kV equipped with EDS spectrometer. The crystal structure of the prepared materials was explored using an XRD; Bruker-AXS D8, Germany. Further, X-ray photoelectron spectroscopy (XPS) was used to specify the oxidation states and elemental composition of the synthesized materials using XPS, Thermo Scientific™ K-Alpha™ with Al-K α micro-focused monochromator operated at an energy range up to 4 KeV. Additionally, the elemental composition and surface area of the biochar were determined using an X-ray fluorescence (XRF, Axios-Advanced sequential WDXRF spectrometer) and BET surface area (BET Belsorp-max automated), respectively. Further, the bandgap of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite was estimated using UV-visible spectrometer (Jasco, V-630 UV-Vis spectrophotometer) based on Tauc plot method.

The concentration of TC was estimated using a Shimadzu UV-Vis spectrophotometer (Jasco, V-630 UV-Vis spectrophotometer) at a wavelength of 357 nm and the generated intermediates were recognized using liquid chromatography-mass spectroscopy (LC-MS, Shimadzu 2020) using acetonitrile (50%) and water (50%) at a flow rate of 0.2 mL/min. Chemical oxygen

demand of samples was determined using the standard method in (Standard Methods for the Examination of Water and Wastewater) ²⁴.

Computational modeling

Biochar adsorption mechanism with tetracycline was carried out by computational simulation model i.e. BIOVIA software. Graphite structure was used to have the 3D structure of the biochar derived from *Corchorus olitorius* on the database.

Probably the graphite could represent the biochar model as reported earlier by ^{13,25,26}. The surface oxygen groups like COOH, OH and C=O were added to the surface of graphite structure to study the effect of biochar activation on adsorption of tetracycline. 3D structures of tetracycline were downloaded from PubChem and optimized with BIOVIA Forcite before adsorption onto biochar. The binding energy of biochar with tetracycline was estimated using Eq. 1 ²⁷.

$$\Delta E = E_{\text{Biochar}@x} - E_{\text{Biochar}} - E_x \quad (1)$$

where, ΔE : is the binding energy, $E_{\text{Biochar}@x}$: is the total energy of complex (biochr@tetracycline), E_{Biochar} is the biochar energy, and E_x : is the tetracycline energy

Results and discussion

Characteristics of *Corchorus olitorius*-derived biochar

Fig.1a. shows the SEM image of the prepared biochar indicating that the morphology is vessel-like with high porosity suggesting its high adsorption ability. The diffraction peak between 20°-30° are imputed to the diffraction plane (002) of the graphite confirming its carbon content as shown in the XRD pattern in Fig. (1b) ¹³. Additionally, other diffraction peaks are indexed to the metal oxides (e.g., SiO₂, CaO, MgO) in the prepared biochar detected by XRF as described in Fig. (1c) ²⁸. The sharp peak at 26.7° is attributed to SiO₂ ²⁸. The XRF analysis of biochar shows

the oxides existed in the biochar and their weight ratios as depicted in Fig. (1c). The surface area of the synthesized biochar is 277.6 m²/g suggesting the high adsorption performance of the biochar.

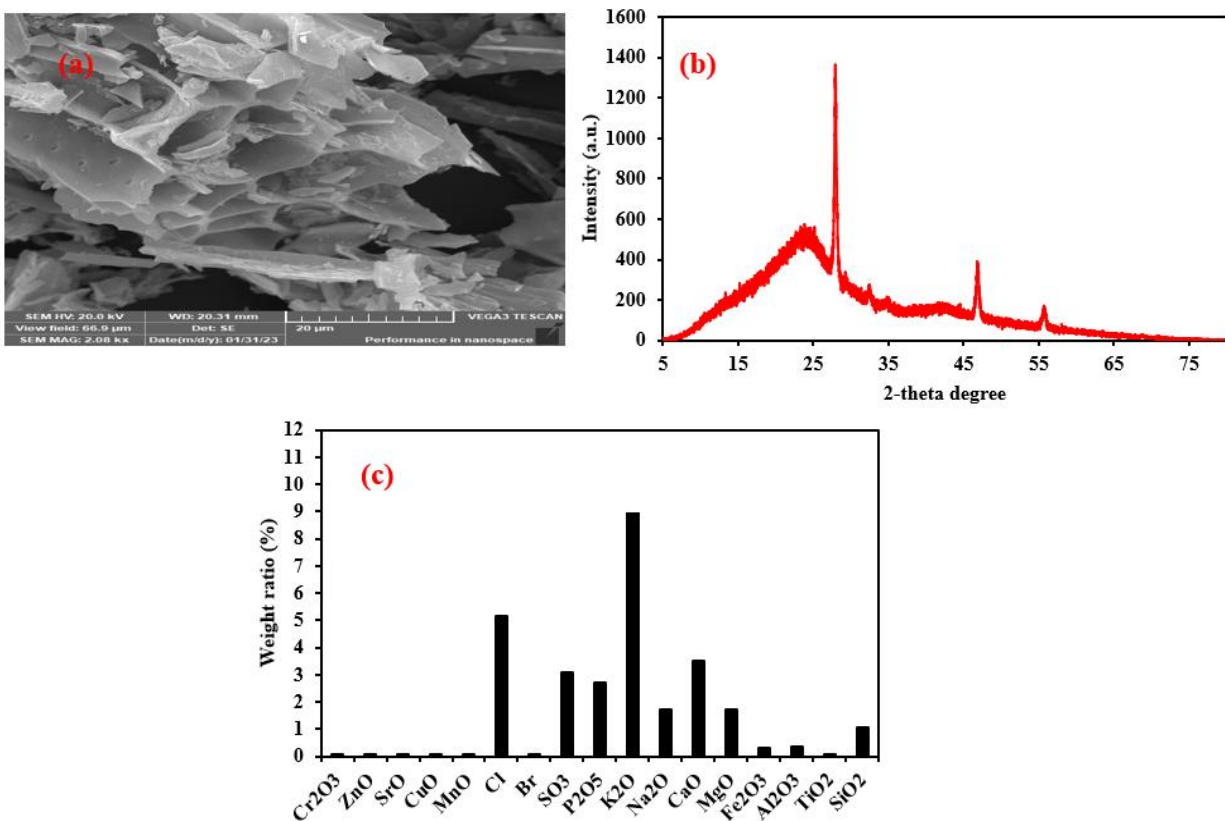


Figure 1. SEM (a), XRD (b) and XRF (c) of the biochar derived from *Corchorus olitorius*.

Bi₁₂O₁₇Cl₂ catalyst and biochar/Bi₁₂O₁₇Cl₂ composite characteristics

The chemical groups in the bare Bi₁₂O₁₇Cl₂ and biochar/Bi₁₂O₁₇Cl₂ composite were determined by Fourier transform infrared (FT-IR) spectrum as depicted in Fig. (2a). The bands at 3438.57 cm⁻¹, (1622.22 cm⁻¹, 1469.84 cm⁻¹), 1392.82 cm⁻¹, 846.4 cm⁻¹ and 528.8 cm⁻¹ in the case of pristine Bi₁₂O₁₇Cl₂ are owing to O-H bond, water molecules, Bi-Cl stretching vibration, O-Bi-O bending vibration, and Bi=O bending vibration, respectively ^{14,29}. A slight shift in the bands in the case of biochar/Bi₁₂O₁₇Cl₂ to 3435.37 cm⁻¹, 1626.56 cm⁻¹, 1471.02 cm⁻¹, 1393.9 cm⁻¹, 846.5 cm⁻¹ and 530.3 cm⁻¹ was observed due to the incorporation of the biochar.

194 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses
 195 of the $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ are presented in Figs. (2b,c,d,e) to show the
 196 morphology and chemical constituents of the catalysts. The particle size of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ was
 197 39.02 nm (Fig.2b), whereas the particle size decreased to 22.799 nm in the case of
 198 biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (Fig. (2c). Further, Fig. (2b,c) shows that $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ particles are in the form
 199 of spheres and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ particles have flower-like structure. The change in the
 200 morphology in the case of the composite compared to the morphology in the case of pure
 201 materials affirmed the interaction between the biochar and pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$.

202 Fig. (2d,e) depicts the EDX pattern of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ showing that there
 203 is no carbon in the case bare $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, whereas carbon mass ratio was 9.66% in the case of
 204 biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ confirming the loading of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst on the prepared biochar. The
 205 mass ratios of Bi in the $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ /biochar composite were 70.06 and
 206 65.97% respectively. The Cl mass ratio was 9.39% in the case of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst and
 207 increased to 10.76 in the case of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$. The mass ratio of oxygen is 8.11% in the
 208 case of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst and 7.55% in the case of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$. The EDX analysis
 209 strongly insures the elemental composition of bare $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite
 210 and the excellent interaction between the biochar and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$. The XRD patterns of
 211 $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ /biochar are illustrated in Fig. (3a). The main peaks observed
 212 at 24.01° , 25.86° , 32.49° , 46.4° , 48.1° , 53.8° and 58.3° are imputed to (113), (115), (200), (2012),
 213 (220), (315) and (317) diffraction planes of the tetragonal $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (JCPDS No. 37-0702) ³⁰. In
 214 the case of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, no significant diffraction peaks were observed compared to the
 215 XRD pattern in the case of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, which might be due to the high dispersion of the
 216 catalyst particles on the biochar surface as well as the small content of biochar in the composite

³¹. The bandgap of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite was estimated Fig. (3b) as reported by He et al. (2015) ¹⁹. The bandgap was 2.9 eV in the case of bare $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and decreased to 2.7 eV in the case of the composite due to the interaction between the biochar and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ phases which could result in the formation of new energy level above the valence band or above the conduction band ^{11,32}. The reduction of bandgap in the case of the composite confirms the role of biochar to narrow the band gap which improved the utilization of solar light.

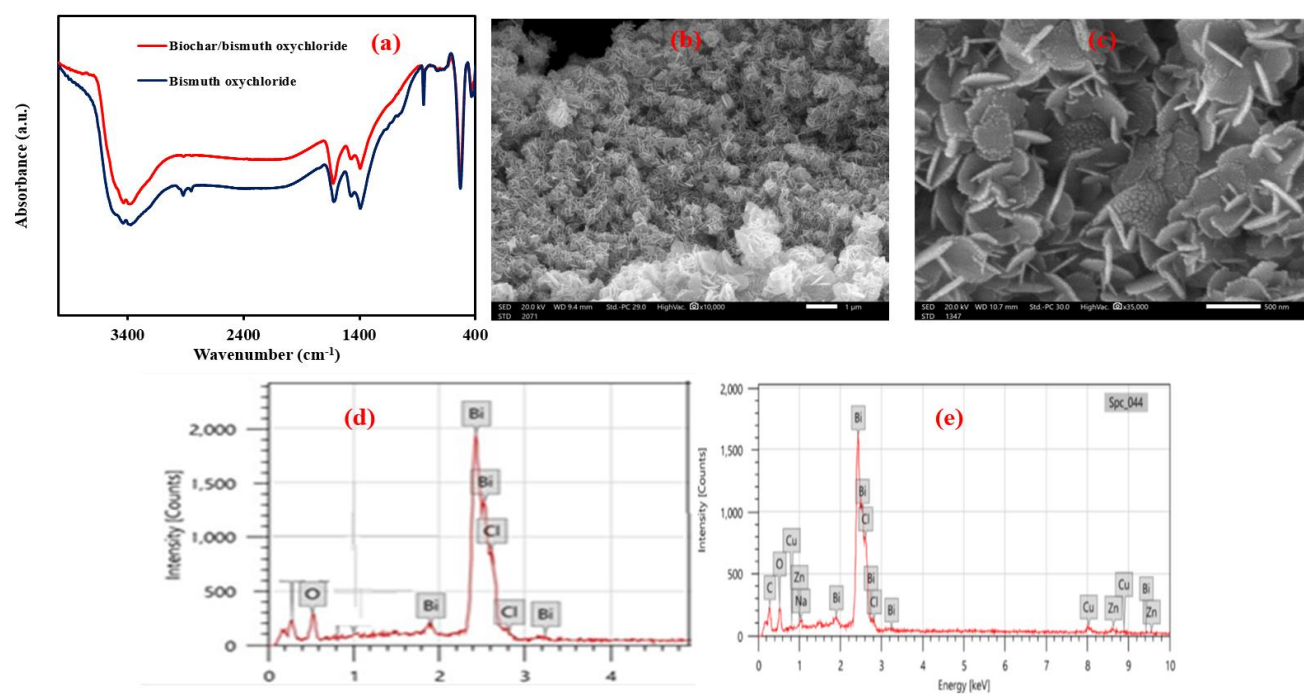


Figure 2. (a) Fourier transform infrared spectrum (FTIR) for $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, scanning electron microscope (SEM) for (b) $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and (c) biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, energy dispersive X-ray spectroscopy (EDX) for (d) $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and (e) biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$.

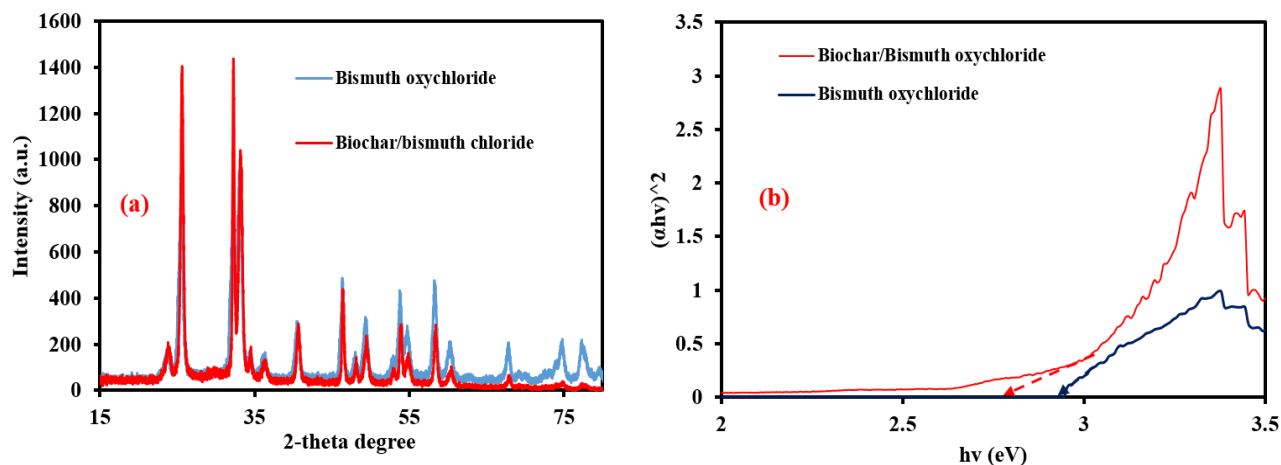
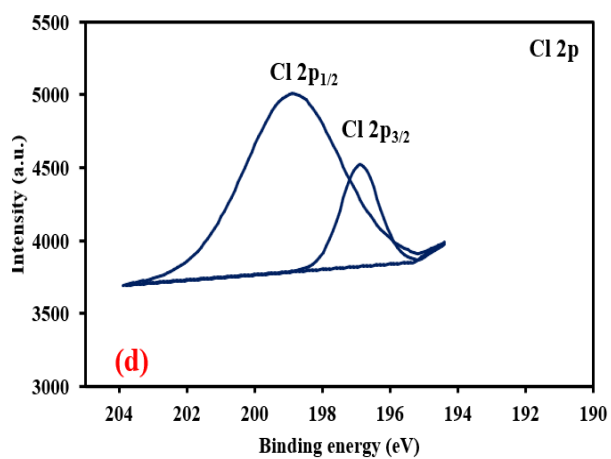
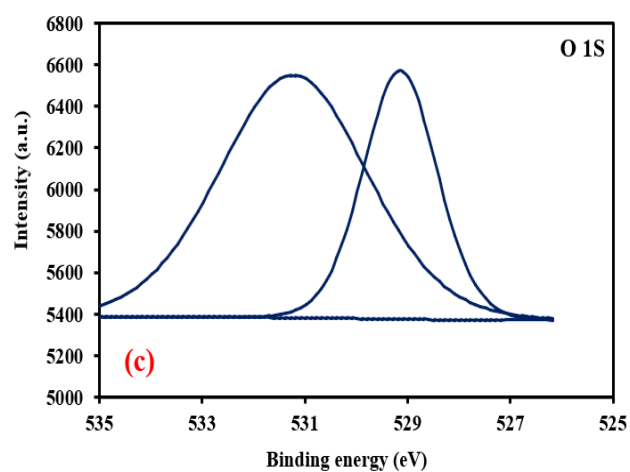
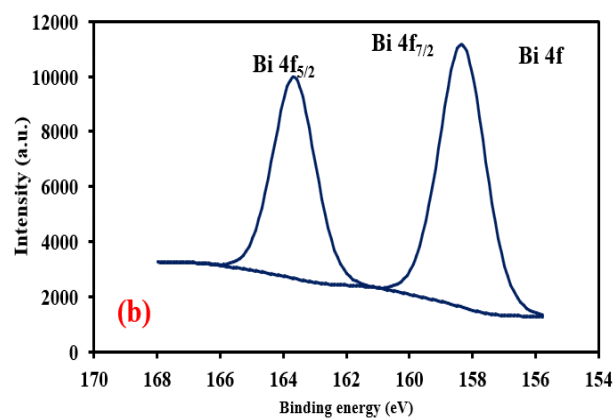
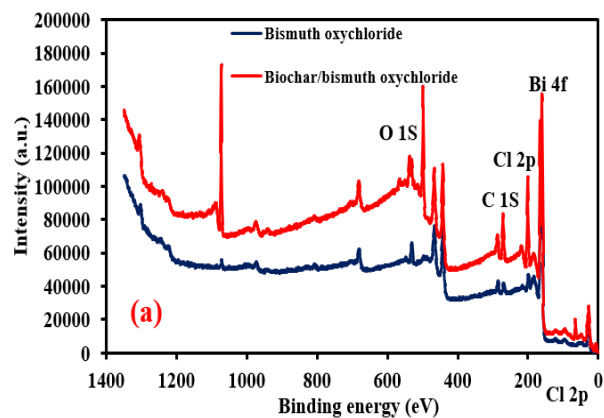


Figure 3. (a) XRD patterns and (b) bandgap of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite

X-ray photoelectron spectroscopy (XPS) analysis for $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ was carried out to show the chemical states of the elements on the catalysts' surface (Fig. 4). XPS survey in Fig. (4a) reaffirmed the growth of Bi, O, Cl and C in the case of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ which confirmed the excellent interaction between the prepared biochar and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$.

The peaks with binding energies at about 158.33 and 163.66 eV are assigned to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively for $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst, whereas the peaks at 160.28 and 165.56 eV are imputed to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively in the case of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ composite confirming the presence of Bi^{3+} species as shown in Fig. (4b,e) ³³. The peaks at 198.82 and 196.93 eV are ascribed to Cl $2p_{1/2}$ and Cl $2p_{3/2}$, respectively in the case of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, while the peaks for Cl $2p_{1/2}$ and Cl $2p_{3/2}$ are at 199.49 and 200.7 eV, respectively in the case of the composite ensuring the presence of Cl as depicted in Fig. (4d, g) ³⁴. Additionally, the peaks at around 529 eV and 530 eV are imputed to O 1s in Bi-O-Bi bond and O-H bond in the case of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (Fig. (4c, f) ³. Further, the peaks at nearly 287 eV and 284 eV are assigned to C 1s of C-C bond in the biochar in the case of the composite which affirmed the interaction between the components of the composite as given in Fig. (4h) ¹⁴.



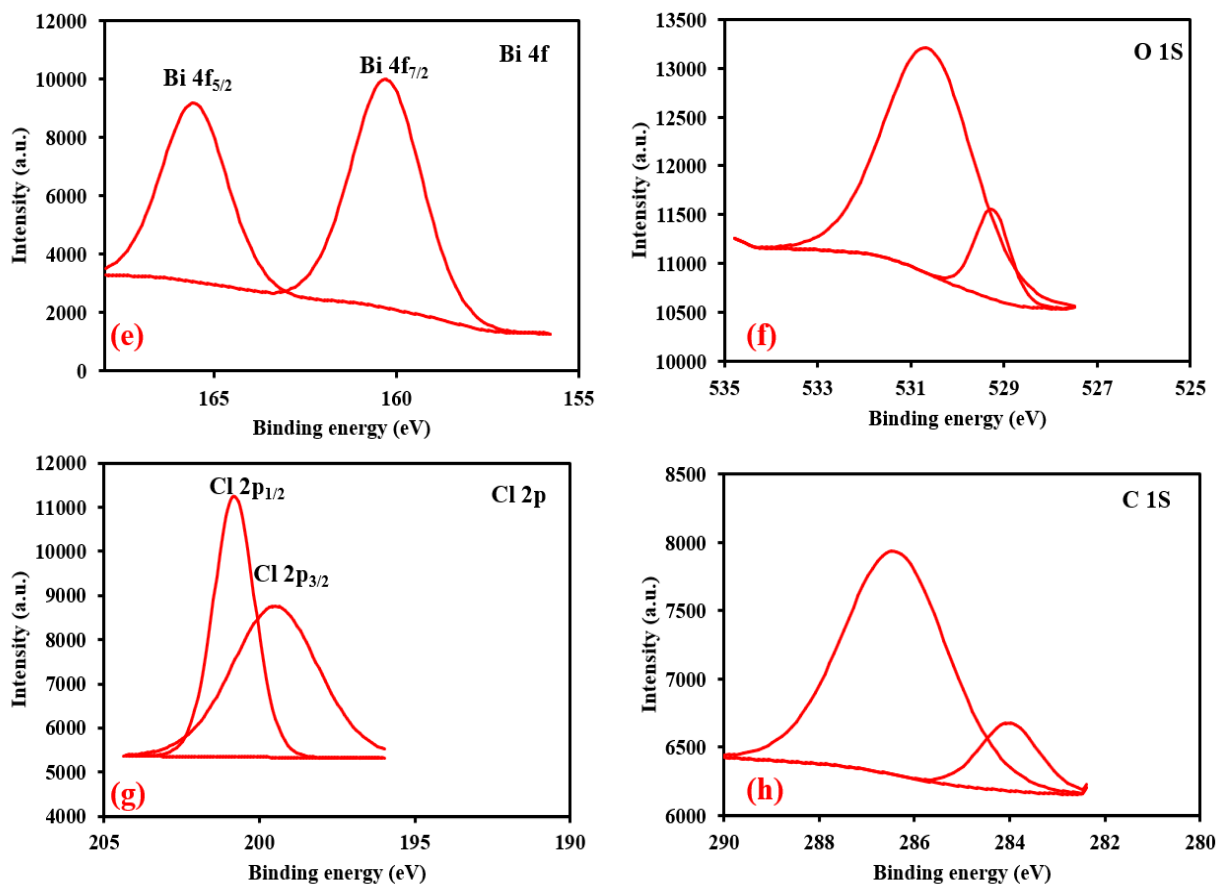


Figure 4. (a) XPS survey spectra of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ and biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, (b) Bi 4f, (c) O 1S and (d) Cl 2p spectra of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$; (e) Bi 4f, (f) O1S, (g) Cl 2p and (h) C 1S spectra of biochar/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$.

Investigation of the prepared biochar performance for removing tetracycline

Figure (5a) shows the removal of TC and the concentration of the generated intermediates over 6 h using 100 mg/L of the prepared biochar at $\text{pH } 4.7 \pm 0.5$, initial TC concentration of 163 mg/L and COD of 1244 mg/L. The removal efficiencies of tetracycline and COD were 37% and 48.15%, respectively after 5 h, whereas they were only 38.2% and 48.4% after 6 h indicating that the optimum contact time was 5 h. After 5 h, the biochar's surface and pores might be saturated by the adsorbed TC molecules^{35,36}. Therefore, the removal of TC after 5 h was limited. Additionally, the removal of TC by the biochar could be due to the generated reactive radicals

that would be generated as a result of the excitation of metal oxides (e.g., TiO_2 , Fe_2O_3 , MgO) in the biochar as explained in the XRF analysis¹³. However, the metal oxides weight ratios are low. Therefore, the removal of biochar was mainly due to adsorption. According to the proposed degradation pathways described in the next sections based on the generated by-products detected by LC-MS, TC could be degraded to simpler by-products such as caprylic acid and pentanedioic acid as a result of the frequent attack by the generated reactive radicals. The concentrations of the generated caprylic acid and pentanedioic acid were 1.77 mg/L and 2.2 mg/L after 5 h, while TC concentration decreased from 163 mg/L to 102.6 mg/L at the same time. The low concentration of the generated by-products was due to the modest degradation by the limited number of reactive radicals generated via the illumination of metal oxides on the biochar's surface which affirmed that most of TC molecules were adsorbed on the biochar's surface.

Prior optimizing the contact time, different biochar doses (50-200 mg/L) were investigated to specify the optimum biochar dose at a reaction time of 5 h, pH 4.7 ± 0.5 , initial TC concentration of 163 mg/L and COD of 1244 mg/L as well as the concentration of the generated intermediates was estimated at different doses as demonstrated in Fig. (5b). The removal efficiencies of COD were 10.8%, 29.5%, 48.1%, 56.3%, 59.6% and 59.8%, while the removal ratios of TC were 11%, 12.3%, 37%, 44.9%, 52.7% and 52.9% at biochar doses of 50 mg/L, 75 mg/L, 100 mg/L, 125 mg/L, 150 mg/L and 200 mg/L, respectively. According to the results, the removal efficiency and COD mineralization percentages went up with raising the biochar dose due to the increase of adsorption sites as well as the increase of the generated radicals as a result of the increase of metal oxides. However, the removal efficiency remained approximately the same with increasing the biochar dose from 150 mg/L to 200 mg/L. The biochar particles might agglomerate with

increasing the biochar loading above 150 mg/L which could result in the decline of active area, thereby suppressing the expected higher removal at excessive biochar doses as reported by Mensah et al. (2022) and Salama et al. (2022)^{37,38}. The same trend was observed for the generated intermediates, where the concentration of the generated by-products increased from 0.9 mg/L to 3.9 mg/L in the case of caprylic acid and from 0.88 mg/L to 3.7 mg/L in the case of pentanedioic acid by raising the biochar from 50 mg/L to 150 mg/L, respectively, while the concentration of the generated nearly remained the same at biochar dose of 200 mg/L.

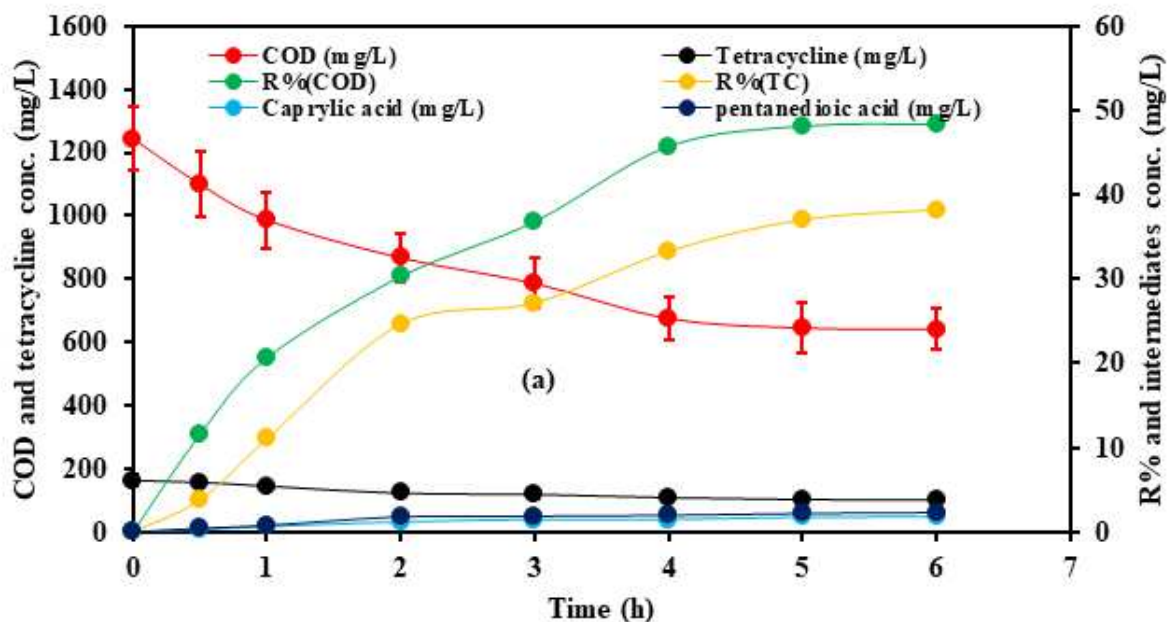


Figure 5. (a) Removal of TC and COD by the prepared biochar

Insert Figure 5(b)

Photodegradation of TC by $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ catalyst

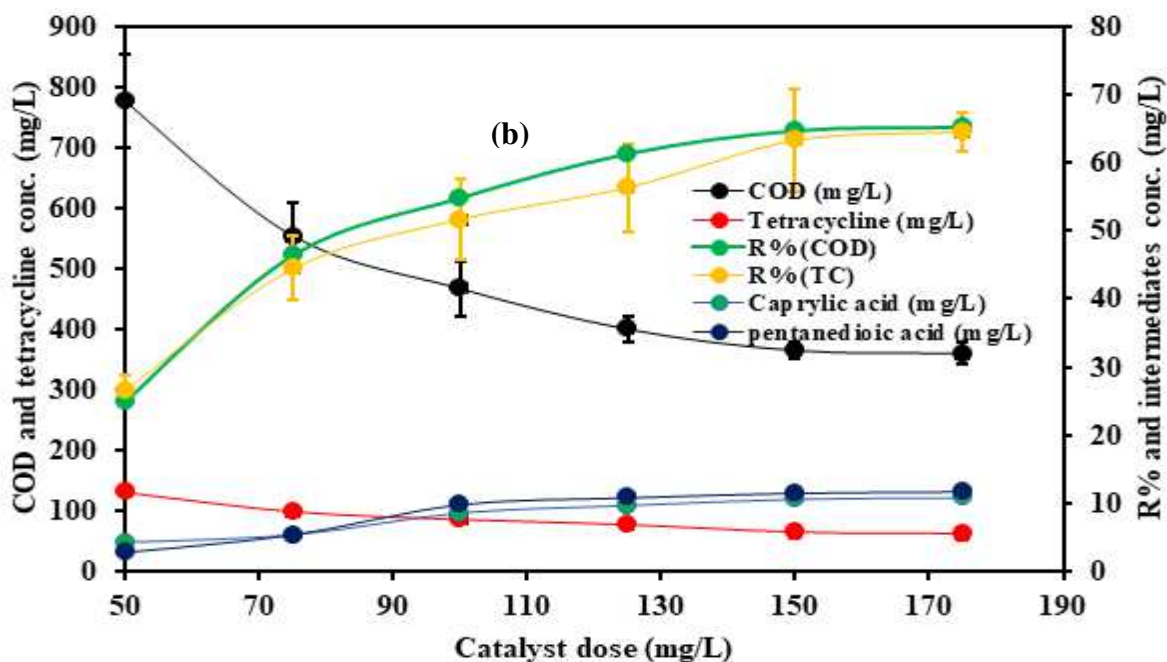
The degradation of TC and monitoring the concentration of the generated intermediates were attained using 100 mg/L of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ photocatalyst at $\text{pH } 4.7 \pm 0.5$, initial TC concentration of 178

300 mg/L and COD of 1034 mg/L as shown in Fig. (6a). The TC degradation and COD mineralization
301 percentages were 55% and 56.5%, respectively after 6 h, while TC and COD removal efficiencies
302 were 51.7% and 54.8% after 4 h. The slight increase of TC removal efficiency after extending the
303 time to 6 h might be due to the block of active sites with time as a result of the accumulation of
304 TC molecules and its intermediates on the catalyst's surface which resulted in the decrease of the
305 generated reactive radicals ³⁹. Additionally, the caprylic acid and pentanedioic acid concentrations
306 were 8.6 mg/L and 9.8 mg/L after 4 h, while they were 9 mg/L and 11.4 mg/L, respectively after 6
307 h. Therefore, the optimum reaction time was 4 h.

308
309 The optimum Bi₁₂O₁₇Cl₂ photocatalyst dose was determined by studying the catalyst dose in the
310 range (50-175 mg/L) at pH 4.7±0.5, initial TC concentration of 178 mg/L, reaction time of 4 h and
311 COD of 1034 mg/L as well as the by-products' concentrations were measured at the different
312 doses (Fig. 6b). The increase of catalyst dose from 50 mg/L to 150 mg/L resulted in the raising of
313 TC degradation efficacy from 26.6% to 63% and COD mineralization ratio from 24.9% to 64.7%,
314 while TC degradation ratio and COD mineralization percentage were 64.5% and 65.2% at a
315 catalyst dose of 175 mg/L. Raising the catalyst dose generally improved the degradation
316 performance due to the increase of active sites which could lead to the generation of more radicals,
317 thereby enhancing the degradation efficiency ⁴⁰. On the contrary, the rising of catalyst dose above
318 150 mg/L did not show a significant change in the degradation performance, as excessive increase
319 of the catalyst dose could raise the turbidity of the solution which might result in the scattering of
320 photons and the inactivation of most of the active sites ²⁰. Additionally, the agglomeration
321 between the catalyst particles might increase in the case of elevating the catalyst dose which
322 reduced the active sites leading to the inhibition of the accelerated degradation performance ⁴¹.

323 Regarding the by-products' concentrations, the caprylic acid and pentanedioic acid concentrations
 324 were 10.6 mg/L and 11.5 mg/L at a catalyst dose of 150 mg/L, whereas they were 10.8 mg/L and
 325 11.7 mg/L, respectively at a catalyst dose of 175 mg/L. Thus, the optimum catalyst dose was 150
 326 mg/L.

327 **Insert Figure 6 (a)**



328
 329 Figure 6. (b) effect of catalyst dose on the degradation performance with tracking the
 330 generated intermediates
 331

332 Photodegradation of TC by biochar/Bi₁₂O₁₇Cl₂ composite

333
 334 The degradation of TC and the concentration of the generated intermediates were studied at a
 335 composite dose of 100 mg/L, pH 4.7±0.5, initial TC concentration of 167 mg/L, reaction time of 6
 336 h and COD of 1044 mg/L as shown in Fig. (7a). TC removal efficiency was 73% after 3 h,
 337 whereas it was only 78.4% by prolonging the time to 6 h. Further, COD mineralization ratios were
 338 70.9% and 72.2% after 3 h and 6 h, respectively. Additionally, the caprylic acid and pentanedioic
 339 acid concentrations increased to 16.4 mg/L and 17.6 mg/L after 3 h and they were 19 mg/L and

21.4 mg/L, respectively after 6 h. According to the results, the optimum reaction time could be 3 h. As we explained in the above section, the degradation and mineralization ratios did not greatly change after extending the time due to the accumulated TC molecules and its intermediates on the composite's surface which blurred the active sites. The degradation efficiencies and mineralization ratios were higher in the case of the prepared hybrid than that of pure $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ under a shorter reaction time which could participate in reducing the treatment cost. The added biochar could accept electrons which improved the separation efficiency between electrons and holes. Additionally, the enhanced performance might be owing to the combined effects of adsorption and photodegradation.

The optimum composite dose was specified using various doses (50, 75, 100, 125, 150 and 175 mg/L) as well as the by-products' concentrations were specified at these values at pH 4.7 ± 0.5 , initial tetracycline concentration of 167 mg/L, reaction time of 3 h and COD of 1044 mg/L as given in Fig. (7b). The increase of composite dose to 150 mg/L raised the degradation efficiency of TC to 85.8% and COD mineralization ratio to 77.7% due to the increase of the generated radicals with elevating the catalyst dose. However, the increase of catalyst dose to 175 mg/L did not improve the degradation efficiency due to the aforementioned explanations (Light scattering and particle agglomeration). As a result, the caprylic acid and pentanedioic acid concentrations were 28.7 mg/L and 22.3 mg/L at catalyst dose of 150 mg/L, whereas their concentrations nearly remained the same in the case of raising the composite dose to 175 mg/L. Therefore, the optimum composite dose was 150 mg/L.

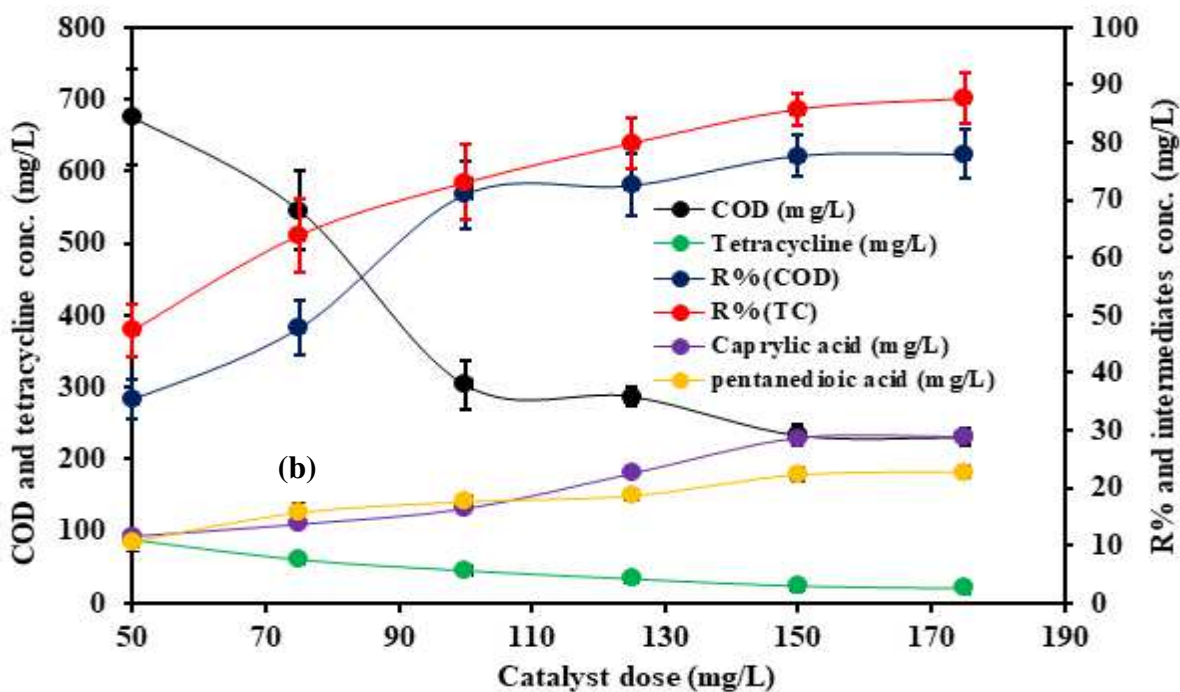
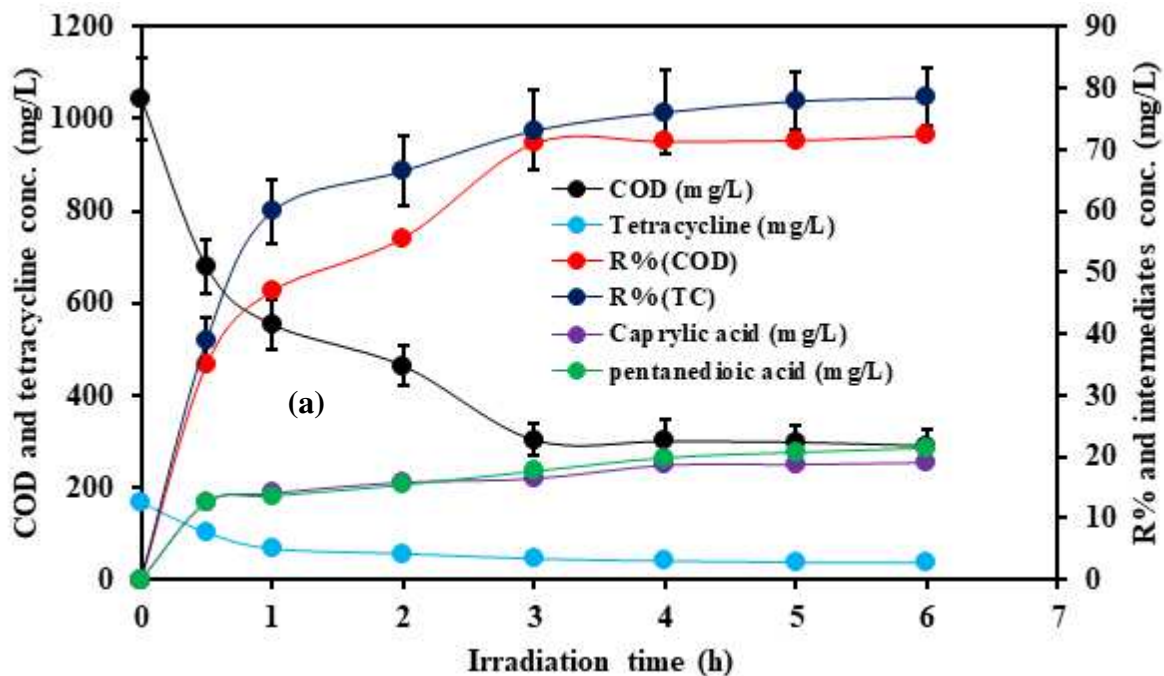


Figure 7. (a) Degradation of TC using the prepared composite and the concentration of the generated by-products with time and (b) effect of composite dose on the degradation performance and the concentration of the formed intermediates under different doses.

Reusability of the prepared composite

Assessing the recyclability of the prepared composite is essential to confirm the stability of the composite under a prolonged reaction time prior the full-scale application. Additionally, using the catalyst in successive cycles could reduce the treatment cost. To evaluate the reusability of the composite, the composite was tested under five succeeding cycles using different composite doses (50-175 mg/L) at pH 4.7 ± 0.5 , initial TC concentration of 167 mg/L and reaction time of 3 has given in Fig. (8). The degradation efficiency of TC was 85.8% in the first cycle and decreased to 52.7% is the fifth cycle in the case of composite dose of 150 mg/L, while the degradation ratio was 79.2% after the fourth cycle indicating the stability of the catalyst under four cycles. In the case of all doses, the degradation percentage started to greatly decrease after the fourth cycle. Thus, the prepared catalyst could be efficiently reused under four cycles. The decrease of degradation efficiencies with cycles might be due to the loss of catalyst particles during samples withdrawal. Moreover, the active sites might be blocked by the pollutant molecules and its intermediates which resulted in the suppression of radicals' generation.

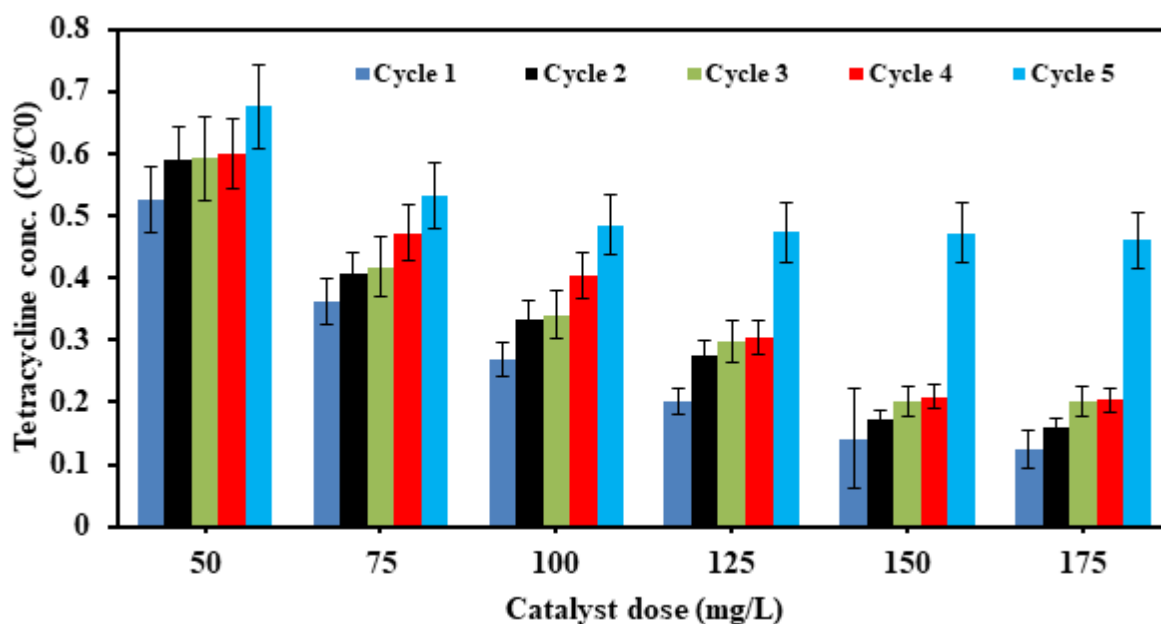


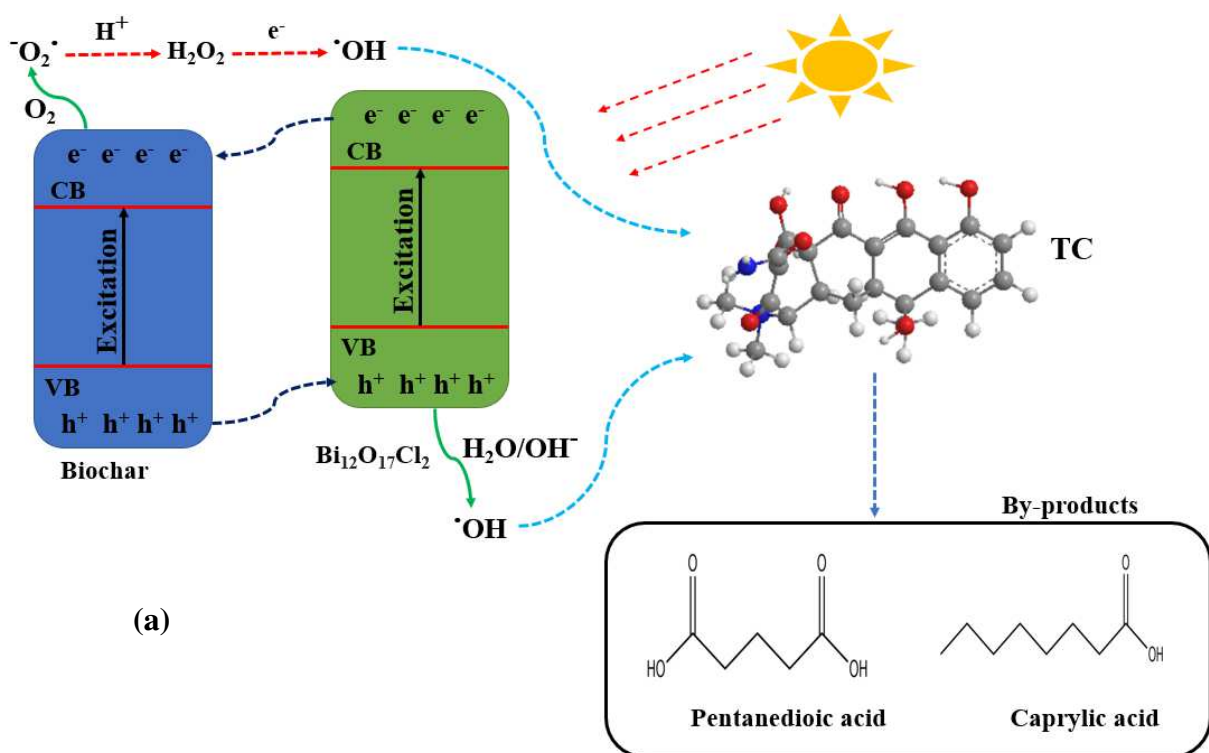
Figure 8. Reusability of the prepared composite at different doses in five succeeding cycles

Degradation mechanism and proposed degradation pathways

Prior the excitation of the composite, electrons and holes could be generated in the biochar and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, then the electrons in the conduction band (CB) of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ started to move the CB of the biochar and the holes in the valence band (VB) of the biochar transferred to the VB of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ which suppressed the recombination between charge carriers as shown in Fig. (9a). Then, the electrons and holes could react with oxygen and hydroxyl ions, respectively to form superoxide radicals and hydroxyl radicals, respectively. Then, the generated superoxide radicals could react with H^+ to form H_2O_2 which could further react with electrons to generate additional hydroxyl radicals¹⁴. For the bare $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, the electrons and holes could recombine rapidly. Thus, the composite showed higher performance. The continuous oxidation of TC by the generated radicals could convert TC to simpler intermediates such as Caprylic acid and pentanedioic acid.

The generated intermediates were identified using LC-MS and the degradation pathways were proposed according to the generated reactive radicals and their reaction with TC as shown in Fig. (S2). The degradation of TC (m/z 445, Fig. (S2a)) could start with the demethylation of TC to produce two by-products with m/z 403 and 417 (Fig. S2b,c)⁴². Additionally, the aromatic ring in TC could be cleaved to produce another intermediate with m/z 277 (Fig. S2b)⁴³. Then, the dehydroxylation, oxidation and C-C bond cleavage in the intermediates with m/z 277 and 403 could result in the formation of an intermediate with m/z 186 (Fig. S2b)⁴³. Additionally, the by-product with m/z 417 could be further attacked by the generated radicals leading to ring opening, dehydroxylation and carbonyl reduction, thereby forming the intermediates with m/z 174 and 194 (Fig. S2a)⁴². Then, the by-products with m/z 186, 174 and 194 could be further degraded to

411 simpler by-products with m/z 144 (Caprylic acid) and 132 (Pentanedioic acid) (Fig. S2b,c) via
 412 the attack of the generated radical, dehydroxylation and cleavage of C-C bonds. Fig. (9b) depicts
 413 the suggested degradation pathways.



414

415

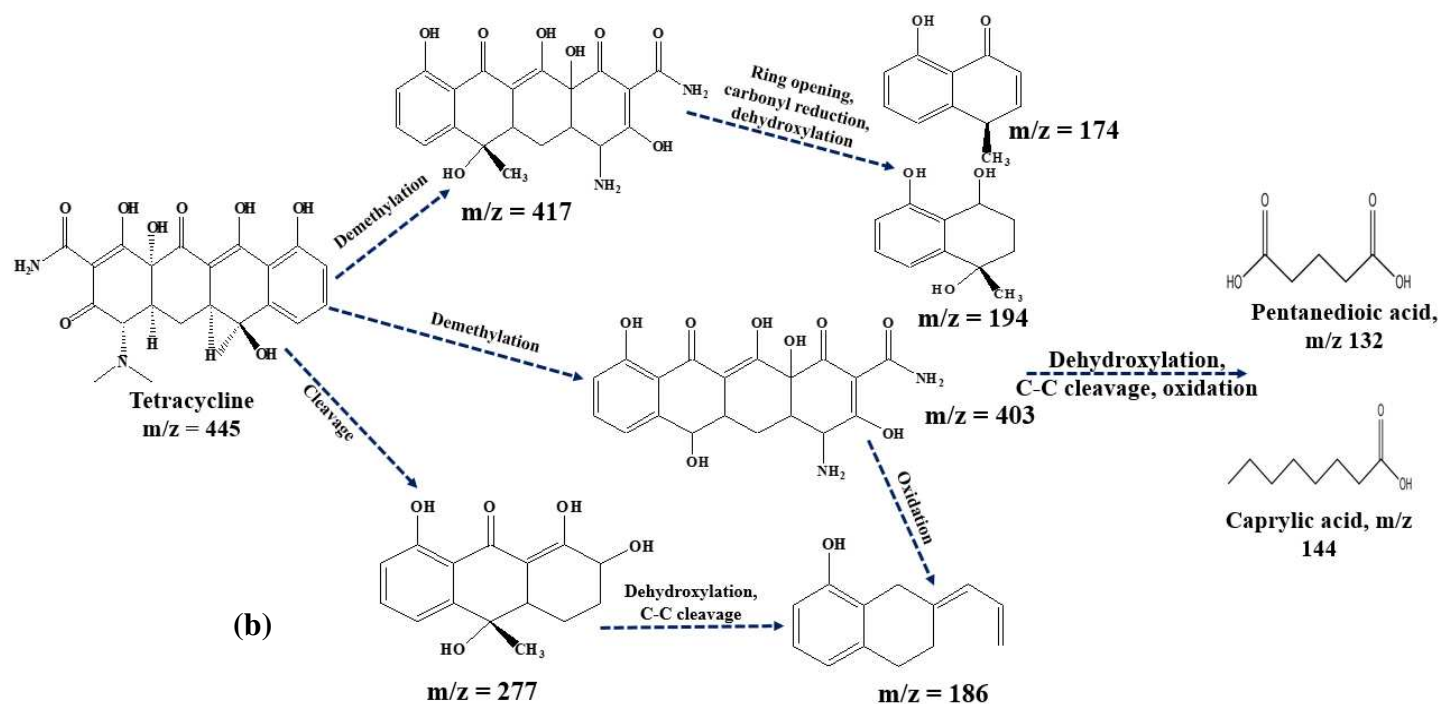


Figure 9. (a) Degradation mechanism of TC over biochar/Bi₁₂O₁₇Cl₂ and (b) proposed degradation pathways.

Computational modeling

The adsorption locator module in BIOVIA was used to quantify the adsorption energy between the prepared biochar (adsorbent) and tetracycline (adsorbate) and to study the effect of surface activation of biochar on the binding energy (Fig. 10), as reported earlier^{13,44}. According to the computational modeling results, biochar exhibited an adsorption energy of -28.68 kJ/mol, while surface activated biochar showed an adsorption energy of -38.86 kJ/mol to capture tetracycline. The adsorption energy increase in the case of activated biochar was due to the presence of numerous surface oxygen groups such as COOH, OH and C=O on the activated biochar surface. Also, in case of activated biochar, hydrogen bond was observed between H and O in tetracycline and the surface oxygen group of activated biochar.

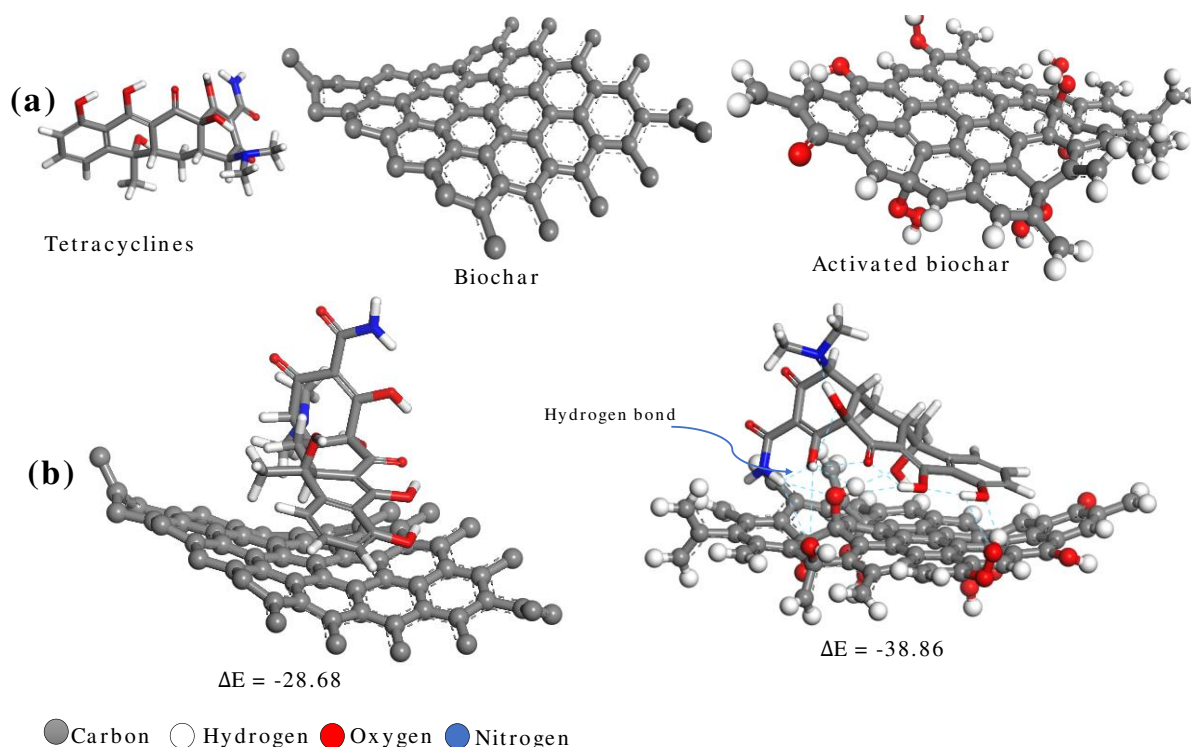


Figure 10. (a) The geometry optimized structure of Tetracycline, biochar, and surface activated biochar. (b) The adsorption of tetracycline on the surface of the biochar and surface activated biochar.

Conclusions

XRD, EDX, XPS and FTIR analyses affirmed the excellent fabrication of biochar/Bi₁₂O₁₇Cl₂ composite. The activation of biochar ameliorated the adsorption energy to capture TC. The optimum biochar dose was 150 mg/L, where the removal efficiencies of TC and COD were 52.7% and 59.6%, respectively within 5 h, while the degradation and mineralization ratios went up to 63% and 64.7%, respectively using 150 mg/L of pristine Bi₁₂O₁₇Cl₂. Biochar/Bi₁₂O₁₇Cl₂ showed higher degradation performance compared to the individual components due to the capability of the biochar to accept electrons which improved the separation efficiency between charge carriers. The prepared composite could be reused for four cycles efficiently, where the degradation efficiency was 85.5% in the first cycle and reduced to 79.2% in the fourth cycle. TC could be mineralized to caprylic acid and pentanedioic acid via oxidation, dehydroxylation, demethylation, ring opening and C-C cleavage. The efficient degradation performance, stability and low-cost provide the synthesized catalyst a superiority to be utilized in large-scale reactors for the mineralization of real industrial effluents.

Data availability

The datasets used and/or analyzed during the current study is available with the corresponding author up on request

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Mahmoud Samy: Writing original draft, Investigation, Writing review & editing; Mohamed Gar Alalm: Writing original draft, Investigation, Writing review & editing; Ali El-Dissouky: Conceptualization, Funding acquisition, Writing review & editing. Ribh S. abodlal: Methodology, writing original draft. Mohamed N. Khalil: Methodology. Ehab R El-Helow: Writing review & editing, Tarek El-Sayed Khalil: investigation, Writing review & editing; Ahmed Tawfik: Conceptualization, Funding acquisition, writing original draft, Investigation, Writing review & editing.

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.

603 **Plant guidelines**

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605 material, complies with relevant institutional, national, and international guidelines and
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