ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 27, No. 1 (2026) 460688c

http://doi.org/10.21743/pjaec/2026/460688c

Transforming Transformer Oil Waste: A Hybrid Biological–Oxidative Strategy for PCB Decontamination

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Received 23 June 2025, Revised 25 January 2026, Accepted 10 February 2026

Academic Editor: Huma Mudassar

Abstract

Polychlorinated biphenyls (PCBs) are dangerous and long-lasting chemicals that bioaccumulate in the food chain. The use of PCBs in transformer oil as heat-resistant compounds is widespread and has received more attention in recent years. This work used a sequential degradation methodology that combined an advanced oxidation mechanism with anaerobic biological treatment, indicating that these methods improved degradation efficiency and resulted in 100% PCB removal from industrial effluent containing transformer oils. Three alternative combinations were used: upflow anaerobic sludge blanket reactor (UASB) for 6 h followed by micro-bubble ozonation for 1 h, UASB for 6 h followed by the Fenton process for 1 h, and ozonation for 1 h followed by the Fenton process. Integrated approaches were shown to significantly reduce PCBs, with levels below detection in both the UASB and ozonation combinations, as well as the ozonation and Fenton combination. The Fenton method and upflow anaerobic sludge blanket reactor (UASB) reduced 2,4,5-trichlorobiphenyl to 0.3 and 2.4 µg/mL, respectively. The treatments significantly reduced chemical oxygen demand (COD). The UASB-ozonation combination reduced COD concentration from 785 mg/L to 364 mg/L, the UASB-Fenton combination reduced it to 407 mg/L, and the ozonation-Fenton combination achieved the greatest reduction, reaching 260 mg/L. The study demonstrated the degradation of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl. The initial concentration of PCBs in wastewater was 24.4 µg/mL for 2,4,5-trichlorobiphenyl and 12.1 µg/mL for 2,3,4-trichlorobiphenyl. However, after treatment, the value went below the detection limit due to an integrated treatment method. In the UASB-Fenton combination, the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were reduced to 2.4 and 0.3 µg/mL, respectively.

Keywords: Environmental chemistry, Environmental toxicology, Wastewater treatment, Transformer oil, PCBs, Sequential degradation

Introduction

The diversity and magnitude of synthetic hazardous chemicals released into the environment have resulted in enduring effects on human health and ecosystems. Polychlorinated biphenyls (PCBs) include a collection of harmful pollutants consisting of 209 distinct chlorinated organic compounds. PCBs persist in the environment due to their exceptional stability and significant hydrophobicity. These properties result in bioaccumulation, biomagnification, and bioconcentration within food chains, leading

to diverse health impacts in people and animals [1]. The persistent nature of PCBs in the atmosphere means that contaminated places, including grid stations, service areas, dumpsites, and sediments in adjacent water bodies, continue to have substantial effects on human health and the environment [2].

In Pakistan, despite being a member of the Stockholm Convention established in 2001, there is no formal monitoring protocol to assess and regulate PCB levels in diverse environmental contexts. PCBs are predominantly utilized in industrial applications, serving as insulators in transformer oil and as coolants, typically amounting to 4000 Mt·year^{-1}; the volume of transformer oil employed is around 1500 Mt·year^{-1} [3].

Diverse treatment methods have been employed for the degradation of PCBs, encompassing physical, chemical, and biological processes [4]. Conventional treatment approaches for PCB degradation, such as biological processes, are largely ineffective due to the resilient nature of the pollutants found in wastewater. There is a necessity to investigate the sequential degradation of PCBs utilizing Advanced Oxidation Processes (AOPs) in conjunction with biological methods for comprehensive degradation. AOPs are regarded as efficient and eco-friendly treatment technologies for the degradation of PCBs, facilitating their conversion into less toxic compounds. Enhanced degradation efficiency can be attained through the integration of sophisticated oxidation methods with biological therapies [5-7]. Nevertheless, considerations such as pollutant concentration, process limitations, and operational parameters must be considered when selecting the most appropriate oxidation treatment for the degradation of a certain contaminant. Various advanced oxidation processes, like the Fenton process and micro-bubble ozonation, can be integrated with biological therapies to attain comprehensive breakdown of PCBs into less hazardous chemicals [8]. Advanced oxidation degradation of PCBs is achieved through the production of free hydroxyl radicals from hydrogen peroxide utilizing several methods, including ultraviolet light, ultrasound, semiconductor photocatalysts, and Fenton's reagent [9].

However, limited additional research has been undertaken to provide an overview of the various types of integrated processes for wastewater treatment. The research aims to elucidate the integrated advanced oxidation methods for wastewater treatment. This study examines the integration of AOPs with anaerobic biological treatment to improve wastewater treatment efficiency and achieve complete destruction of PCBs.

Materials and Methods

Chemicals and Reagents

Trichlorobiphenyl (PCB No. 29), with a purity of 99.4%, a formula of $C_{12}H_7Cl_3$, and a molecular weight of 257.54, along with other necessary chemicals, was acquired from Sigma-Aldrich, located at 3050 Spruce Street, Saint Louis, MO 63103, USA. Sulfuric acid (95–97% purity), methanol, and n-hexane were acquired from Sigma-Aldrich.

Experimental Setup

Effluent waste oil, or wasted oil, was gathered from the transformer maintenance and repair sector in Multan, Pakistan. The sequential deterioration of wastewater was investigated through the application of advanced oxidation technologies alongside biological treatment. Three distinct

combinations were employed: Upflow Anaerobic Sludge Blanket Reactor (UASB) with Fenton process, UASB with micro-bubbles ozonation, and micro-bubbles ozonation combined with Fenton process. The attributes of the gathered sample were as follows: pH value of 7.96; electrical conductivity (EC) of 995 µS/cm; total dissolved solids (TDS) of 765 mg/L; chemical oxygen demand (COD) of 785 mg/L; and a concentration of 2,4,5-Trichlorobiphenyl at 24.4 µg/mL.

Upflow Anaerobic Sludge Blanket Reactor and Fenton Combination

Sequential degradation of PCBs was done using all processes in different combinations. In the first combination, the UASB reactor was combined with the ozonation process. For this, initially, the UASB reactor was fed with a nutrient solution for 2 months to produce granulation. Afterwards, wastewater containing transformer oil was fed into the UASB reactor. Wastewater sampling was done for 6 h. Sampling was done for each hour interval, and all physicochemical parameters were studied. Similarly, the concentration of PCBs was measured for all samples using GC-MS. After treatment of wastewater for 6 h, the wastewater was fed into the UV reactor for Fenton treatment. Wastewater was treated for 1 hr using Fenton treatment, and sampling was done after 10 min interval. All physicochemical parameters were analyzed, and PCB concentration was studied using GC-MS.

Upflow Anaerobic Sludge Blanket Reactor and Ozone combination

In a second combination, the UASB reactor and the ozonation process were combined. UASB reactor was activated using a nutrient solution for 2 months. Afterwards, wastewater containing transformer oil was fed into the reactor and was treated for 6 h. Sampling was done after a 1 h interval, and then all physicochemical parameters were analyzed, and the PCB concentration was measured using GC-MS. Then the effluent was fed into the ozonation column and was treated for 1 h. Finally, samples were collected after 10 min and all physicochemical parameters were studied and GC-MS analysis was performed.

Ozonation and Fenton Combination

In the third combination, wastewater was treated by the ozonation process for 1 h. Sampling was done after 10 min interval. All physicochemical parameters were analyzed, and the concentration of PCBs was measured using GC-MS. Then the effluent was transferred to the Fenton reactor. It was operated for 1 h, and sampling was done in intervals of 10 min. Similarly, all physicochemical parameters were analyzed, and PCB concentration was studied using GC-MS.

Analytical Procedures

Wastewater was treated for 60 min, and samples were collected after every 10, 20, 30, 40, 50, and 60 min of treatment. Raw and treated wastewater samples were analyzed for their COD, pH, EC, TDS, and PCB concentration according to the standard methods for wastewater analysis [10].

The pH of the wastewater samples was monitored using a digital pH Meter (Jenway model 520). Before recording the measurements, the pH meter was calibrated using buffer solutions (pH 4, 10, and 7). According to NEQS of Pakistan, pH of wastewater should be in the range of 6 to 9. Electrical conductivity (EC) is an important

parameter to assess the wastewater quality. It measures ionic concentration in water or wastewater. It is also an indicator of salinity and is measured in µS/cm. Conductivity of the samples was determined using a conductivity meter, Jenway model 470.

The COD of the samples was determined by the closed reflux colorimetric method using a digester (HACH - LTG 082.99.40001) according to Standard Methods (APHA 2005). Firstly, 1.5 mL of the digestion solution was taken in a COD vial, then 3.5 mL of sulfuric acid along with other reagents was added to the vial, and after that, 2.5 mL of the sample was added to the vial. It was then placed in a digester for digestion.

Extraction of PCBs from Wastewater

Sequential extraction was done in order to prepare the samples for analysis. n-Hexane was used in a 1:1 for extraction of PCBs from wastewater. Initially, the samples were sonicated in order to extract TCB from a water complex mixture at 45 °C for 35 min. Afterwards, samples were centrifuged at 4000 rpm for 10 min [11]. Supernatant was extracted and analyzed by GC-MS.

GC-MS Conditions

GCMS (Thermo Scientific (DSQ)) was used for the identification of compounds. The sample was examined on a GC with a detector (FID). Helium was employed as a carrier gas, with a flow rate of 1.2 cm^3 min^{-1}. The gas chromatograph was equipped with a TR5-MS silica capillary column. The column employed was TR5-MS, 30 m long with 0.25 mm internal diameter and 0.25 µm film thickness [11]. The temperature was programmed to rise from 50 °C (1 min hold time) to 330 °C (20 min) at a rate of 10 °C per min, with a total run time of 25 min for the sample. The sample injection volume was 1 µL Fig. 1.

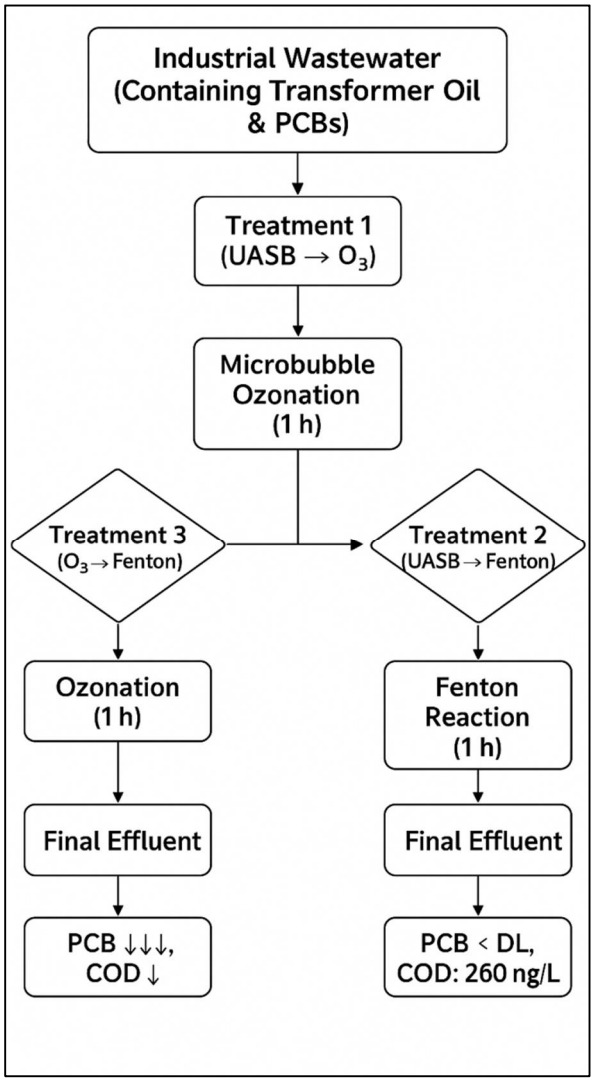

Figure 1. **Treatment combinations for the treatment of PCBs**

Results and Discussion

Upflow Anaerobic Sludge Blanket Reactor - Ozonation Integration Effect on pH

The pH of the wastewater was 7.96 at first, but after 6 hours of treatment in a UASB reactor, it was reduced to 7.82, as shown in Fig. 2A. When the effluent of the UASB reactor was treated with an ozonation procedure for 1 hour, the pH altered to 8.31 at the end of the experiment. The increase in pH was caused by the formation of hydroxyl ions during the oxidation of organics in wastewater. The pH of the control sample was adjusted from 7.96 to 7.91. Teimouri [12]

found that the pH values of both biological reactors were approximately 5.5 - 6 at the commencement of the experiment. After treatment, the pH of the effluent was increased, indicating that the reactors were functioning well and that the environment for microorganism growth and activity was favorable.

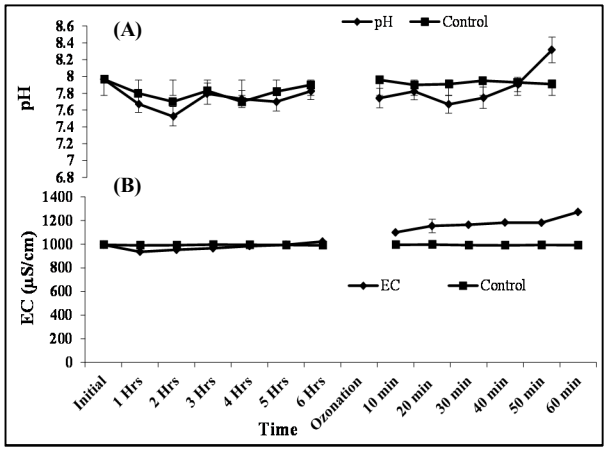

Figure 2. **Effect on pH by UASB-ozonation combination (A); Effect on Electrical Conductivity by UASB-ozonation combination (B)**

Effect on Electrical Conductivity

The electrical conductivity of wastewater was measured both before and after treatment. The initial EC of wastewater was 995 µS/cm, but after treatment with a UASB reactor, it was 1021 µS/cm (Fig. 2B). After ozonating the same effluent for 1 hour, the EC increased to 1272 µS/cm. Ozone treatment caused a rapid increase in the EC of effluent. The control EC was adjusted from 995 µS/cm to 991 µS/cm.

Effect on Total Dissolved Solids

Initially, the TDS of the wastewater sample was 791 mg/L; however, after treatment using the UASB reactor, it was reduced to 765 mg/L, as shown in Figure S1. TDS levels may have decreased as a result of degradation products combining to generate new compounds that were not previously dissolved. After ozonation treatment of UASB reactor effluent, the TDS of the wastewater sample increased to 877 mg/L. TDS levels in wastewater samples increased rapidly during ozonation treatment. After 30 min of therapy, it had climbed to 858 mg/L. The control TDS increased from 791 mg/L to 795 mg/L (Fig. S1).

Reduction of Chemical Oxygen Demand

The initial COD of the wastewater sample was 785 mg/L; however, after 6 h of treatment in the UASB reactor, it decreased to 691 mg/L, as shown in Fig. 3. When this effluent was treated using ozonation, the COD level was reduced to 364 mg/L. The COD level was lowered to 597 mg/L after 30 min of therapy and to 364 mg/L after 1 h. The control COD was reduced from 785 mg/L to 653 mg/L.

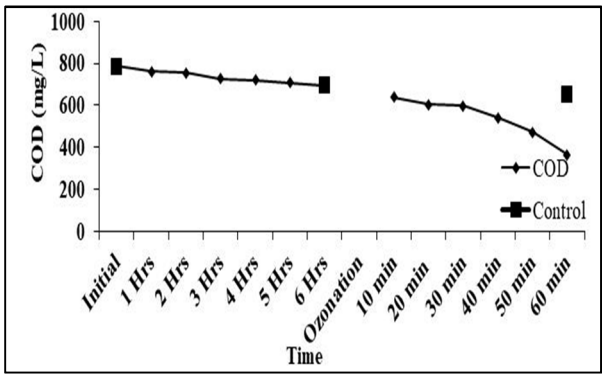

Figure 3. **Reduction of COD by UASB-ozonation combination**

Effect on Concentration of Compounds

Effect on PCB concentration after 2 h UASB treatment

Initially the concentration of PCBs in wastewater was 24.4 µg/mL for 2,4,5-trichlorobiphenyl and 12.1 µg/mL for 2,3,4-trichlorobiphenyl as seen in Fig. S2. After treatment by UASB reactor for 2 h the concentration of 2,4,5-trichlorobiphenyl was reduced to 23.5 µg/mL and of 2,3,4-trichlorobiphenyl was reduced to 10.6 µg/mL.

Other intermediate compounds that were identified were 2,3-dimethyl- pentane and 2-methyl- pentane in a concentration of 12 µg/mL, 1-chloro- octadecane and 1,2-benzenedicarboxylicacid diisooctyl ester in a concentration of 0.3 and 0.4 µg/mL (Fig. S2).

Effect on PCBs Concentration After 4 h UASB Treatment

After further treatment of wastewater by UASB reactor for 4 h, the concentration of PCBs was further reduced (Fig. S3). The concentration of 2,4,5-trichlorobiphenyl was reduced to 18.1 µg/mL, and that of 2,3,4-trichlorobiphenyl was reduced to 9.2 µg/mL, as seen in Fig. S3. Other compounds found by GC-MS analysis were 2,3-dimethyl-pentane and 2-methyl- pentane in a concentration of 15 µg/mL, 2,5-dimethyl- benzaldehyde, 4-methyl-2-propyl-1-pentanol, 26,11-trimethyl-dodecane and 2,4-bis(1,1-dimethyl)- phenol in a concentration of 17.0, 0.16, and 17.4 µg/mL. The chlorinated compound identified was in the form of 1-chloroeicosane in a concentration of 0.17 µg/mL. Similarly, 1,2-benzenedicarboxylic acid, diisoctyl ester and 1,2-benzenedicarboxylic acid, mono) 2-ethylhexyl) ester were found in a concentration of 1.49 µg/mL (Fig. S3).

Effect on PCB Concentration after 6 h UASB Treatment

After 6 h of treatment with an UASB, the concentration of PCB compounds dropped to 15.6 µg/mL for 2,4,5-trichlorobiphenyl and 8.3 µg/mL for 2,3,4-trichlorobiphenyl (Fig. 4). The concentrations of 2,3-dimethyl-pentane and 2-methyl-pentane were 28 µg/mL, whereas cyclohexane and 1,3-dimethyl-benzene were 0.86 and 8.72 µg/mL, respectively. The concentrations of 2,4-bis(1,1-dimethyl)-phenol, 2, 6, 10, 14-tetramethyl-hexadecane, 9-hexyl-heptadecane, and 22-tricosenoic acid were 11.6, 6.3, 2.9, and 0.096 µg/mL. The chlorinated chemical found was 1-Chloroeicosane at a concentration of 0.24 µg/mL. Similarly, 1,2-benzenedicarboxylic acid, diisoctyl ester, and 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester were detected in a concentration of 1.55 µg/mL (Fig. 4).

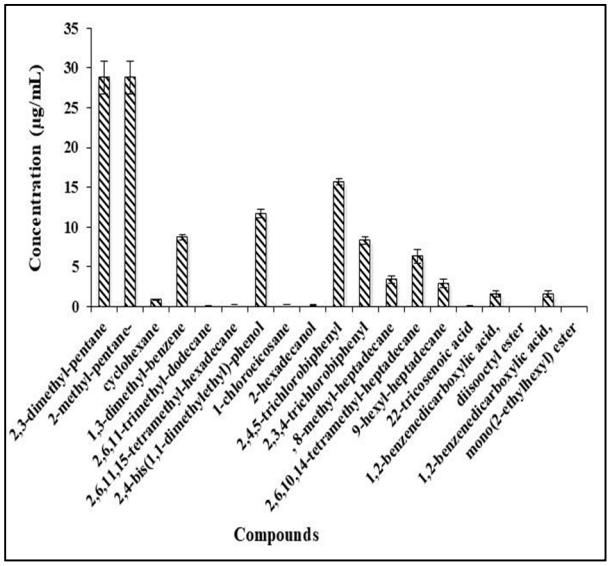

Figure 4. **Effect on PCB concentration after UASB treatment (6 h)**

Effect on PCB Concentration after 20 min Ozonation Treatment

After treatment of effluent from UASB reactor by ozonation for 20 min, the concentrations of PCBs were reduced to 9.7 µg/mL for 2,4,5-trichlorobiphenyl and 5.8 for 2,3,4-trichlorobiphenyl, as seen in Fig. S4. The concentrations of 2,3-dimethyl- pentane and 2-methyl- pentane was 38 µg/mL, of 2,4-dimethyl- benzaldehyde, 2,5-dimethyl-benzaldehyde and 3,4-dimethy- benzaldehyde was 0.17 µg/mL and of 2,4-trimethylbenzene were 0.36 µg/mL. The concentrations of 1-chloro- octadecane and 1-chloroeicosane were 0.88 µg/mL. Similarly, the concentration of 1,2-benzenedicarboxylic acid, mono) 2-ethylhexyl) ester was 3.5 µg/mL (Fig. S4).

Effect on PCB Concentration after 40 min of Ozonation Treatment

After treatment of effluent by ozonation for 40 min, the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were 3.2 and 2.6 µg/mL, as seen in Fig. S5. The concentration of 2,3-dimethyl- pentane and 2-methyl- pentane was 15.1 µg/mL, and of cyclohexane, 1, 3-dimethyl- benzene and 1-(1,3-dimethyl-3-butenyl)-4-(triflouromethyl)- benzene were 0.67, 8.2, and 0.16 µg/mL. Similarly, the concentration of 2-tetrahydrofurylmethyl ester-4-ethylbenzoic acid was 0.27 µg/mL. 1-chloro- octadecane and 1-chloroeicosane were found in concentrations of 0.22 and 2.0 µg/mL. 4-tetradecyl ester benzeneacetic acid and 1,2-benzenedicarboxylic acid, diisooctyl ester were also found in concentrations of 0.22 and 4.5 µg/mL (Fig. S5).

Effect on PCB Concentration after 60 min Ozonation Treatment

The concentration of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl was further lowered by treating the effluent with ozonation for 60 minutes. The quantity of 2,4,5-trichlorobiphenyl was lowered to 0.9 µg/mL, whereas 2,3,4-trichlorobiphenyl was below the detection limit (Fig. 5). Similarly, the concentrations of 2,3-dimethyl-pentane, 2,4-dimethyl-benzaldehyde, and 1,3-dimethyl-benzene were 18.2, 0.95, and 8.7 µg/mL. Similarly, 1-chloro-octadecane and 1-chloroeocosane were detected at concentrations of 0.29 and 2.7 µg/mL. The concentration of 1,2-benzenedicarboxylic acid and diisooctyl ester was 6.15 µg/mL. According to several studies, the degree of PCB breakdown varies from organism to organism and may differ based on the initial amount as well as the nature of the PCB mixture [11].

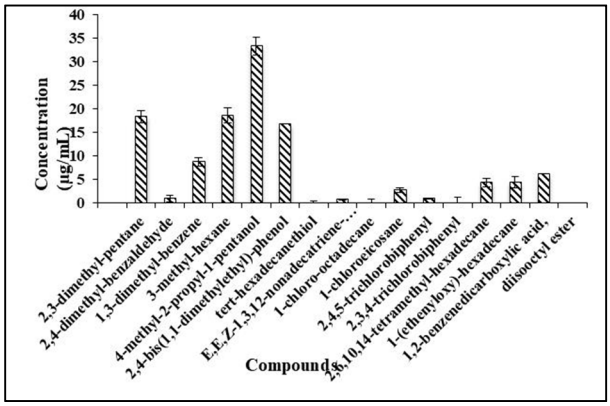

Figure 5. **Effect on PCBs concentration after ozonation treatment (60 min)**

The study, conducted by Adebusoye et al., [12], showed that employing ozonation and biological combination improved PCB degradation. Ozonation demonstrated increased degradation of PCB 138, 180, and 203 using a biological technique, including *A. xylosoxidans*. A single biological procedure using *A. xylosoxidans* resulted in the breakdown of 55% of the total concentration of nine selected PCB compounds; however, the ozonation process reduced the overall quantity of the nine specific PCB compounds by 86%. However, combining biological and chemical methods, namely ozonation and *A. xylosoxidans*, resulted in 94 percent breakdown of the selected PCB compounds, which was higher than both procedures when employed separately (Fig. 5).

Upflow Anaerobic Sludge Blanket Reactor and Fenton Integration Effect on pH and Electrical Conductivity

The pH of the wastewater sample was 7.96 before treatment, but after 6 h of treatment in an UASB reactor, it had changed to 7.82, as shown in Fig. 6A. When Fenton reagent was added to the effluent from the UASB reactor, the pH was reduced to 5.75. After one hour of Fenton process treatment, the pH of the effluent was altered to 4.46. The control pH was adjusted from 7.96 to 7.91.

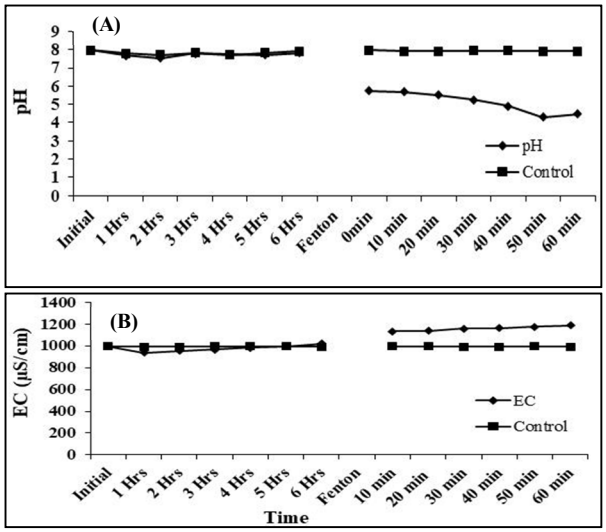

Figure 6. **Effect on pH by UASB-Fenton combination (A); Effect on Electrical Conductivity by UASB-Fenton combination (B)**

The initial EC of the wastewater sample was 995 µS/cm, but following treatment by the UASB was 1021 µS/cm, as shown in Fig. 6B. The Fenton treatment improved the effluent's EC to 1187 µS/cm. The EC of the effluent increased considerably following treatment with ozonation. The control EC was adjusted from 995 µS/cm to 991 µS/cm.

Effect on Total Dissolved Solids

The wastewater sample before treatment had a TDS of 791 mg/L, and after treatment by UASB reactor for 6 h, it was reduced to 765 mg/L, as seen in Fig. S6. When effluent was treated by the Fenton process, the TDS was increased to 986 mg/L. The TDS of the wastewater sample started to increase as the effluent was treated by the Fenton process. After 30 min of treatment, TDS was increased to 887 mg/L and finally to 986 mg/L after 1 h of treatment. There was a significant increase in TDS after treatment by the UASB-Fenton combination.

Reduction of Chemical Oxygen Demand

Initially, the wastewater sample had COD of 785 mg/L, and after treatment in the UASB reactor for 6 h, the COD was reduced to 691 mg/L, as seen in Fig. 7. When the effluent was further treated by the Fenton process, the COD was reduced to 407 mg/L. The Fenton process effectively reduced the COD of wastewater. After treatment for 30 min, COD was reduced to 532 mg/L, and after further treatment for 1 h, it was reduced to 407 mg/L. There was a significant change in the COD of the wastewater after treatment by the Fenton process. For the control, COD was changed from 785 mg/L to 653 mg/L.

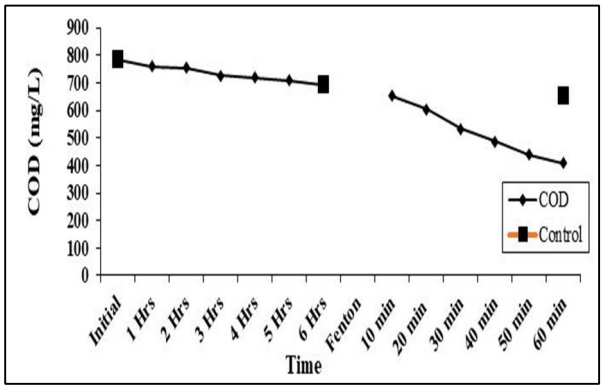

Figure 7. **Reduction of COD by UASB-Fenton combination**

Effect on Concentration of Compounds

Effect on PCB concentration after 20 min of Fenton treatment

After treating the effluent in the UASB reactor, the concentration of PCBs was lowered for 20 min using the Fenton procedure. Fig. S7 shows that the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were 11.2 and 6.1 µg/mL, respectively. The concentrations of 1-ethyl-2-methyl-benzene, cyclohexane, 4H-furo[3,2-d]-1,3-dioxin-6 (7H)-one, 4a, 7a-dihydro-7-hydroxy-2,2-dimethyl-, 3-deoxy-á-D-glucopyranose, and 3,4-dimethyl-benzaldehyde were 1.5, 0.93, 0.45, and 0.2 µg/mL, respectively. The concentrations of 1-dichloromethyldimethylsilyloxynonane and 1,2-benzenedicarboxylic acid, diisooctyl ester were 0.36 and 4.5 µg/mL, respectively.

Effect on PCB concentration after 40 min of Fenton treatment

After 40 minutes of Fenton process treatment, effluent concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were lowered to 7.5 µg/mL and 2.9 µg/mL, respectively (Fig. S8). The concentrations of 2,4-dimethyl-benzaldehyde, 3,4-dimethyl-benzaldehyde, and 2,5-dimethyl-benzaldehyde were 2.5 µg/mL, while 2-ethyl-benzaldehyde was 0.16 µg/mL. Similarly, the concentrations of 1-cyclohexyldimethylsilyloxy-3, 5-dimethylbenzene, 1,2-benzenedicarboxylic acid, diisooctyl ester, and 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester were 1.5, 5.7, and 5.1 µg/mL. The concentration of 9-(2',2'-dimethylpropanoilh-ydrazono)-3,6-dichloro-2,7-bis-[2-(diethylamino)-et hoxy]fluorine was 3.9 µg/mL.

Effect on PCB concentration after 60 min of Fenton treatment

After 60 min of treatment by the Fenton process, the concentration of 2,4,5-trichlorobiphenyl and 2,3,4- trichlorobiphenyl was reduced to 2.4 and 0.3 µg/mL, as seen in Fig. 8. The concentration of 2,4-dimethyl-benzaldehyde, 3,4-dimethyl- benzaldehyde, 1-ethyl-2-methyl- benzene was 2.5, 2.5, and 2.2 µg/mL. The concentration of 1-dichloromethyldimethylsilyloxynonane was 3.8 µg/mL. It has been seen in a study conducted by Dudasovaa et al., [13] that the amount of two compounds, which were PCB28 and PCB52, decreases quickly in the first 24 h of the experiment, while the other two, which were PCB101 and PCB138, were degraded partially. The degradation of PCB138, PCB153, PCB180, and PCB209 was greater than 95%, and for PCB138, it was a maximum of 97%. PCB28, PCB52, and PCB101 were not identified by GCMS after 3 h of reaction, respectively (Fig. 8).

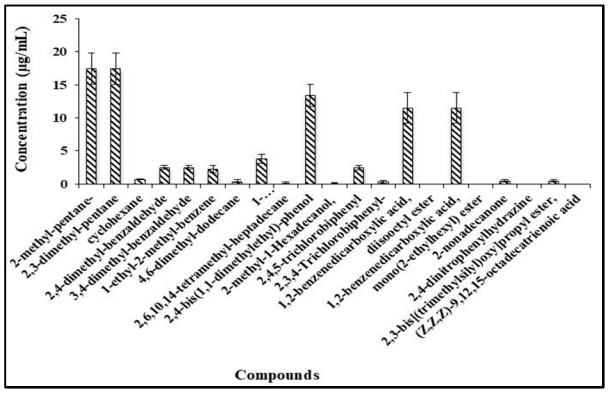

Figure 8. **Effect on PCBs concentration after Fenton treatment (60 min)**

Ozonation and Fenton Integration Effect on pH and EC

Initially, the pH of the wastewater was 7.96, and after treatment by ozonation for 10 min, it was changed to 8.1; after 30 min, it was 8.3, and after treatment for 1 h, it was changed to 8.6, as seen in Fig. S9. After addition of Fenton reagent to the effluent, the pH was lowered to 5.3. When the effluent was treated by the Fenton process, after 10 min of treatment, the pH was changed to 5.13, after 30 min to 4.5, and after 1 h of treatment to 3.9. For the control, the pH was changed from 7.96 to 7.91.

Initially, the wastewater sample had an EC of 971µS/cm, and after treatment by ozonation for 1 h, it was reduced to 907 µS/cm, as seen in Fig. S10. When the effluent was further treated by the Fenton process, the EC of the wastewater started to increase. After 10 min of treatment, it was increased to 1065 µS/cm. After 30 min of Fenton treatment, the EC was further increased to 1234 µS/cm. After 1 h of treatment, the EC was increased to 1309 µS/cm. For the control, the EC was changed from 971 µS/cm to 991 µS/cm.

Effect on Total Dissolved Solids

The wastewater sample before treatment had a TDS of 791 mg/L, and after

treatment by ozonation for 1 h, it was reduced to 688 mg/L, as seen in Fig. S11. There was a gradual decrease in the TDS of wastewater after treatment by ozonation for 1 h. When effluent was treated by the Fenton process, TDS started to increase, and after 30 min of treatment was 983 mg/L. After 1 h, the treatment was changed to 1085 mg/L. It has been estimated that a large increase in the amount of ferrous ions can cause an enhanced accumulation of iron salts, which results in the rise of the TDS of the wastewater, which is not allowed [14]. For the control, the TDS was changed from 791 to 795 mg/L.

Reduction of Chemical Oxygen Demand

The initial wastewater sample had COD of 785 mg/L, and after treatment by ozonation for 1 h, COD was reduced to 494 mg/L, as seen in Fig. S12. When effluent was further treated by the Fenton process for 1 h, COD was further reduced to 260 mg/L. For the control, the COD changed from 785 mg/L to 717 mg/L. Studies have been conducted [17,18] showed that the removal efficiency of COD by using Fenton treatment was 43– 55% after 24 h of treatment.

Concentration of Compounds

Wastewater was treated by ozonation for 60 min, then the effluent was fed into the Fenton reactor and was treated for 60 min. Initially, the concentration of PCBs in wastewater was 24.4 µg/mL for 2,4,5-trichlorobiphenyl and 12.1 µg/mL for 2,3,4-trichlorobiphenyl.

Effect on PCB Concentration after 20 min of Ozonation Treatment

After treatment of the wastewater for 20 min by ozonation, the concentrations of PCBs were reduced. The concentration of 2,4,5-trichlorobiphenyl was 16.3 and of 2,3,4-trichlorobiphenyl was 8.2 µg/mL, as seen in Fig. S13. The concentration of 2,5-dimethyl-benzaldehyde and 1,3-dimethyl- benzene was 2.0 and 0.4 µg/mL. Similarly, the concentration of 1-chloro- octadecane and 1-chloroeicosane was 0.9 and 1.0 µg/mL. The concentration of 1,2-benzenedicarboxylic acid, diisooctyl ester was 3.1 µg/mL.

Effect on PCBs Concentration after 40 min Ozonation Treatment

The concentration of PCBs was further reduced by treatment of wastewater for 40 min by ozonation. The concentration of 2,4,5-trichlorobiphenyl was 10.2 and of 2,3,4-trichlorobiphenyl was 5.7 µg/mL, as seen in Fig. S14. The concentration of 1,3-dimethyl-benzene, 4-tetradecyl ester-3-trifluoromethyl-benzoic acid, and 4-pentadecyl ester-3-trifluoromethylbenzoic acid was 0.53, 0.9, and 0.9 µg/mL. The concentration of 1-dichloromethyldimethylsilyloxynonane found was 0.86 µg/mL. Similarly, the concentration of 1,2-benzenedicarboxylic acid and diisooctyl ester was 3.4 µg/mL.

Effect on PCB Concentration after 60 min Ozonation Treatment

After 60 min of treatment by ozonation, the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were 8.4 and 3.3 µg/mL, as seen in Fig. S15. The concentrations of cyclohexane, 2,5-dimethyl- benzaldehyde, and 1,3-dimethyl-benzene were 1.7, 2.7 µg/mL, and 0.68 µg/mL. The chlorinated compounds identified were 1-chloroeicosane and 1-chloro-octadecane with a concentration of 0.28 µg/mL. The 1,2-benzenedicarboxylic acid, diisooctyl ester, 1,2-benzenedicarboxylic acid, mono (2-ethylhexyl) ester were also identified in a concentration of 3.3 µg/mL (Fig. S15).

Effect on PCB Concentration after 20 min Fenton Treatment

When effluent from the ozonation column was further treated by the Fenton process for 60 min, the concentration of PCBs was also reduced. After treatment of effluent by the Fenton process for 20 min, the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were 4.3 and 1.9 µg/mL, as seen in Fig S16. The concentrations of 2,5-dimethyl- benzaldehyde, 2,4-dimethyl-benzaldehyde and 3,4-dimethyl-benzaldehyde were 0.21 µg/mL, and of 1,3-bis (1,1-dimethylethyl)- benzene was 2.0 µg/mL. The concentration of 4-chlorophenyl ester -2-trifluoromethylbenzoic acid and 3,4-dichlorophenyl ester-2-trifluoromethylbenzoic acid was 2.0 µg/mL. The chlorinated compounds identified were 1-dichloromethyldimethylsilyloxynonane, 1-chloro- octadecane and 1-chloroeicosane in a concentration of 1.3, 0.8, and 0.83 µg/mL. 1,2-benzenedicarboxylic acid, diisooctyl ester, 1,2-benzenedicarboxylic acid, mono (2-ethylhexyl) ester were also found in a concentration of 13.0 µg/mL (Fig. S16).

Effect on PCB concentration after 40 min of Fenton treatment

The concentrations of 2,4,5-trichlorobiphenyl and of 2,3,4-trichlorobiphenyl after treatment of effluent for 40 min by the Fenton process were 1.1 µg/mL and 0.4 µg/mL, as seen in Fig. S17. The concentrations of 2,5-dimethyl-benzaldehyde, 2,4-dimethyl- benzaldehyde and 3,4-dimethyl- benzaldehyde were 0.5 µg/mL, and of 1-ethyl-2-methyl- benzene was 0.3 µg/mL. The chlorinated compounds identified were 1-chloro- octadecane and 1-chloroeicosane in a concentration of 0.29 µg/mL. Similarly, the concentration of 1-cyclohexyldimethylsilyloxy-3,5-dimethylb-enzene and 2,2,7,7-tetramethyl-4,5-diphenyl-3,6-dioxa-2,7-disilaoctane was at concentrations of 1.5 and 1.4 µg/mL. 1,2-benzenedicarboxylic acid, diisooctyl ester, 1,2-benzenedicarboxylic acid, mono (2-ethylhexyl) ester were also found in concentrations of 4.2 and 3.2 µg/mL.

Effect on PCB Concentration After 60 min of Fenton Treatment

After 60 minutes of Fenton treatment, the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl were below detectable levels. In Fig. S18, the concentrations of 2,4-dimethyl-benzaldehyde and 2,5-dimethyl-benzaldehyde were 0.59 µg/mL, while 1-ethyl-2-methylbenzene was 0.37 µg/mL. The quantity of 3,4-dichlorophenyl ester trifluoromethyl benzoic acid was 2.3 µg/mL, while 1-chloroeicosane was 0.4 µg/mL. The concentration of 1,2-benzenedicarboxylic acid, diisooctyl ester, and mono (2-ethylhexyl) ester was found to be 4.2 µg/mL. Dennis [11] found that the Fenton process is effective in treating water containing 2,2',4,4',5,5'-hexachlorobipheny (PCB153), reducing its concentration by 98%. According to Riaza-Frutos' research [15], 98% degradation of the original PCB congeners was seen after 3 days of treatment. In the study, up to 53% of PCBs were removed during the first half hour after Fenton treatment, with up to 94% removed after 24 hours. Fig. 8-11 demonstrates the degradation products created following various treatments. It was evident that the numerous degradation products were simple organic compounds that rarely contained a chlorine atom, making them easily biodegradable and safe to dispose of in the environment.

The study demonstrated the degradation of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobipenyl. Initially, the concentration of PCBs in wastewater was 24.4 µg/mL for 2,4,5-trichlorobiphenyl and 12.1

µg/mL for 2,3,4-trichlorobiphenyl, however, after treatment, it was below the detection limit with the application of an integrated treatment procedure in UASB-ozonation and ozonation-Fenton the concentration of 2,4,5-trichlorobiphenyl and 2,3,4- trichlorobiphenyl were reduced below the detectable level. However, in the UASB-Fenton combination, the concentration of 2,4,5-trichlorobiphenyl and 2,3,4- trichlorobiphenyl was reduced to 2.4 and 0.3 µg/mL.

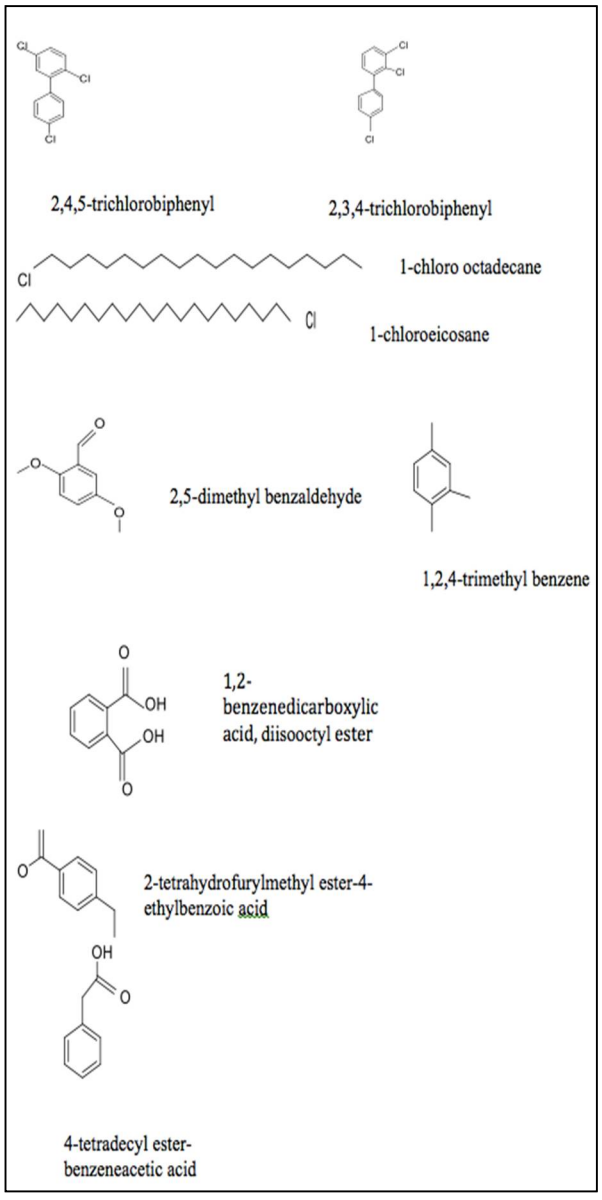

Figure 9. **Degradation products by UASB-ozonation combination**

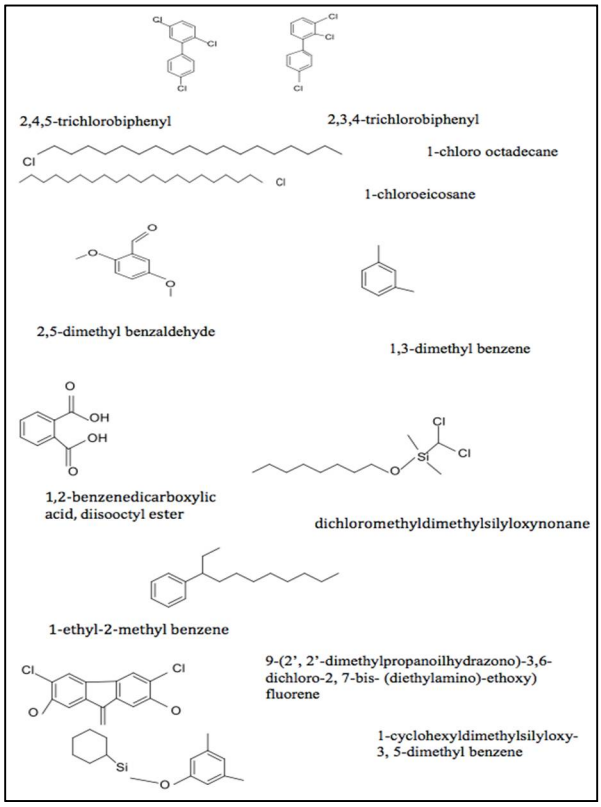

Figure 10. **Degradation products for UASB-Fenton combination**

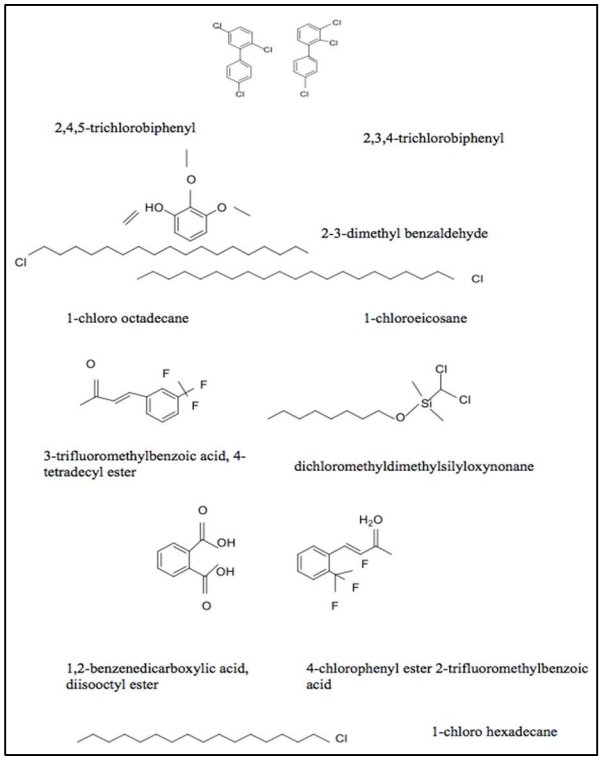

Figure 11. **Degradation products for ozonation-Fenton combination**

Conclusion

The sequential degradation of PCBs was investigated utilizing various combinations, including UASB and ozonation, UASB and Fenton, and finally ozonation and Fenton. The initial concentration of PCBs in wastewater was 24.4 µg/mL for 2,4,5-trichlorobiphenyl and 12.1 µg/mL for 2,3,4-trichlorobiphenyl. Integrated procedures were found to significantly degrade PCBs. The PCB concentrations were decreased below detectable levels in both the UASB and ozonation combinations, as well as the ozonation and Fenton combination. UASB and Fenton lowered the concentrations of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobiphenyl to 2.4 and 0.3 µg/mL, respectively. The primary degradation byproducts generated during UASB-ozonation combination were 1,2-benzenedicarboxylic acid, diisooctyl ester, 2-tetrahydrofurylmethyl ester-4-ethyl benzoic acid, and 4-tetradecyl ester-benzeneacetic acid. After ozonation-Fenton treatment, the main byproducts discovered were 4-tetradecyl ester-3-trifluoromethylbenzoic acid and 4-chlorophenyl ester 2-trifluoromethylbenzoic acid. The study demonstrated that degradation of 2,4,5-trichlorobiphenyl and 2,3,4-trichlorobipenyl was below the detection limit when an integrated treatment procedure (UASB followed by ozonation and ozonation followed by the Fenton process) was utilized.

Conflict of Interest

All authors declare that they have no conflicts of interest.

Availability of Data and Materials

All the data and materials are available with authors. Supplementary data file can be requested from authors or PJAEC.

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