



Research article

Ozone oxidation of wastewater containing trichlorobiphenyl and used transformer oil

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ABSTRACT

Trichlorobiphenyl (TCB) is a persistent toxic organic compound and exerts more hydrophilicity than other polychlorinated biphenyl (PCB) compounds. PCBs have been used on large scale in transformer oil. To observe the strong ozone oxidation effect on the degradation of TCB in aqueous medium, synthetic wastewater was prepared from transformer oil with TCB. Microbubbles ozonation of TCB was done in order to completely oxidize it. A batch treatment system was used for 60 min in glass column with a diffuser at the bottom to convert ozone gas into microbubbles. GCMS analyzed TCB and other toxic compounds before and after the treatment. TCB was reduced to below detection limit during the first 20 min of ozonation. Ethylbenzene and 1-chloroheptacosine were identified after 10 and 20 min, the concentrations of these compounds increased to 1.45 and 3.9 mg/L after 60 min. Alkane with chlorine containing compounds were identified more than any other compounds. The alkanes compounds with chlorine, such as tetradecane 1-chloro, hexadecane 1-chloro, heptadecane 1-chloro, octadecane 1-chloro and nonadecane 1-chloro were found during 60 min of ozonation. Chemical oxygen demand (COD) in the wastewater reduced from 700 to 390 mg/L. Small increase in pH was observed from 7.7 to 8.3. In this study it was concluded that TCB and other pollutants in transformer oil were degraded with ozone dose, 0.05 g/min L in the shortest period of 60 min.

1. Introduction

The Polychlorinated Biphenyls (PCBs) are hazardous chemical compounds which are released in the environment due to many anthropogenic activities [1]. In the past, PCBs were used in transformer oil at a concentration of 50 mg/L to enhance its electrical insulating properties. PCBs were also used in pesticides, hydraulic oil, flame retardants and in adhesives etc. Since late 1960's, PCBs have been considered as a contaminant which caused environmental pollution due to their slow degradability and their toxicity at even trace concentrations [2]. Many anthropogenic activities are the most important to focus such as incineration [3] which release PCBs in environment [4]. PCBs are naturally stable, capable of bio-accumulation which are potentially toxic to humans and wildlife.

Despite ban on their use since many years, PCBs are still present in the environment with certain levels in soil, sediments and water affecting human health through the contaminated agriculture crops [5, 6]. PCBs

have been considered by Stockholm Convention as persistent organic pollutants and need to reduce their concentrations from the environment [7]. From prolonged exposure certain health impacts can occur such as skin cancer, immune deficiencies, thymus gland problems, reproductive disorder, nervous system damage and enhanced cancer risks [8, 9]. The chronic toxicity of PCB compounds was noticed after usage for many years. It has been estimated that more than 1.2 million tons of PCBs were produced and commercialized throughout the world. Subsequently, PCBs have been manufactured and used globally up to 1985, they are found today in all environmental components such as air, surface & groundwater, soil and sediments [10]. Therefore, it is necessary to remediate number of areas and equipment's such as transformer oil [11]. Different processes can be used in order to decontaminate materials that contain PCB congeners. The water solubility of the PCBs depends on the number of chlorine atoms attached to biphenyl; more chlorine attached to biphenyl causes less solubility. Tetrachlorobiphenyl and pentachlorobiphenyl is less soluble in water than TCB so these PCBs have

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tendency to be found in sediments. Therefore, the contamination of TCB and related PCBs in water is of great concern due to its toxicity to aquatic life [12, 13, 14].

Pakistan, despite of being participated in Stockholm Convention 2001, there is still need to define monitoring mechanism and control PCB levels in different environmental conditions. The manufacturing and usage of PCBs needs more control and must be included in the list of National Environmental Quality Standard (NEQS) as important chemicals of major concern [15]. Currently, PCBs are not being used in transformer oil but left over from old transformer still exist which need to be degraded. Many old transformers were grounded to avoid oil spillage. An initial survey regarding the concentrations of polychlorinated biphenyl compounds in air and soils across industrial and agricultural areas of Punjab Province, Pakistan, was conducted from January to March 2011. The total amount of all PCBs ranged from 34 to 389 $\mu\text{g}/\text{m}^3$ in air and from 7 to 45 ng/g dry weight in soils, where both ranges were like the average ranges in other areas of the world [16]. PCBs can be destroyed at 1200 °C [17] but this technology is expensive for developing countries. Biological processes are slow and require specific growth condition to successfully run the process. In this proposed study, low cost and simple treatment option was explored by using ozone as oxidizing agent in wastewater treatment technology [18]. Ozone degradation of PCBs in soil were more focused than in wastewater. Ozonation may be an efficient and effective method for the degradation of PCBs [19]. Ozonation process has also been extensively used for water and wastewater treatment, such as for disinfection and for breakdown of toxic organic pollutants. Different organic compounds such as phenols, pesticides, dyes, pharmaceuticals, PCBs, nitrobenzene, phthalic acid esters etc. can be degraded by ozonation process [20]. It has been shown in other studies that 86 % of the total concentration of the nine selected PCB congeners present in Delor 103 were removed by the ozonation method which were PCB 8 (2,4-dichlorobiphenyl), PCB 28 (2,4,4-trichlorobiphenyl), PCB 52 (2,2,5,5-tetrachlorobiphenyl), PCB 101 (2,2,4,5,5-pentachlorobiphenyl), PCB118 (2,3,4,4,5-pentachlorobiphenyl), PCB 138 (2,2,3,4,4,5-hexachlorobiphenyl), PCB 153 (2,2,4,4,5,5-hexachlorobiphenyl), PCB 180 (2,2,3,4,4,5,5-heptachlorobiphenyl), and PCB 203 (2,2,3,4,4,5,5,6-octachlorobiphenyl) [21]. The effects of ozone oxidation on single TCB in aqueous medium still need to be explored; therefore, focused area in this study was to see the effectiveness of ozone oxidation of TCB in wastewater and other compounds present in transformer oil. In view of lack of knowledge about degradation of TCB by ozone microbubbles, the main objective of this research was to study degradation of TCBs in wastewater by ozonation process.

2. Methodology

Treatment was performed in a glass column locally prepared and synthetic wastewater was added into the column.

2.1. Chemicals

TCB (PCB No 29) having 99.4% purity, formula $\text{C}_{12}\text{H}_7\text{Cl}_3$, molecular weight 257.54 and other required chemicals were purchased from Sigma Aldrich, 3050 Spruce street Saint Louis, MO 63103 USA. Sulfuric acid (95–97% purity), methanol and n-hexane were also purchased from Sigma Aldrich.

2.2. Preparation of synthetic wastewater

Synthetic wastewater was prepared at the rate of 10 mL transformer oil per liter of distilled water and the concentration of 2, 4, 5-trichlorobiphenyl 18 mg/L was adjusted. Prior to addition in the reactor, the synthetic wastewater was continuously stirred in the presence of methanol for 30 min in fume-hood to complete mixing in water and later methanol was evaporated from the solution. Methanol was used to dissolve PCBs in

synthetic wastewater. Wastewater was fed to glass column for oxidation just after homogenous mixing. The ozone was used as oxidant of PCB in the current work.

Table 1 showed the initial characteristics of wastewater. The synthetic wastewater containing model PCB was treated by ozonation at various rates to find out appropriate dosage for the oxidation of PCB. Desired wastewater characteristics like COD, pH, Electrical Conductivity (EC), total dissolved solids (TDS) and PCB concentrations were monitored based on standard methods prior to and after ozonation.

2.3. Experimental setup

Diffuser was used to convert ozone gas into microbubbles (average diameter of 100 μm), ozone was generated from the ozonator, and diffuser was placed at the bottom of the glass column (Figure 1). The arrangement allowed microbubbles to slowly rise towards to water surface and reacted with TCB and other organics present in the wastewater during the reaction. The height of the column is very important through which the maximum ozone bubbles reacted with TCB by travelling upward long distance inside the wastewater in column. Ozone generator was connected to the diffuser with the Teflon pipe (Figure 1). This was batch process where wastewater was fed into the column and was treated by microbubbles at a rate of 3 g/Lh .

2.4. 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 (APHA, 2005).

The pH of the wastewater samples was monitored by using digital pH Meter (Jenway model 520). Before recording the measurements, pH meter was calibrated by using buffer solutions (pH 4, 10 and 7). According to NEQS of Pakistan, pH of wastewater should be 6 to 9. Electric 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 measured in $\mu\text{S}/\text{cm}$. Conductivity of the samples was determined by using conductivity meter, Jenway model 470.

The COD of the samples was determined by closed reflux colorimetric method using a digester (HACH - LTG 082.99.40001) according to Standard Method [22]. Firstly, 1.5 mL of the digestion solution was taken in a COD vial, then 3.5 mL of sulfuric acid along other reagents were added in vial, after that 2.5 mL sample was added in vial. It was then placed in digester for digestion at 150 °C for 2 h. COD spectrophotometer recorded the readings.

2.5. Extraction of TCB from wastewater

Sequential extraction was done in order to prepare the samples for analysis. N-Hexane was used in 1:1 for extraction of PCBs from wastewater. Initially, the samples were sonicated, in order to extract TCB from water complex mixture at 45 °C for 35 min (Figure 2). Afterwards samples were centrifuged at 4000 rpm for 10 min [23]. Supernatant was extracted and analyzed in Gas chromatography mass spectrometry (GCMS).

2.6. GCMS conditions

GCMS was used made by Perkin Elmer. The sample was analyzed on gas chromatograph, consisting of a detector (Electron Impact). Helium was used as a carrier gas at flow rate of 1.2 $\text{cm}^3 \text{min}^{-1}$. The gas chromatograph was fitted with silica capillary column elite 5. The model of column used was Elite-5 MS that was 30m long with 0.25 mm internal diameter and 0.25 μm film thickness. The temperature was programmed

Table 1. Initial characteristics of wastewater containing transformer oil.

Parameters	Results
pH	7.7
Electrical Conductivity	289 $\mu\text{S}/\text{cm}$
TDS	230 mg/L
COD	700 mg/L
2,4,5-Trichlorobiphenyl	17.88 $\mu\text{g}/\text{mL}$

from 50 °C (1 min hold time) to 330 °C (20 min), at a rate of 10 °C min⁻¹, and total run time for sample was 25 min. Sample injection volume was 1 μL .

2.7. Calibration

Initially n-Hexane was run on GCMS in order to check its calibration. Then afterwards sample was run with internal standard that was meta-xylene with concentration of 400 ng/mL. About 20 μL sample was taken in Eppendorf and 20 μL of internal standard was added. Then 160 μL of n-Hexane was added in it and analyzed on GCMS. The concentration of compounds present in sample were determined by multiplying area of sample peak with concentration of standard then dividing by peak area of standard.

2.8. Ozone detection

Portable ozone generator was purchased from Water 2000, Inc. company, Lahore, Pakistan. Model used was HY-002 with Ozone output of 3 g/h with the dimensions of 230*180*420 mm. As ozone reacts quickly with pollutants or microorganisms and degenerates in wastewater quickly so measurements of its concentration is not accurate. Hence, we only considered its generation rate and role in the oxidation of PCB in synthetic wastewater.

The meter consists of sensor head that is placed at the top of the reactor to measure ozone concentration. Ozone meter gave the concentration of ozone in mg/L. Highly sensitive sensor measures ozone even in very small concentration. Ozone concentration was detected at the start of the experiment and for every 10 min throughout the experiment. The ozone molecule absorbs UV light and most of the sensors use UV absorption to measure the concentration of ozone. According to Beer law the amount of light absorb is proportional to the concentration of ozone. For ozone 254 nm wavelength of light is created by mercury lamp. The amount of light absorbed is used to measure the concentration of ozone

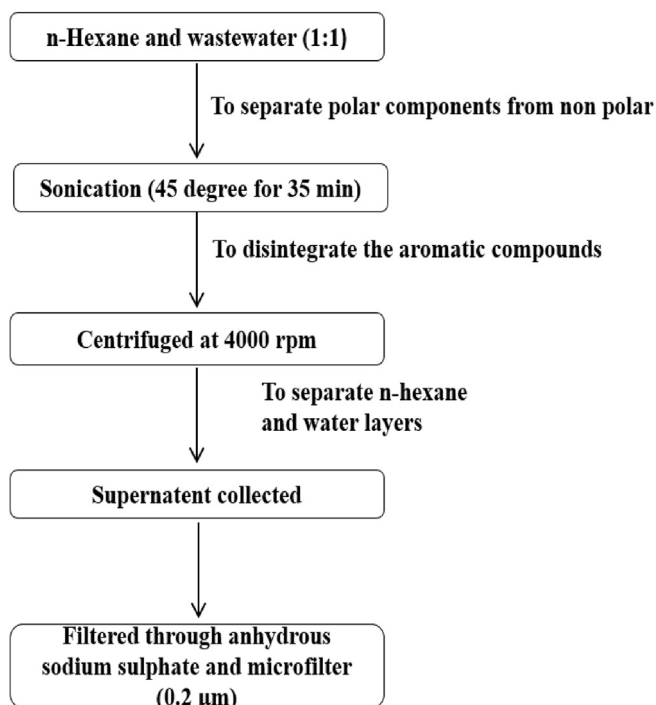


Figure 2. Sample preparation flow chart.

gas. Various operating parameters of current treatment have been shown in Table 2.

3. Results and discussion

3.1. Effect on pH

Initially the pH of wastewater sample was 7.7 and after treatment for 30 min by ozonation it increased to 8.1. The pH gradually increased within 20 min of ozonation and then it remained uniform till 60 min of treatment (Figure 3). The maximum pH value of 8.1 was recorded after a treatment for 60 min. The increase in pH was due to the generation of hydroxyl ions during the oxidation of organic waste in synthetic wastewater. Hydroxyl radicals were produced when ozone molecules reacted with organics mainly TCB in wastewater (transformer oil) and decomposed into simple compounds. A study has shown that there was a gradual increase in pH of wastewater after ozonation. The pH of

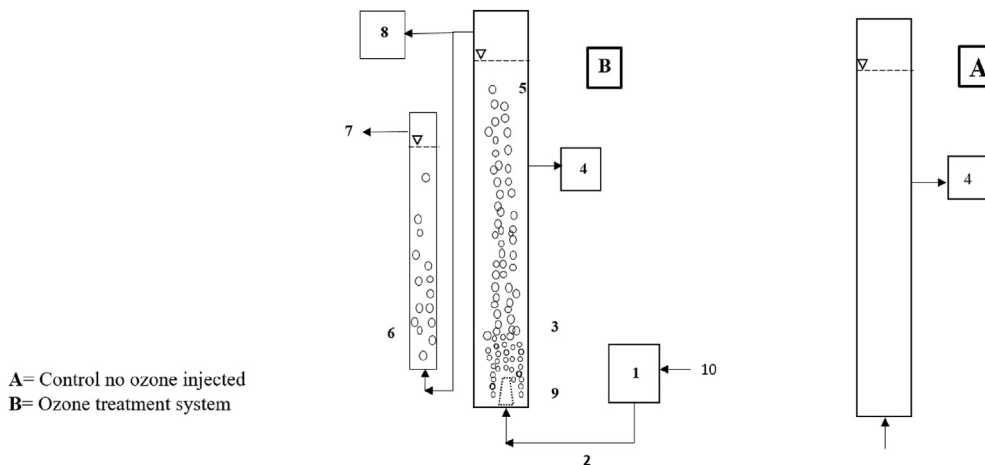


Figure 1. 1. Ozonator, 2. Teflon pipe, 3. Glass column, 4. Waste water sampling point, 5. Ozone bubbles, 6. Ozone destruction column, 7. Gasses out, 8. Ozone detection point, 9. Ozone diffuser, 10. Air inlet.

Table 2. Advanced oxidation operating parameters for the current treatment.

Parameters	values
Ozone generation	0.05 g/min
Ozone diffuser size	1.5 cm × 2.5 cm
Ozone diffuser diameter	1.5 cm
Ozone bubble diameter	100–10000 μm
Working temperature	15–25 °C
Reaction column height	0.914 m
Total reaction time	60 min
Sample collection time	After every 10 min

wastewater sample increased from 6.97 to 8.39 [24]. The increase in pH of wastewater might be due to the accumulation of H₂O₂ during the treatment.

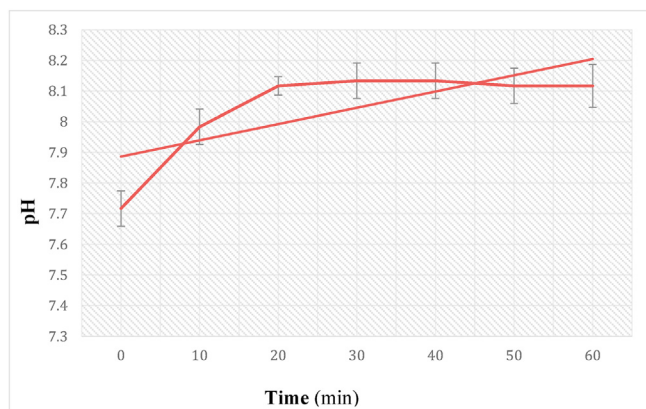
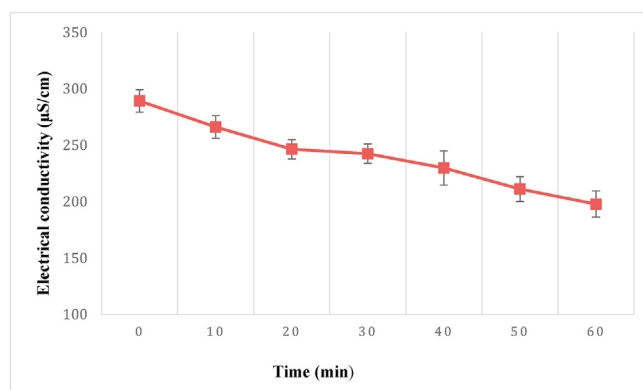
The pH increases could be attributable to different reasons depending on the wastewater and the following oxidation reactions; but also, because a bubble column was used in the experiment, and displaced the CO₂ from the wastewater to the air, hence the pH increased. Ozone degrade organic pollutants through the formation of hydroxyl radicals (HO·). HO· are produced during degradation of organic compounds by ozone due to which pH increases. As the current experiment was carried out in bubble column, and CO₂ was being displaced from the wastewater to the air, hence the pH increases.

3.2. Reduction of Electrical Conductivity

Initially, the electrical conductivity (EC) of wastewater sample was 289 μS/cm and after treatment for 60 min with ozone it was reduced to 210 μS/cm. EC of wastewater reduced rapidly for first 20 min (Figure 4). However, after 20 min–60 min it was reduced gradually. EC was reduced as chloride ions were not released but they were attached to strait chain alkane compounds, similarly ions get attached to different compound and were not in free form. Another study showed that the average EC for five samples prior to ozone treatment was found to be 1380.80 μS/cm. However, the mean conductivity values were 1423.75 μS/cm after treatment with ozone [24]. Another reason behind the reduction of EC could be reduction of TDS which resulted in EC reduction.

3.3. Effect on Total Dissolved Solids

Initially wastewater had 230 mg/L of total dissolved solids and after treatment of wastewater for 60 min, wastewater had 120 mg/L of total dissolved solids. There was gradual decrease in TDS from 0 min to 20 min, afterwards no apparent decrease in TDS was observed and it remained between 120 - 140 mg/L, as noted in Figure 5. Decrease in TDS

**Figure 3.** Effect on pH during TCB degradation.**Figure 4.** Reduction of Electrical Conductivity during ozonation.

might be due to the combining of degradation products to form new products which were not in dissolved form.

3.4. Effect on COD

Initially, wastewater had COD of 700 mg/L which reduced to 390 mg/L after 60 min treatment. Initially COD of the wastewater decreased rapidly up to 20 min (Figure 6). Another study showed that the mean COD value of inlet and outlet samples from wastewater treatment plant were found to be 368.8 and 43.6 mg/L respectively. After ozonation these values decreased significantly to 275.2 and 31.9 mg/L respectively [24]. When ozone could enter in wastewater containing TCB, it accomplished a complex chain of reactions which lead to the generation of radicals such as HO· and the superoxide radicals (O₂·), which are more strong oxidants than O₃ which also catalyzed the depletion of molecular O₃.

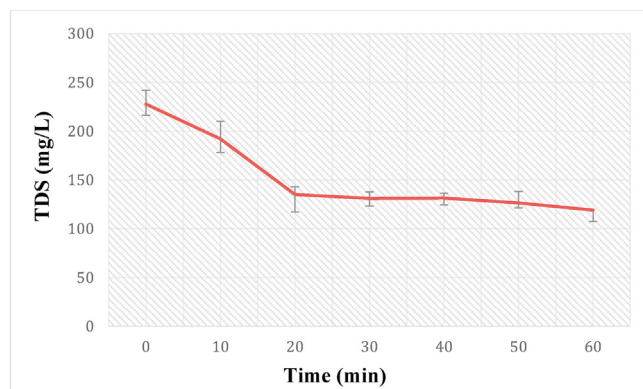
3.5. COD Removal and Reaction Kinetics

Kinetic evaluations was also determined that the ozonation of wastewater was a pseudo-second order reaction with respect to the COD of wastewater, as shown in Figure 7. A logarithmic relationship was found between the rate constants and the applied ozone dose. As the applied ozone dose was continued, COD removal efficiency increased.

The initial concentration of 2,4,5-TCB at the rate of 17.88 mg/L, and 2,3,4-TCB was 7.7 mg/L after prepared synthetic wastewater.

3.6. Results after 10 min treatment with ozone

After 10 min treatment with ozone, total eleven compounds were identified out of them only three were containing chlorine such as tetradecane 1-chloro, nona-decane 1-chloro, hexa-decane 1-chloro with

**Figure 5.** Effect on Total Dissolved Solids during ozone treatment.

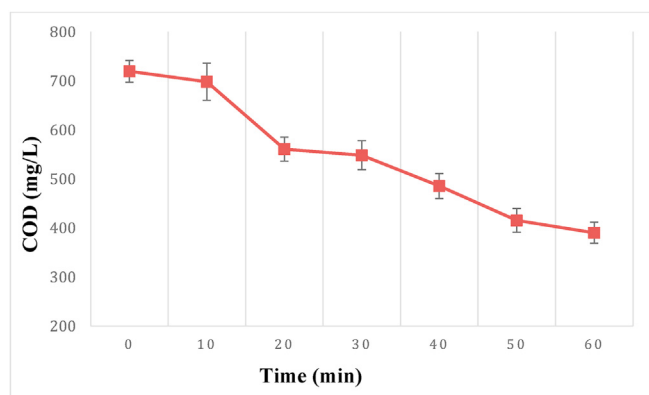


Figure 6. Effect on COD in wastewater containing TCB.

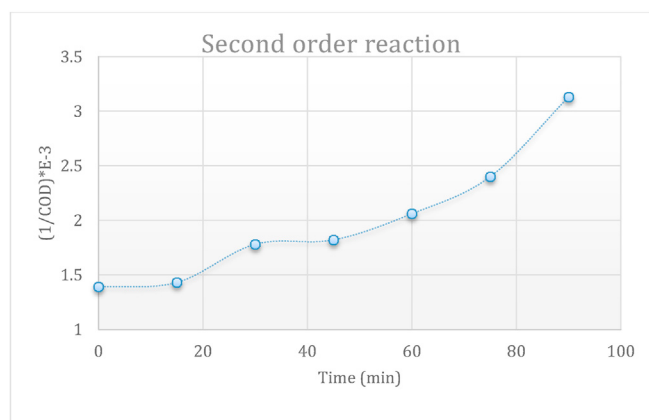


Figure 7. COD Removal and Reaction Kinetics of TCB degradation.

concentration 6.75, 0.53 and 7.0 mg/L. Concentration of 2,4,5 TCB was found 2.77 mg/L after 10 min and no 2,3,4 TCB. The PCB 2,3,4 TCB was found in the sample transformer oil. Four aromatic hydrocarbons compounds identified which were O-xylene, Benzene acetic acid, Benzene,1-methyl dodecyl, benzene, 1-methylhexadecyl with respective concentrations of 16.9, 8.5, 12 and 12.5 mg/L. Other compounds identified were dodecane 4,6 dimethyl, undecane 3,5 dimethyl and oxalic acid 2-ethyl-hexyl and these were less toxic and not identified in following samples collected at different times till one hour, as shown in Table 3.

After treatment for 20 min with ozonation, ten compounds were identified; six of them contained chlorine such as tetradecane 1-chloro, nonadecane 1-chloro, 1-chloroeicosane, heptacosane 1-chloro, hexadecane 1-chloro and octadecane 1-chloro with concentration of 0.46, 4.5, 1.5, 0.20, 2.1 and 1.75 mg/L.

Benzene containing compounds were four, such as ethyl benzene, o-xylene, benzene acetic acid 2-tetradecane and benzene 1,3,3-trimethylnonyl with the respective concentrations of 0.335, 20.10, 9.08 and 2.9 mg/L. The comparison of the results after 10 and 20 min, ethyl benzene, o-xylene and benzene acetic acid 2-tetradecane were also present after 10 min of ozonation. Other compounds which were also present after 10 min of ozone treatment such as nona, tetra and hexadecane 1-chloro with concentration of 4.5, 0.46 and 2.5 mg/L (Table 3). After 20 min, two new chlorine containing compounds octadecane 1-chloro and 1-

chloroeicosane were identified. In this sample 2,4,5 TCB was found below detection limit or very small amount. Increase in chlorine containing compounds suggested that oxidation of TCB resulted in increased concentration of chlorine containing compounds. O-xylene was observed in high concentration which was 20 mg/L as compared to the concentration found at 10 min sampling.

After 30 min treatment, a total of 12 compounds were identified and only one compound was found containing chlorine which was heptacosane 1-chloro with concentration of 0.29 mg/L. Two compounds were containing benzene structure such as ethyl benzene and o-xylene with concentration of 0.43 and 1.36 mg/L. The compounds like o-xylene, ethyl benzene and heptacosane 1-chloro were present after 20 min and found again after 30 min. Other compounds identified after 30 min of ozonation were octatricontane 1,38-dibromo, octadecanoic acid 2-oxomethyl, tritetracantane, penta tricontane, tetrapenta contane 1 54-bibromo, octatriacontyl pentafluoropropane, tetratetracantane, docosyl octyl ether and carbonic acid octadecyl vinyl.

After 40 min only six compounds were identified which were ethyl benzene, o-xylene and only one compound was chlorine containing compound which was heptacosane 1-chloro. Other two compounds tritetracantane and tetrapentacontane 1,54-dibromo were also present after 40 min and only one new compound was identified 1-dodecanol 2-octyl.

After 50 min of ozone treatment total 8 compounds were identified out of 8 compounds following compounds were also identified after 30 min and 40 min of reaction time such as ethyl benzene, o-xylene, heptacosane 1-chloro, tritetracantane and tetrapentacontane 1, 54-dibromo. After 50 min of reaction time concentration of these compounds were 0.7, 1.83, 0.16, 1.72 and 1.7 mg/L. New compounds identified were 1 dodecanol 2 octyl and carbonic acid octadecyl vinyl ester with concentration of 9.86 and 0.8 mg/L.

After 60 min of ozone treatment total 12 compounds were identified. Ethyl benzene, heptacosane 1-chloro, tritetracantane were identified as after 10, 20, 30, 40 and 50 min time of treatment, after 60 min concentration of these compounds were 1.45, 3.9 and 1.25 mg/L. Carbonic acid octadecyl vinyl ester were also identified after 50 min of treatment time as well as after last 60 min with concentration of 0.8 mg/L. Other new compounds identified after 60 min were as followed: 1-decanol 2-hexyl, 17-pentatricontane, octacosyl trifluoroacetate, docosyl ethyl carbonate, benzene 1-methyl dodecyl, benzene 1-methyl hexadecyl, silane trichloro octadecyl, 2-nonadecane 2, 4-dinitrophenylhydrazine with concentration of 1.16, 1.16, 2.26, 0.9, 18.6, 19.55, 13.12 and 12.48 mg/L.

The selected compounds, ethyl benzene and heptacosane 1-chloro, were not found at zero minutes and after 10 min. These compounds were found during all reaction time with different concentration. TCB which was 17.88 mg/L before treatment and after 20 min its concentration was below detection limit. There may be possibility that increase in ethyl benzene and heptacosine due to oxidation of TCB (Table 3). Various other compounds identified at various time intervals have been presented in Table 4.

3.7. Ozone feed and dissolved oxygen (DO) in wastewater for 60 min reaction

Ozone was continuously injected into the wastewater treatment column at the rate of 3 g/L.hr. As the Figures 8 and 9 show ozone utilization and its impact on change in DO of the treated wastewater. Ozone utilization was measured as difference of feed concentration and

Table 3. Changes in concentration of three selected compounds during ozonation.

Compounds	0 min	10 min	20 min	30 min	40 min	50 min	60 min
Ethyl benzene (mg/L)	NF	0.25	0.335	0.43	0.62	0.7	1.45
Heptacosine 1-chloro (mg/L)	NF	NF	0.21	0.29	0.06	0.16	3.9
TCB (mg/L)	17.88	2.77	BDL	BDL	BDL	BDL	BDL

Table 4. Compounds identified after every 10 min.

S.#	0 min	10 min	20 min	30 min	40 min	50 min	60 min
	Compounds	Compounds identified					
1	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	-	-	-	-	-	-
2	Hexadecane, 2,6,10,14-tetramethyl-	-	-	-	-	-	-
3	Octadecane, 3-ethyl-5-(2-ethylbutyl)-2-hexadecanol	-	-	-	-	-	-
4	2-Nonadecanone	-	-	-	-	-	-
5	2,4-dinitrophenylhydrazine	-	-	-	-	-	-
6	Octadecane, 3-ethyl-5-(2-ethylbutyl)- E,E,Z-1,3,12-Nonadecatriene-5,14-diol	-	-	-	-	-	-
7	Octadecane, 3-ethyl-5-(2-ethylbutyl)- Z-(13,14-Epoxy) tetradec-11-en-1-ol acetate	-	-	-	-	-	-
8	Neronine, 4á,5-dihydro- diisooctyl ester Bis (2-ethylhexyl) phthalate	-	-	-	-	-	-
9	2,4,5-Trichlorobipheny, 2,3,4-Trichlorobiphenyl	2,4,5-Trichlorobipheny	-	-	-	-	-
10	-	Ethyl benzene	Ethyl benzene	Ethyl benzene	Ethyl benzene	Ethyl benzene	Ethyl benzene
11	-	o xylene	o xylene	o xylene	o xylene	o xylene	-
12	-	benzene acetic acid, 2, tetradecyl ester	benzene acetic acid, 2, tetradecyl ester	-	-	-	-
13	-	Benzene, (1-methyldodecyl)-	-	-	-	-	-
14	-	Benzene, (1-methylhexadecyl)-	-	-	-	-	-
15	-	nonadecane 1-chloro	nonadecane 1-chloro	-	-	-	-
16	-	hexadecane 1-chloro	hexadecane 1-chloro	-	-	-	-
17	-	tetra decane 1-chloro	tetra decane 1-chloro	-	-	-	-
18	-	dodecane 4,6-dimethyl	-	-	-	-	-
19	-	undecane 3,5-dimethyl	-	-	-	-	-
20	-	oxalic acid,2- ethylhexyl hexyl ester	-	-	-	-	-
21	-	-	benzene, (1,3,3,trimethylnonyl)-	-	-	-	-
22	-	-	1 chloroheicosane	-	-	-	-
23	-	-	heptacosane 1-chloro	Heptacosane, 1-Chloro	Heptacosane, 1-Chloro	heptacosane 1-chloro	heptacosane 1-chloro
24	-	-	octadecane 1-chloro	-	-	-	-
25	-	-	-	Octatriacontane 1,38-Dibromo-	-	-	-
26	-	-	-	Octadeconoic acid, 2-Oxo-Methyl	-	-	-
27	-	-	-	Tritetracontane	Tritetracontane	Tritetracontane	Tritetracontane
28	-	-	-	Pentatriacontane	-	-	-
29	-	-	-	Tetrapentacontane, 1,54-Dibromo	Tetrapentacontane, 1,54-Dibromo	Tetrapentacontane, 1,54-Dibromo	-
30	-	-	-	Octatriacontyl Pentafluoroprop	-	-	-

(continued on next page)

Table 4 (continued)

S. #	0 min	10 min	20 min	30 min	40 min	50 min	60 min
	Compounds	Compounds identified					
31	-	-	-	Tetratetracontane	-	-	-
32	-	-	-	Docosyl Oetyl Ether	-	-	-
33	-	-	-	Carbonic Acid, Octadecyl Vinyl	-	-	-
34	-	-	-	-	1-Dodecanol, 2-OctylL-	1-Dodecanol, 2-octylL	-
35	-	-	-	-	-	-	-
36	-	-	-	-	-	carbonic acid octadecyl vinyl ester	carbonic acid octadecyl vinyl ester
37	-	-	-	-	-	-	1-Decanol, 2-HexylL-
38	-	-	-	-	-	-	17-Pentatriacontene
39	-	-	-	-	-	-	Octacosyl Trifluoroacetate
40	-	-	-	-	-	-	Docosyl ethyl carbonate
41	-	-	-	-	-	-	Benzene, (1-methyldodecyl)-
42	-	-	-	-	-	-	Benzene, (1-methylhexadecyl)-
43	-	-	-	-	-	-	Silane, trichlorooctadecyl-
							2-Nonadecanone 2,4-dinitrophenylhydrazine

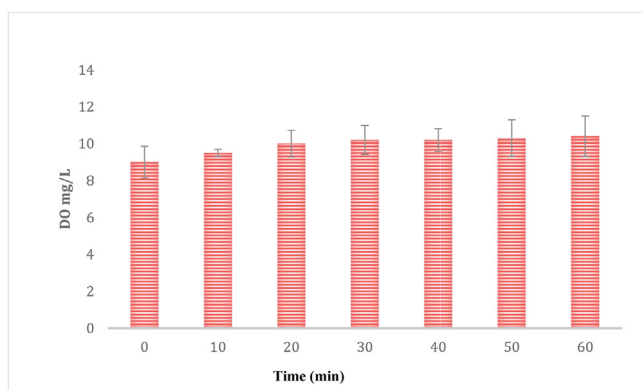


Figure 8. Change in dissolved oxygen concentration during ozone treatment.

concentration measured at the surface of treated water column. In Figure 9 it was obvious that the ozone concentration was increasing at the surface, exit point, of the treatment column from 0 min till 60 min. During the first 20 min, ozone concentration was measured with gradual increasing rate 0.056, 0.061 and 0.06 mg/L and from 40 to 60 min time concentration was increasing sharply as 0.084 and 0.1 mg/L. The difference line shows that ozone utilized in reaction, which was decreasing gradually at time 0, 10, 20, 30, 40, 50 and 60 min with concentration 2.97, 2.95, 2.94, 2.93, 2.94, 2.91 and 2.89 mg/L. This means that effective utilization of ozone during reaction was in between 0 to 40 min.

The present investigation on the use of ozonation to degrade TCB produced promising results. Ozonation of TCBs and other aromatic compounds resulted in significant reduction in their concentration and the degradation products have been mentioned in Table 4. Different compounds were identified after every ten minutes of ozone treatment. The concentration of TCB started to decrease very fast and after 20 min no TCB was found at detectable range of the equipment (0.05 µg/L). Ozone dose (3 g/L h) was found very effective to reduce the TCB. Ethyl benzene was slowly increasing from concentration 0.2 mg/L at 10 min and after 60 min its concentration increased to 1.45 mg/L. The concentration of O-xylene was 16 mg/L after 10 min; while it was observed slight increasing till 20 mg/L after 20 min, later its concentration was found decreasing to 1.6 mg/L at 50 min and not found after 60 min. Benzene acetic acid was started to increase after 10 and it was also found after 20 min but at this time no TCB was observed. There may be conversion of TCB into other compounds like benzene acetic acid etc. Benzene acetic acid is an organic compound containing functional groups of phenyl and carboxylic.

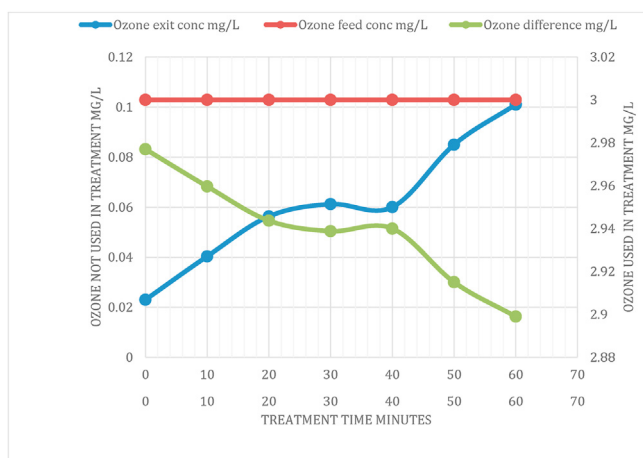


Figure 9. Ozone concentration used in reaction.

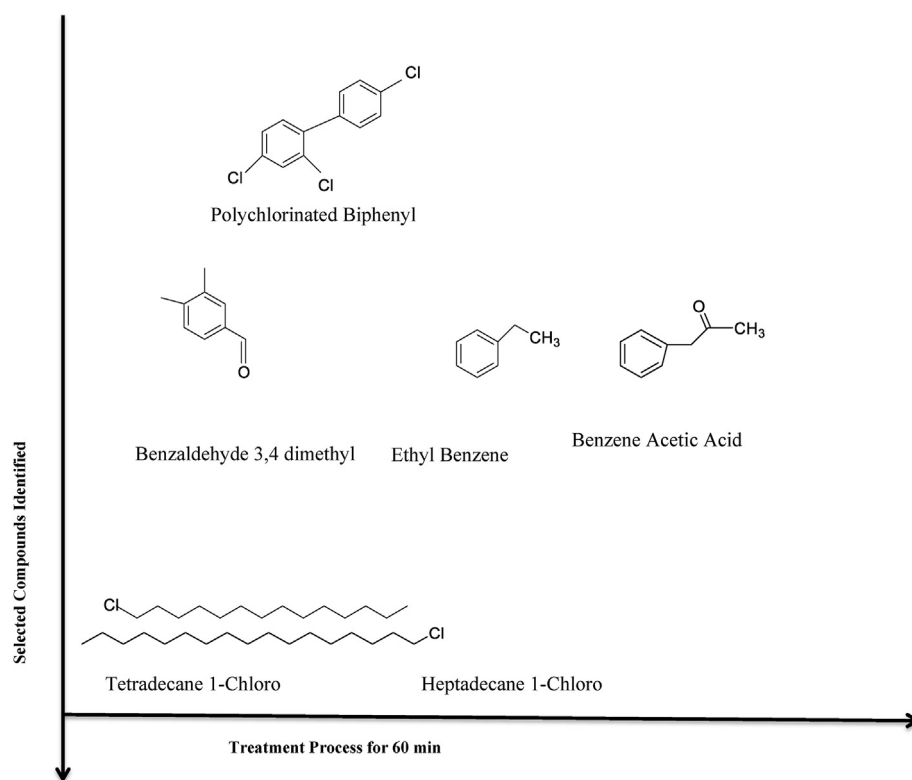


Figure 10. Selected series of degradation products of TCB.

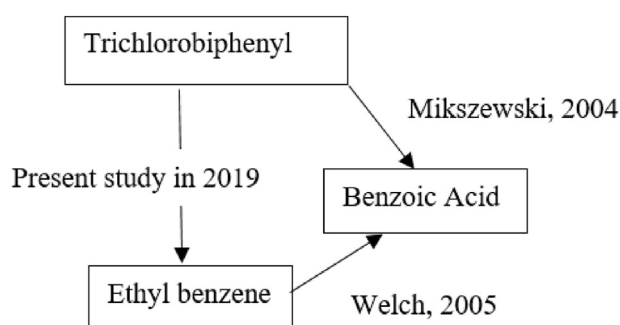


Figure 11. Interconversions of intermediate products of PCB degradation.

In another study by Dudasova [21], it was found that TCB was reduced to less than 0.1 g/m^3 (volume of soil) from initial concentration 0.6 g/m^3 after 20 min of ozone treatment and the ozone concentration injected was 5 g/h . In this study nine different PCBs congeners mixture were used in sediments for ozone treatment. Comparing results with present study where it was observed that TCB was reduced to below detection limit when ozone dose was applied 0.05 g/min after 20 min of continuous treatment. Chen [25] reported that 47% of TCB was reduced by using photosensitized process in the presence of dissolved organic matter. The degraded products were 4-chlorobenzoic acid, 2, 5-dichlorobenzoic acid, hydroxyl-2,5-dichlorobenzoic acid and hydroxyl-TCB. Comparing these degraded compounds with the present study shows different compounds identified which include benzoic acid, ethyl benzene, o-xylene, nonadecane-1-chloro, hexadecane-1-chloro, tetradecane-1-chloro, heptacosane-1-chloro and octadecane-1-chloro. These were different from study by Chen [25]. This may be due to ozone treatment in aqueous solution in the presence of used transformer oil. Based on the prevalence and potential toxicity, the effect of ozonation was studied on the degradation of TCB [26].

It has been shown in other studies [20, 21] that ozonation reduced the concentration of majority of the low chlorinated compounds such as PCB 8 by 97%, PCB 28 by 95% and PCB 52 by 96% however, removal efficiency of PCBs that had more chlorines such as PCB 101, PCB 118, PCB 138, PCB 153, PCB 180 was lower, that was up to 80%, and the removal of octachlorobiphenyl was only about 70% [20]. In this present study, similar compounds identified after 10 min treatment were further degraded into new compounds. Studies have shown that the greatest removal rate for PCB 118 occurred after 10 min of the ozonation process with the corresponding removal efficiency of 85% [21].

The concentration of heptacosane 1-chloro was gradually increased with time by ozonation treatment showing that PCBs may be degraded and chlorine was found along with long chain alkanes like tetradecane 1-chloro, heptadecane 1-chloro, octadecane 1-chloro, hexadecane 1-chloro and nonadecane 1-chloro, these all compounds detected at different time during one hour of treatment. A study found that chlorine was started to accumulate in *Lysinibacillus* sp., during degradation of aroclor 1260

Table 5. Other compounds identified by GCMS in synthetic wastewater.

Name of compounds	Concentration mg/L
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	0.40
Hexadecane, 2,6,10,14-tetramethyl-	0.95
Octadecane, 3-ethyl-5-(2-ethylbutyl)-2-hexadecanol	2.44
2-Nonadecanone	0.73
2,4-dinitrophenylhydrazine	-
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	0.10
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	-
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	0.89
Z-(13,14-Epoxy)tetradec-11-en-1-ol acetate	-
Neronine, 4á,5-dihydro- diisooctyl ester Bis(2-ethylhexyl) phthalate	0.76
2,4,5-Trichlorobiphenyl	17.88
2,3,4 -Trichlorobiphenyl	7.7

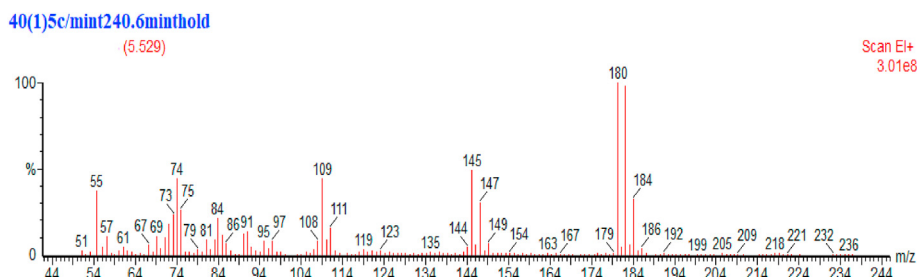


Figure 12. Sub peaks showing other compounds found in sample other than TCB.

(PCB) with 60% chlorine in it, this indicates that chlorine was detached from biphenyl and assimilated by *Lysinibacillus* sp. The current research showed that all alkanes were found with chlorine which may be released during ozone oxidation of TCB as mentioned above in Table 4.

In another study by Deng [27], found tetradecane and pentadecane as product during photocatalytic degradation of 2,4,4-TCB. Comparing results of present study with, Deng [27], tetradecane 1-chloro only one similar compound was found. Other compound, nona, hexa, hepta and octadecane 1-chloro was not found in study by Deng. In our research shows that all alkanes were found with chlorine which may be released during ozone oxidation of TCB.

The Removal of chlorine from PCBs depends upon its position. A study was conducted by Furukawa [28], showing that position of chlorine in the PCB 101 compound structure was two meta, one para and two ortho, while in PCB 118 it was two meta, two para and one ortho. According to Furukawa [28], in the congener structure two ortho positions were responsible for the lower degradation rate. In this study two chlorine was attached at para and meta position of TCB, from these positions' chlorines may release and found with different alkanes.

When present study results were found during ozone treatment aliphatic compounds; Ethylbenzene, aromatic compounds; o-xylene, benzene acetic acid and benzene 1-methyl dodecyl were compared with study by Mikszewski [29] found benzoic acid biphenyl in soil and sediments during bioremediation. One year later, Welch [30] found that benzoic acid was formed during bioremediation of ethyl benzene as seen in Figures 10 and 11. The Sub peaks showing other compounds found in sample other than TCB mentioned in Table 5 were shown in Figure 12. These two different researches by [29, 30] giving evidence that ethylbenzene can be formed during TCB oxidation. Because Mikszewski [28], found benzoic acid formation during TCB degradation and Welch [30] found benzoic acid formation from Ethyl benzene. Our study shows ethylbenzene concentration was increased after 60 min of ozone oxidation of wastewater containing TCB. This shows that TCB oxidation for 60 min may results to form ethylbenzene along with alkanes.

There was a significant effect of ozone treatment on COD. It has been shown that the type of PCB compounds determined the COD removal rate because the PCBs-spiked reactors having initial CODs of 2,300 mg/L and 2,400 mg/L showed low removal efficiency of 11 %. The lower removal efficiency of the reactor was possibly due to the accumulation of volatile acids, especially acetic acid [31].

Studies show that ozone when gets dissolved in wastewater it initiates series of chain reactions to degrade large organic molecules in water and thus decrease COD [24]. To see the effect of ozone reaction on pH and EC of the wastewater before and after ozone treatment. An especially important finding was the reduction in EC which indicated that chloride ions were not released but built up within the structures of alkanes compounds resulting simpler organic compounds [32]. Increase in pH might be due to the increased generation of hydroxyl ions. Ozone has numerous oxidizing properties so that it can be used in treatment of wastewater. Ozone unlike other oxidants, has two

specific mechanisms by which it can cause degradation of organic pollutants. It can be either direct electrophilic attack or indirect attack by the generation of hydroxyl radicals [33]. Organic compounds are degraded by either direct electrophilic attack by ozone molecule or by hydroxyl radicals generated by ozone decomposition [34]. Direct attack of molecular ozone to organic pollutants commonly occurs under acidic or neutral conditions and it is a selective process resulting in the production of carboxylic acids as end products which cannot be oxidized further by molecular ozone. At high pH value, ozone decomposes to hydroxyl radicals, which then attack the organic pollutants. Therefore, it has been examined that the pH of the effluent is a major factor that determines the efficiency of ozonation as it can affect pathways of degradation as well as kinetics. Many researchers [35, 36] studied that by increasing pH the rate of ozone decomposition is accelerated to generate HO· radical, which then degrade the organic compounds more effectively than ozone itself. Thus, the degree of ionization would have increased the pH value.

Kinetic evaluations also determined that the ozonation of wastewater was a pseudo-second order reaction with respect to the COD of wastewater. A logarithmic relationship was found between the rate constants and the applied ozone dose. As the applied ozone dose was increased, COD removal efficiency increased [37]. Studying PCBs degradation in wastewater measured as COD decreasing represented as first order reaction [21].

4. Conclusion

In this study, it was proposed that TCB and other aromatic organic pollutants from transformer oil in wastewater could be oxidized into simpler compounds in one hour of ozonation at the rate of 0.05 g/min could be simple option to decompose TCB and related compounds from wastewater. This concentration of ozone was found more effective decomposition of TCB. During first 20 min, TCB was reduced to concentration below detection limit. Effective utilization of ozone for oxidation reaction was observed in first 40 min and DO remained below 10 mg/L. During this time, ethylbenzene and heptacosane 1-chloro compounds was found in first 10 and 20 min of ozonation and no degradation was noted upon further ozonation. During last 20 min of treatment ethylbenzene, heptacosane 1-chloro, tritetracosane and carboxylic acid were repeatedly observed.

Declarations

Author contribution statement

Umara Abbasi: Performed the experiments; Wrote the paper.
Zulfiqar A Bhatti: Conceived and designed the experiments.
Qaisar Mahmood: Conceived and designed the experiments; Wrote the paper.

Farhana Maqbool, Malik Tahir Hayat: Analyzed and interpreted the data.

Farid Ullah: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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