

UV-OXIDATIVE TREATMENT OF BIO-REFRACTORY ORGANIC HALOGENS IN LEACHATE: Comparison Between UV/O₃, UV/H₂O₂, and UV/H₂O₂/O₃ Processes

Tahir Imran Qureshi¹ and Young-Ju Kim^{2*}

¹Department of Chemical Engineering, NFC-Institute of Engineering and Technological Training, Multan, Pakistan

²Department of Environmental Engineering, Kyungpook National University, Daegu 702-701, Korea
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Abstract : UV-catalytic oxidation technique was applied for the treatment of bio-refractory character of the leachate, which is generally present in the form of adsorbable organic halogens (AOX). Destruction of AOX was likely to be governed by pH adjustment, quantitative measurement of oxidants, and the selection of oxidation model type. Peroxide induced degradation (UV/H₂O₂) facilitated the chemical oxidation of organic halides in acidic medium, however, the system showed least AOX removal efficiency than the other two systems. Increased dosage of hydrogen peroxide (from 0.5 time to 1.0 time concentration) even did not contribute to a significant increase in the removal rate of AOX. In ozone induced degradation system (UV/O₃), alkaline medium (pH 10) favored the removal of AOX and the removal rate was found 11% higher than the rate at pH 3. Since efficiency of the UV/O₃ increases with the increase of pH, therefore, more OH-radicals were available for the destruction of organic halides. UV-light with the combination of both ozone and hydrogen peroxide (UV/H₂O₂ 0.5 time/O₃ 25 mg/min) showed the highest removal rate of AOX and the removal efficiency was found 26% higher than the removal efficiency of UV/O₃. The system UV/H₂O₂/O₃ got the economic preference over the other two systems since lower dose of hydrogen peroxide and relatively shorter reaction time were found enough to get the highest AOX removal rate.

Key Words : UV-catalytic treatment, AOX, Hydrogen peroxide, Ozone

INTRODUCTION

Bio-refractory organic halogens also known as adsorbable organic halogens (AOX) are defined as the sum of all halogen-organic compounds, which can be adsorbed by activated carbon. It is a complex mixture of more than 300 halogenated compounds of aliphatic as well as aromatic origin. A large number of these compounds have been known for their potential toxicity on microorganism and adverse effects on the health of human beings.¹⁾ For instance, halogenated furanone is an extremely

potent mutagen.²⁾ 2,4-dichlorophenol causes irritation in respiratory tract and its detrimental effects on kidneys, liver, and blood are known. Trichloroethylene increases risk of cancer and complicates liver circulatory problems. Sewage water legislation provides very strict regulation for the discharge of AOX containing wastewater since their treatment entails financial problems for specific industrial branches. AOX may be removed by reverse osmosis, air stripping, adsorption by activated carbon, activated sludge or by chemical pre-treatment.³⁻⁶⁾ Unfortunately all of these methods are non-destructive and do not end up with complete mineralization. The rates of AOX degradation through biological treatment, in most of the cases, are too

* Corresponding author
E-mail: yjukim@knu.ac.kr
Tel: +82-53-950-6585, Fax: +82-53-950-6579

slow to be practical. Scientists have been working on the effective removal of AOX by different chemical means since last decade. Kazuaki *et al.*,⁷⁾ concluded that in advanced oxidation processes (AOPs), the rate of destruction of trihalomethane formation potential was found higher than that of dissolved organic carbon removal. And a large reaction time did not contribute to the quantitative increase in the biodegradable components but supported to greater mineralization. Hofl *et al.*⁸⁾ observed appearance of new organohalides, so called AOX *de novo*¹⁵⁾ during the oxidative treatment of pharmaceutical wastewater. However, these organohalides were destroyed in the progressive stages of the reaction since chloride content in the sample was very low (<200 mg/l). Singer⁹⁾ while working on the control of disinfection by-products also pointed to AOX development phenomenon to some extent.

While past studies have been primarily focused on the study of AOX phenomenon in UV-oxidative treatment, a very little work has yet been undertaken on investigating the characteristic role of different oxidants in eliminative degradation of AOX. In this study, we worked on the destruction of AOX in AOPs treatment of the leachate. Synergy of UV-light with two oxidants in three

systems, i.e. UV/O₃, UV/H₂O₂, and UV/H₂O₂/O₃ was tested. An underlying objective of the work had been to examine how oxidation systems could be run facilitating maximization of AOX removal in the most cost effective manner.

MATERIALS AND METHODS

Equipment

UV- reflecting type reactor was employed for this work with dimension of 19 cm high, 24 cm long, and 18 cm wide. A high-pressure UV-lamp consisted of one 20 cm synthetic quartz tube with inner and outer diameters of 2.5 cm, and 4.0 cm, respectively was installed in the upper lid of the reaction vessel. To get the highest possible penetration depth of the UV-radiation, the lamp was fixed at a level of 2 cm above the reaction mixture. Power and specific power of the UV-lamp could be regulated between 300-3000 W, and 15-150 W/cm², respectively. Intensity of the light was set at a minimum value of 0.69 W/cm² by the variable voltage transformer. The high energy UV radiation is generated by briefly vaporizing the mercury inside the lamp and igniting the gases that are released radiation at 254 nm. Dosage of UV-light was

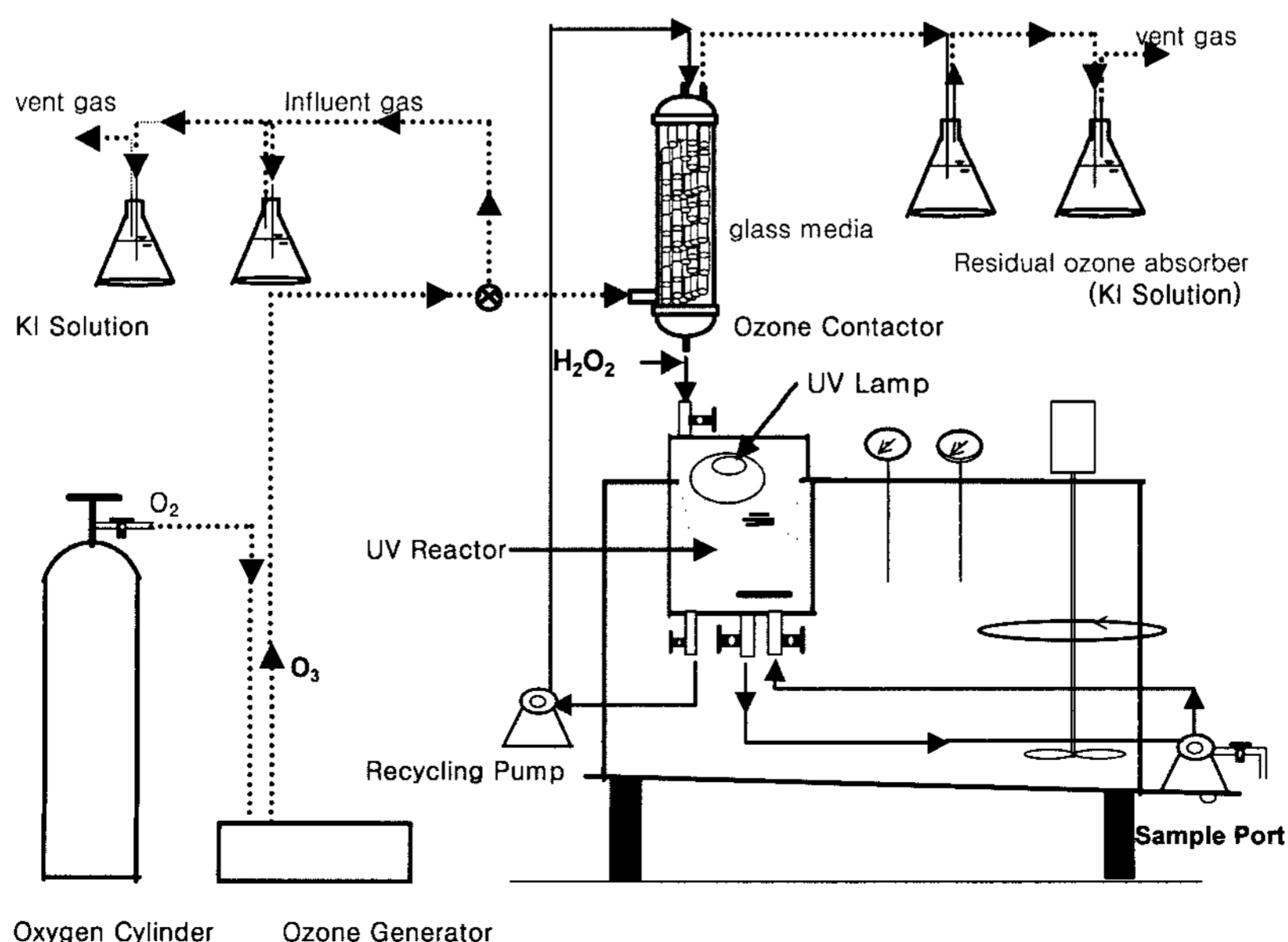


Figure 1. Schematic diagram of UV-reflecting type reactor.

measured in watt seconds of UV-energy per sq. cm of water surface (Ws/cm^2). Input of the UV-light was 1500 W, which continued until the completion of reaction time of 3 hours. Reflection of the UV-light was facilitated with the help of an arc-shaped reflector (24 cm long, and 12 cm in diameter) adjusted over the UV-lamp. Cooling system of the UV-lamp was maintained with the supply of air at a flow rate of 400 m^3/hr . To increase the contact time of ozone with the sample, an ozone contactor (450 cm high, and 8 cm in diameter) was installed at the inlet of the main reaction vessel and the reaction mixture was recycled at a flow rate of 2 L/min. The column was packed with cylindrical shaped glass media (8 mm high, and 4 mm in diameter). Ozone was produced from dry oxygen by an ozone generator (COM-CD-HF2, Anseros, Germany). Ozone concentration in the gas phase was determined by iodometric titration after fixing it in potassium iodide solution. All the mechanical parts of the photo reactor assembly contacting either with the gas phase or the liquid phase were made of high chemical resistant materials; such as low carbon stainless steel, per fluorinated plastics or glass. Final treated samples for laboratory analyses were collected from the bottom of the photo reactor. All the reactions were carried out at $20 \pm 2^\circ\text{C}$ with a feed volume of 8 L. Figure 1 shows schematic diagram of the UV- reflecting type reactor.

Sample and Operating Modes

Sample of leachate was taken from the landfill, which is located in the suburb of Daegu city, the third largest city of Korea having a population of about 3 million. The site covers a surface area of 60 ha having total capacity of 1500×10^4 tones and has been in operation since 1990. The waste collected breaks down into the fractions like: household solid waste (55%), non-toxic industrial waste (NIW) (20%), inert waste (18%), auto wreckers waste (AWW) (9%), for a total of 700,000 tones/year. The quantity of leachate produces is approximately $328,500 \text{ m}^3/\text{year}$. The leachate collected was tested without any pre chemical or

biological treatment. Color of the sample was dark black and its pH was 7.8. pH of the reaction mixture was adjusted to pH 3, 7, and pH 10 by the addition of 0.5 N H_2SO_4 (120 ml/8L of sample), 0.5 N H_2SO_4 (9 ml/8L of sample), and 2 N NaOH (220 ml/8L of sample), respectively. Measurement of pH was done by a pH meter (Model NO., S/N 41882, Orion, 1996 Orion Research Inc., USA). Characteristics of raw leachate are given in Table 1.

Batch experiments were carried out and a solution of H_2O_2 (30% w/w) was injected at a stoichiometric amount equivalent to the chemical oxygen demand (COD) of the sample. Ozone gas was supplied at different rates (Table 2) to the reaction mixture. Samples were taken at different time intervals, i.e. 15, 30, 60, 120 and

Table 1. Characteristics of raw leachate at pH 7.8

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
BOD ₅	718	T-P	48.2
COD	5,000	Cl ⁻	300
TOC	1,700	Cd	*ND
AOX	7~8	As	*ND
Acidity	7,671	Cr	3.2
Alkalinity	12,280	Cu	3.5
TSS	1,105	Fe	0.98
VSS	554	Mn	2.1
TKN	2,246	Pb	1.8
NH ₄ -N	1,854	Zn	2.1
Color	6,138 (Pt-Co units)	CN	0.34

Table 2. Operation conditions in different modes of oxidation systems

Oxidation process	*Dose of hydrogen peroxide and ozone
UV/H ₂ O ₂	H ₂ O ₂ alone (0.5 time)
	UV/H ₂ O ₂ (0.2 time)
	UV/H ₂ O ₂ (0.5 time)
	UV/H ₂ O ₂ (1.0 time)
UV/O ₃	UV/O ₃ (25 mg/min)
	UV/O ₃ (50 mg/min)
UV/H ₂ O ₂ /O ₃	UV/H ₂ O ₂ (0.5 time)/O ₃ (25 mg/min)
	UV/H ₂ O ₂ (1.0 time)/O ₃ (25 mg/min)

* stoichiometric amount equivalent to the amount of COD of the sample

180 minutes taking aliquots of 20 ml. COD was calculated by heating the sample with potassium dichromate solution in sulfuric acid for two hours at 148 °C followed by determination of transmittance of the cooked solution at 600 nm. Samples for AOX were tested by using photometer (Nanocolor 400 D, Machinery-Nagel, Germany). Systems were run within the broad range of pH values (3~10).

RESULTS AND DISCUSSION

Peroxide Induced Degradation (UV/H₂O₂)

Peroxide induced degradation facilitated chemical oxidation of organic halides in acidic medium (pH 3). Least AOX removal rate was observed in alkaline medium at pH 10 (Table 3). Reaction at acidic medium showed about 8.1% higher AOX removal than the alkaline medium. This trend could be explained on the basis that the rate of oxidation of organic compound in UV/H₂O₂ system depends upon the relative concentration of H₂O₂ species (H₂O₂ and HO₂⁻) in the solution ($pK_a = 11.7$)¹⁰. An increase in pH of the solution would increase both the generation rate of hydroxyl radicals and the scavenging effect of H₂O₂. Also, efficiency of the UV/H₂O₂ process is not affected by the pH for pH values lower than 8, but

decreases for increasing pH from 8 to high pH value. Peroxide induced degradation system, however, showed the least AOX removal efficiency than the other two-oxidation systems. Increased dose of hydrogen peroxide (from 0.5 times to 1.0 time concentration) even did not contribute to a significant increase in the removal rate of AOX (Table 3) as many routes of destruction govern degradation efficiency of UV/H₂O₂ system. They may follow the direct oxidation by H₂O₂, the direct photolysis by UV light, and the indirect oxidation by OH-radical produced from H₂O₂ excited by UV-light.

The result also showed that the mode UV/H₂O₂ (0.5 time) leads to a high degradation level in comparison to the mode H₂O₂ alone (data not shown). It could, therefore, be beneficial to use lower dose of H₂O₂ in combination with UV than a high dose of H₂O₂ without UV. COD and total organic carbon (TOC) removal rate followed almost the similar trend with that of the removal rate of AOX (Table 3).

Ozone Induced Degradation (UV/O₃)

In ozone induced degradation system, alkaline medium (pH10) favored the removal of AOX and the removal rate was found 11.3% higher than the rate at pH 3 (Table 3). High pH refers

Table 3. AOX, COD, and TOC removal in different modes of oxidation systems

System	UV/H ₂ O ₂			UV/O ₃		UV/H ₂ O ₂ /O ₃
Mode	*(0.2 time)	(0.5 time)	(1.0 time)	*(25 mg/min)	(50 mg/min)	(0.5 time/25 mg/min)
AOX removal (%)						
pH						
3	32.13	44.25	46.32	45.29	46.19	64.13
7	29.41	40.41	39.05	48.17	50.12	71.24
10	24.36	36.17	38.46	56.35	57.47	83.46
COD removal (%)						
3	70.13	82.20	89.19	44.21	44.39	85.18
7	58.32	69.31	65.26	42.47	43.10	87.29
10	37.43	43.04	45.09	50.19	51.43	91.37
TOC removal (%)						
3	68.29	79.38	87.17	46.39	48.21	86.34
7	61.15	70.44	66.14	49.18	49.45	89.21
10	40.37	49.27	48.38	58.13	59.32	94.37

*stoichiometric amount of H₂O₂ and O₃ equivalent to the amount of COD of the sample

to the presence of a high concentration of hydroxyl ions (OH^-) that may lead to hydroxyl radical formation (OH^\bullet), the main oxidizing character, through an indirect route. The OH^- reacts with ozone to form HO_2 and conjugated base of H_2O_2 . Also, the rate of decomposition of ozone increases with increasing pH, consequently, beyond some critical pH, hydrogen radical could become the predominant oxidizing species.¹³⁾ This phenomenon could lead the ozone induced degradation system to higher AOX removal trend. According to data, low dose of ozone (25 mg O_3/min), with the combination of UV, showed comparable results (Table 3) with the high dose of ozone UV/ O_3 (50 mg O_3/min). It could be inferred that applying higher dose of ozone might not be necessarily advantageous for the enhancement of the destruction of bio-refractory character of the leachate, and a lower dose of ozone was already sufficient to achieve the specific target of AOX removal. Excessive dose of ozone (50 mg O_3/min) would only contribute to the increased residual amount of ozone in the reaction mixture. Experiments done by Weichgrebe *et al.*¹¹⁾ also confirmed that higher ozone rate is only benefited at the lower energy output. The mode with lower dose of ozone could be adopted owing to have economic advantage over the other one.

UV/ H_2O_2 / O_3 System

UV with the combination of both hydrogen peroxide and ozone (UV/ H_2O_2 0.5 time/ O_3 25 mg/min) showed the highest AOX removal rate and it was found about 26% higher than the removal rate of UV/ O_3 at pH 10 (Table 3). Also, the combination system required relatively shorter reaction time to achieve the highest possible removal rate of AOX as compared to the other two systems. Higher efficiency of the UV/ H_2O_2 / O_3 system could be attributed to the fact that, synergy of UV with two oxidants increases the oxidation level to a strength, which would be unlikely to exist with the combination of peroxide or ozone alone. In ozone-hydrogen peroxide system, hydrogen peroxide leads to the decomposition of ozone into hydroxyl radicals, mechanism showed in Figure 3.

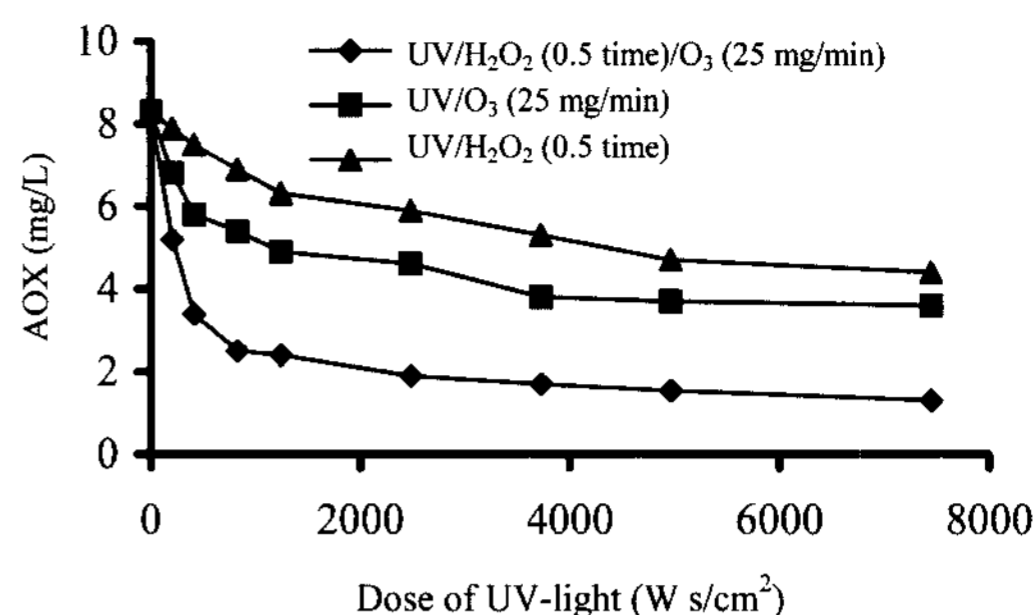


Figure 2. Energy consumption requirement of AOX removal in different modes of oxidation system.

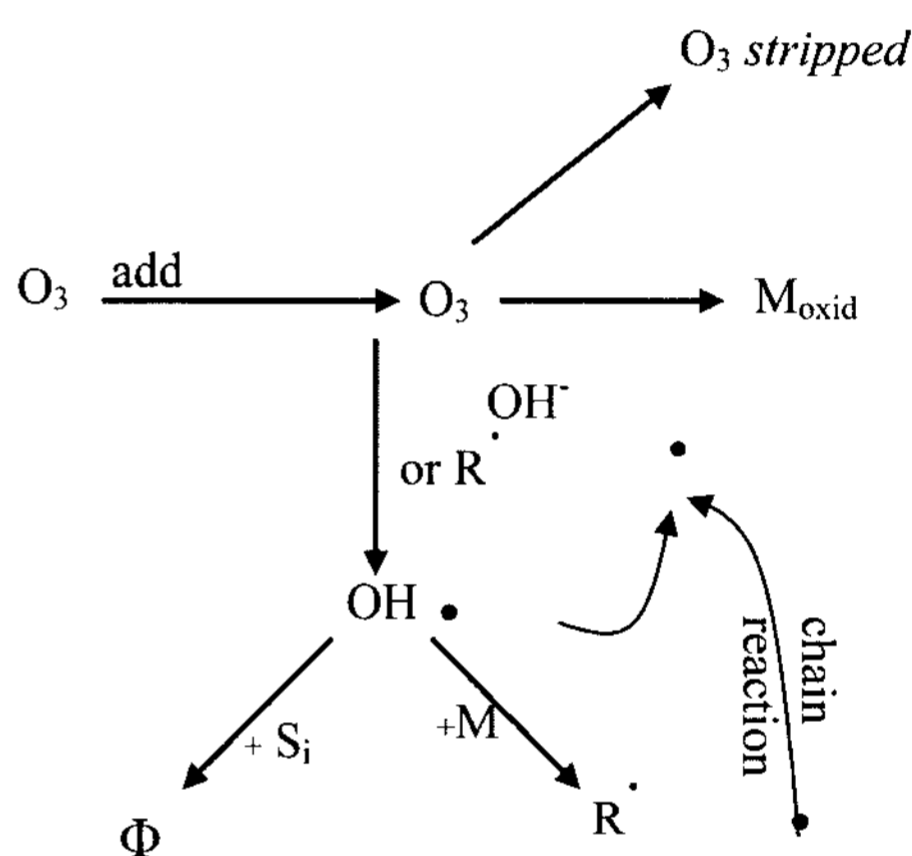


Figure 3. The decomposition mechanism of ozone to form hydroxyl radical.¹⁴⁾

Where M = solute,

M_{oxid} = oxidized solute,

S_i = free radical scavenger,

Φ = product which do not catalyze the ozone decomposition, and

R^\bullet = free radicals

Higher efficiency of UV/ H_2O_2 / O_3 system could be assumed that like ozone, H_2O_2 / O_3 reacts with organic halogen compounds. These conditions make AOX removal rate higher than with ozone or hydrogen peroxide alone. In UV/ H_2O_2 / O_3 system, expected enhancement of the reaction rate by the addition of H_2O_2 did not occur since the organic compounds can also be destroyed rapidly via direct molecular attack of ozone. This observation is in accordance with the recent studies conducted with H_2O_2 / O_3 combination for the treatment of industrial wastewater.¹²⁾

Economic Analysis

Energy consumption sketch drawn on the basis of dosage of UV-light consumed against degradation potential of AOX suggested economic preference of UV/H₂O₂/O₃ over the other oxidation systems. In order to get the highest possible degradation rates with the utilization of minimum amount of energy, intensity of the UV-light, throughout the experiment, was kept at a minimum value (0.69 W/cm²). In term of UV-light dosage supplied to different oxidative systems, UV/H₂O₂/O₃ was found the most cost-effective system as compared to the other two systems (Figure 2). A dosage of UV-light (7452 W s/cm²) successfully achieved 84% AOX removal in UV/H₂O₂/O₃ system while the other two systems with one oxidant could not compete in securing similar removal efficiency with the supply of equal dosage of UV-light. Energy consumption requirement for TOC and COD removal followed the same trends as with that of AOX removal in all the three oxidative systems.

CONCLUSION

Removal of bio-refractory halogens in leachate was successfully achieved by the application of UV-oxidative treatment system. Peroxide induced degradation facilitated the AOX removal in acidic medium while ozone induced degradation favored the same in alkaline medium. UV with the combination of both ozone and hydrogen peroxide showed the highest removal rate of AOX. The system UV/H₂O₂/O₃ got the economic preference over the other two systems since the reduced amount of hydrogen peroxide and relatively shorter reaction time were found enough to get the highest AOX removal rate.

Nomenclature

AOX	Adsorbable organic halogens
AOPs	Advanced oxidation processes
AWW	Auto wreckers waste
BOD ₅	Biochemical oxygen demand in 5 days
COD	Chemical oxygen demand
NIW	Non-toxic industrial waste

TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
T-P	Total phosphorous
TSS	Total suspended solid
UV	Ultra violet
VSS	Volatile suspended solid
W	Watt

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