



Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water

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Abstract

Removal of low levels of organic pollutants can be quite challenging to many water treatment processes. Ketones, such as acetone, are often found in groundwaters and wastewaters at levels too low for supporting a bioreactor, yet since acetone is so soluble, it does not adsorb onto activated carbon very well, nor does it volatilize from water influent using air stripping. This study was undertaken to evaluate three advanced oxidation processes for their comparative ability to remove acetone from aqueous media. Optimization of the oxidation processes was attempted via adjustments of oxidizer inputs. The results indicated that all of the AOPs tested showed promise for removing acetone from water; however, ozonated systems undergoing UV photolysis achieved the highest rate and extent of treatment observed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ketones; Advanced oxidation processes; Water treatment

1. Introduction

Removal of low levels of organic compounds from water can be difficult and expensive. Traditional treatment processes such as biological degradation, carbon adsorption, and air stripping have proven to be effective for many pollutants [1]. However, ever-tightening regulations and process limitations with certain pollutants and their respective concentrations within an influent make development of innovative and more efficient water treatment processes a necessity [1–4]. Chemical oxidation processes offer a high degree of process flexibility and the ability to degrade pollutants and concentration levels that can be challenging to

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the treatment processes listed above [5,6]. Chemical oxidation processes are well established in terms of municipal water treatment [7] but still lack a proven track record for many pollutants, including ketones. Advanced oxidation processes (AOPs) are chemical oxidation technologies that rely on the formation of the hydroxyl radical (OH^\bullet) to further oxidize organic and/or inorganic contaminants. Examples of AOPs that have been proven to be effective in removing pollutants from contaminated waters include ultraviolet (UV) photolysis of ozone (UV/O_3), UV photolysis of hydrogen peroxide ($\text{UV}/\text{H}_2\text{O}_2$), peroxone (the dark reaction of H_2O_2 with O_3), and the illumination of photocatalysts, such as titanium dioxide [5,8–15]. Investigations on the mechanisms of oxidation of specific pollutants, as well as how these reactions are affected by different process variables are necessary to support the potential wider application of these AOPs for site remediation and wastewater treatment activities.

Ketones are used as raw materials, intermediates, and waste products for the manufacture of several types of products including pharmaceutical, plastics, paints, and lubricants [16]. The wide-spread use of ketones has resulted in their appearance in various types of waters and locations in the environment [15,17,18]. The simplest ketone, acetone, is one of the most frequently found water-borne organic compounds in the United States [18]. It has been found in groundwater at various Superfund sites in combination with other hazardous pollutants [15,19]. The EPA regulated level for acetone varies from site to site, depending on the future usage planned for the groundwater resource [20]. Nevertheless, acetone concentration discharge limits have been regulated in the part per billion (ppb) range during past Superfund clean-ups [19].

Acetone is a relatively easy to biodegrade compound [20,21]. Unfortunately, many groundwaters contain acetone along with other organics that are not easily biodegradable. In addition, levels of acetone are often too low to support a stable biomass [17–19]. Granulated activated carbon technology has been used as an alternative in some of these cases, but spent carbon has to be transferred off-site for disposal or regeneration. Additionally, activated carbon has a relatively low adsorptive capacity for acetone [22]. Stripping of acetone is not feasible at ambient temperatures because of its relatively low Henry's law constant [6]. Finally, bench-scale and pilot scale studies using various AOPs have shown a build-up of acetone in waters contaminated with explosives, 2-propanol, solvents, and 1,2-dibromo-3-chloropropane [23–25]. This indicates that acetone is likely produced during the oxidation of some organic pollutants.

This study compares the efficiency of three popular AOPs (UV/O_3 , $\text{UV}/\text{H}_2\text{O}_2$, and $\text{H}_2\text{O}_2/\text{O}_3$) for treating water contaminated with acetone. The quantitative effect of batch and or semi-batch added oxidizer (H_2O_2 and O_3) dosages and contact time on acetone degradation was defined for the three AOPs. The best operating conditions for each candidate AOP in terms of acetone oxidation were identified via performance of a series of bench-scale experiments.

2. Theory on candidate advanced oxidation processes

The goal of any AOP design is to utilize and maximize the oxidizing potential of the hydroxyl radical which is one of the most reactive intermediate chemical species known [26]. This fact is shown in Table 1, which compares the relative oxidation potentials of several

Table 1
Thermodynamic oxidation potential of common oxidation agents used in water treatment [27]

Comparative oxidation potentials	
Species	Volts
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Hypochlorous acid	1.5
Chlorine dioxide	1.5
Chlorine	1.4
Oxygen	1.2

chemical oxidizers. The hydroxyl radical typically attacks organic species by abstracting a hydrogen atom or by adding to the double bond of unsaturated molecules. Radical production includes photolytic, alkaline (high pH), and ozone–hydrogen peroxide reactions [27]. The hydroxyl radical can be consumed by reacting with the contaminant, inorganic constituents present in the influent matrix, and/or the parent oxidizers themselves. All reactions that do not result in the degradation of the contaminant are called “scavenging reactions”. Mineral scavengers (bicarbonates, carbonates, etc.) present in many influents can drastically reduce the efficiency of pollutant oxidation in direct proportion to their concentrations via the reactions [8]:



Also, it has been observed that reduced cations (e.g. iron) and excessive amounts of the primary oxidizers (e.g. ozone and hydrogen peroxide) can serve as significant scavengers of the hydroxyl radical [27,28]. There is an optimum dose for each oxidizer added and stoichiometric mass ratio for systems, such as peroxone, that use two or more chemical oxidizers. It is difficult to add an excessive amount of ozone due to mass transfer limitations (gas–water transfer), but an excessive amount of hydrogen peroxide (a fully water-soluble liquid) can be added; thereby, serving as a potential scavenging source [24,28,29].

Many of the reactions and variables that govern each of the AOPs examined in this study are similar. However, it is important to understand the differences between each AOP because these differences affect treatment efficiency and process economics. The process parameters associated with each AOP evaluated in this study and how they potentially impact treatment are briefly discussed below to provide a framework for the rationale for the design of the study.

3. UV/hydrogen peroxide

The photodecomposition of hydrogen peroxide is the most direct and efficient technique for the generation of the hydroxyl radical [29]:



The most common UV lamp used in this AOP is the medium pressure mercury vapor UV lamp (MPUV). It has significant emittance within the 200–250 nm range, which is the primary absorption band for hydrogen peroxide. The high energy photons produced by the MPUV lamps can degrade, via photolysis, many organic contaminants within water matrices. The combination of MPUV with H_2O_2 dosing make the degradation kinetics achieved with this AOP to be typically more rapid than the other AOPs due to the presence of the increased amounts of the hydroxyl radical and higher intensity UV irradiation fields.

The production of hydroxyl radicals within a MPUV/ H_2O_2 system can be affected by variables such as temperature, pH, concentration of H_2O_2 , and presence of scavengers. For example, the pH effect is due to the acid–base decomposition of hydrogen peroxide, as shown in Fig. 1 (step 3). This type of decomposition is undesirable in the MPUV/ H_2O_2 system because it consumes hydrogen peroxide without generating hydroxyl radicals. However, as in the UV/ O_3 system, the effect of the pH on the efficiency of hydroxyl radical production and its final reaction will depend on the nature of the contaminant. Another important variable is hydrogen peroxide concentration. In a batch system, the gain in efficiency of degradation for an organic or inorganic species obtained by increasing the initial concentration of hydrogen peroxide due to the increase in the rate of formation of hydroxyl radicals predicted by reaction (4) is limited. Hydrogen peroxide can act as a scavenger at relatively high concentrations [28]. Hydrogen peroxide reacts with the hydroxyl radical as follows:



The rate constant for reaction (5) is 2.7×10^7 l/mol s [27]. The negative effect of this reaction will depend on the residual concentration of hydrogen peroxide in the system. The optimum concentration of hydrogen peroxide in the system will depend on the rate constant for the reaction of the hydroxyl radical with the contaminant of interest.

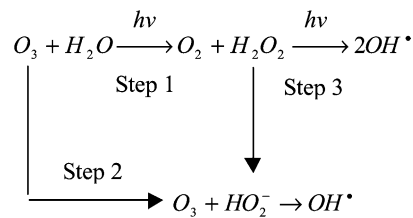


Fig. 1. Photodecomposition of ozone [29].

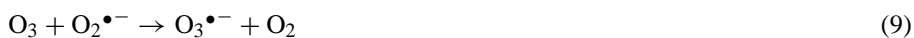
4. UV/ozone

Ozone is a powerful oxidizer having an oxidation potential of about 1.5 times that of chlorine gas, which is the most common oxidizer used in drinking water treatment [7]. As illustrated in step 1 of Fig. 1, the photolysis of ozone within aqueous solutions yields hydrogen peroxide directly, which in turn initiates the further decomposition of residual ozone into hydroxyl radicals [29]. Because of their high reactivity, ozone and the hydroxyl radical are known to oxidize a high variety of organic and inorganic pollutants [11,15].

The UV/O₃ system is similar to the peroxone (H₂O₂/O₃) process where once hydrogen peroxide is formed, there is a “dark” pathway (the other is lighted) that produces the hydroxyl radical. In the former, the H₂O₂ is formed during the photolytic treatment of ozone instead of being added by an external source. Nevertheless, UV light plays an important role in the UV/O₃ system. Some compounds are degraded by direct photolysis due to the reaction with the photons emitted by the mercury vapor lamps used in UV/O₃ systems [9,14]. Furthermore, UV light can excite organic pollutants molecules making them more susceptible for hydroxyl radical attack [30]. Ozone absorption of UV irradiation occurs primarily at 254 nm. Low pressure mercury vapor UV lamps (LPUV) are the most common sources of UV radiation used for this process since they emit the vast majority of their radiation spectrum at the 254 nm wavelength. Systems of this type represent the oldest commercialized AOP that have been used for wastewater and groundwater treatment [11]. In the late 1970s, the EPA selected the UV/O₃ process as a “best practicable technology” for the removal of PCBs from water sources [11]. The efficiency of the system is affected by many variables such as pH, temperature, scavengers in the influent, turbidity, UV intensity, lamp spectral characteristics, influent UV transmissivity, and pollutant type(s).

5. Peroxone (H₂O₂/O₃)

The path for the formation of hydroxyl radicals in the peroxone process is similar to those radical production mechanisms associated with the UV/O₃ system. In this case, hydrogen peroxide is added from an external source instead of forming it via the photolytic breakdown of ozone. The reaction steps during peroxone oxidation for the formation of the hydroxyl radical as described [8] are:



The system is affected by the same variables that affect the UV/O₃ system, except for UV lamp related issues. One advantage over the UV/O₃ system is that it can be used in turbid

or dark waters because it is a dark AOP that is not dependent on the UV transmissivity of the influent being treated.

6. Experimental methodology

6.1. Apparatus and materials

A 1 l glass borosilicate reactor, illustrated in Fig. 2, was used in all of the experiments performed during this study. The reactor has an inner immersion well which houses the UV lamp which allows the UV lamp to be inserted into the reactor volume for the effective application of photolysis within a large portion of the water undergoing treatment. The immersion well is jacketed to control reactor temperature because the UV lamps can produce significant heat (especially the MPUV lamps). Cooling is accomplished by circulation of chilled water through the cooling jacket. The MPUV lamp and LPUV lamps used in this study as light sources had input power ratings of 200 W and 12 W, respectively. Both lamps were manufactured by Hanovia Inc. and marketed by Ace Glass Inc.

Ozone was sparged into the reactor using an OzonologyTM ozone generator with the capability to control the percent of ozone composition in the sparged gas up to 3% by weight. Sparging was accomplished by insertion of a ceramic air-stone into the reactor as illustrated in Fig. 2. Gas phase ozone measurements were analyzed for ozone concentration using an in-line ozone monitor (Fig. 2). The ozone monitor was a PCI Model HC-1 which utilizes a photoionizing UV detector system to measure the percent ozone levels within inlet and outlet gases. Gas flow into the reactor was controlled using a rotameter with regulatory capability mounted on the ozone generator. The volumetric flow rate of gas into the reactor was maintained at approximately 2.5 SCFH (standard cubic feet per hour). The generator ozone output was determined by making a calibration curve of ozone production versus voltage for the O₃ generator before the initiation of the experiments. The exhaust gas from the monitor was passed through a catalyst bed (a mixture of MgO₂ and CuO) for ozone destruction prior to venting to the atmosphere.

Samples for acetone analysis were periodically collected from the reactor at predetermined time increments to develop kinetic information. During each sampling event, approximately 40 ml of sample were removed and stored in 40 ml vials with teflon lined caps. The vials were precleaned to USEPA specifications for organics sampling. To prevent further oxidation within the sample bottle beyond the intended reaction time, approximately 0.01 g of bovine catalase was added to the vials. Catalase is an enzyme produced in the liver of cows to destroy oxidizer species (radicals and hydrogen peroxide) produced during metabolic activity. Analysis of a water control dosed with catalase did not show interference with the analysis of water samples nor did acetone appear as a product of catalase oxidation. Samples were stored at 4 °C for no more than 7 days before analysis. Effluent pH and temperature were measured each time a sample was collected. The pH and temperature of each sample were measured with a Beckmann pH meter equipped with a combination electrode calibrated using a standard two point calibration (Fisher brand pH 4 and pH 10 buffers were used as pH standards).

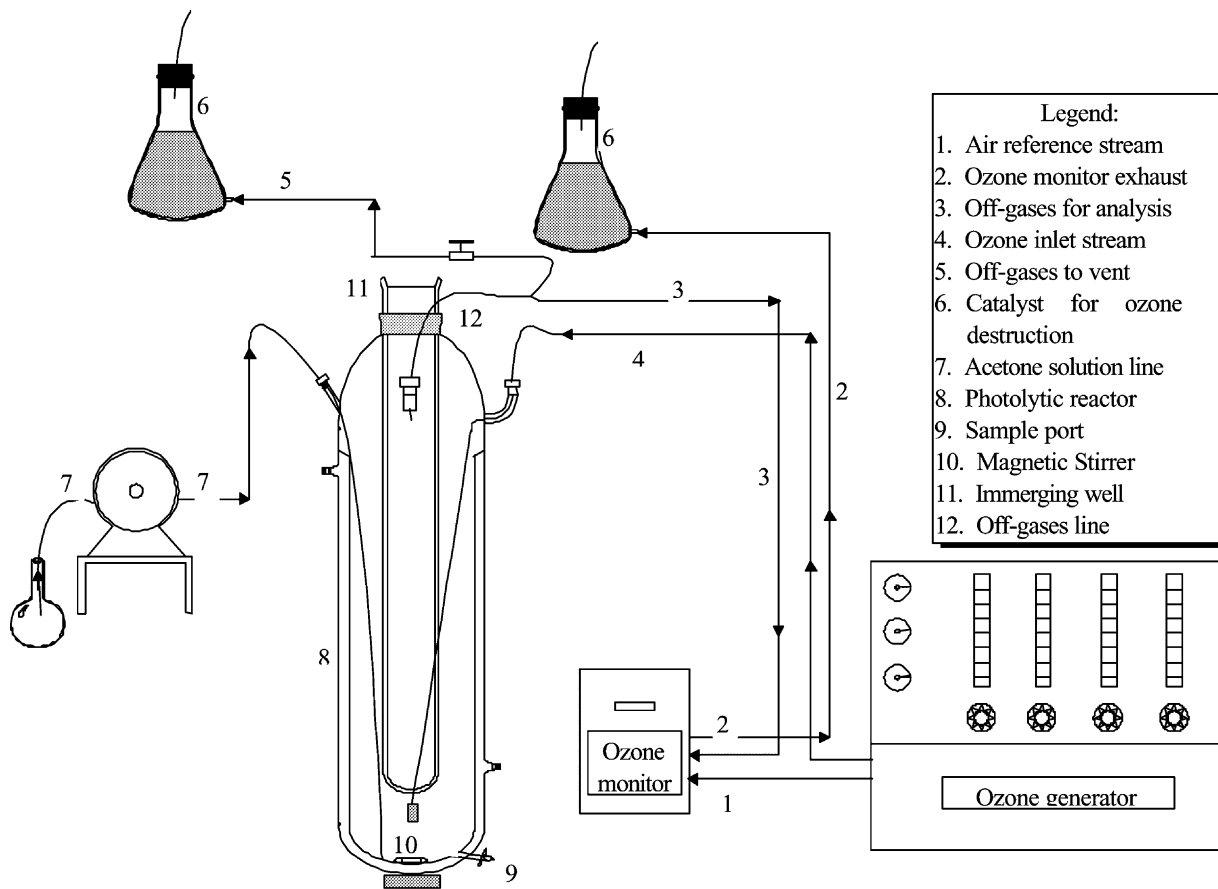


Fig. 2. Bench-scale AOP reactor (not to scale).

Analytical grade reagents were used in all of the experiments. A 50% (w/w) hydrogen peroxide stock solution was used to dose the AOP reactor according to the targeted dose. Distilled and deionized (DDI) water was spiked with the acetone and oxidants. Borate buffers were used to maintain the test solutions at pH 7. The buffer was prepared by mixing 7.455 g potassium chloride, 6.184 g boric acid and 2.0127 g sodium borate into 3 l of DDI water.

A Hewlett-Packard mass spec/gas chromatography unit equipped with an OI analytical sample concentrator was used for all acetone analyses following the techniques described in USEPA analytical method 8260A. The method detection limit for acetone using this method and instrumentation is approximately 25 µg/l. Preliminary testing determined that the presence of the pH buffer reagents or catalase in the sample matrices did not pose significant analytical interference to the method.

7. Experimental procedures

All AOP experimental runs were conducted as detailed below:

1. One liter of water spiked with a known concentration of acetone (approximately 5 ppm acetone) was placed in the reactor. An initial sample (before the addition of oxidants) was collected for analysis as the test influent. H₂O₂ was added according to the specific run conditions (H₂O₂/O₃ and UV/H₂O₂ experiments) to give the desired initial concentration.
2. The UV lamps were turned on for 5 min before adding the test liquids into the reactor to allow the lamps to reach full irradiation output.
3. The acetone spiked water and hydrogen peroxide (when appropriate) were added into the reactor and ozonation was rapidly initiated thereafter (when appropriate). Ozonation was initiated by adjusting the ozone generator to the desired level (wt.%) and by adjusting the O₃ flow introduced into the reactor (this was considered $t = 0$).
4. All reactions were allowed to proceed for 60 min. A temperature of 20 °C was maintained during all of the experimental runs. Samples were collected periodically for the chemical analyses as described above. All experiments were performed in duplicate with the data shown herein representing an average of the two replicates.

8. Discussion of results

8.1. MPUV/H₂O₂

A set of experiments was performed to track hydrogen peroxide concentrations during treatment. The results of these experiments are presented as Fig. 3. While the effect of hydrogen peroxide dosing on the degradation of acetone was later tested during performance of a second set of experiments, the results of these experiments are shown in Fig. 4, which presents the fraction of acetone remaining versus reaction time. Note that two separate experiments were performed to evaluate hydrogen peroxide and acetone fate because the amount of sample volume required for both analyses was too large to allow

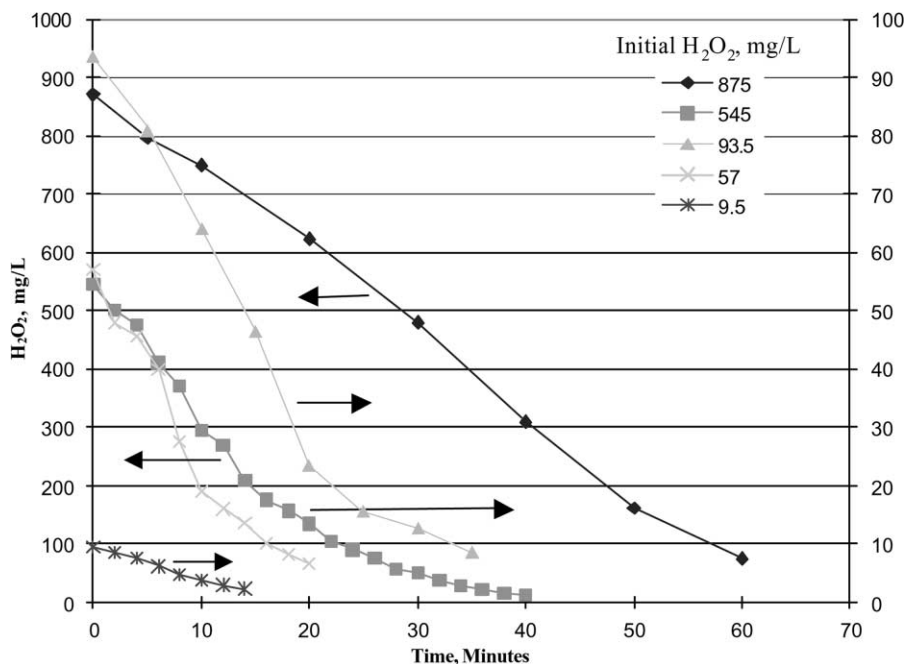


Fig. 3. Time-course of the hydrogen peroxide concentration (MPUV/H₂O₂) system.

for performance of a single series of experiments. Since two separate experimental series were performed, the initial hydrogen peroxide concentrations varied slightly from one series to the other because of variability in the hydrogen peroxide test used during analysis of the initial hydrogen peroxide at $t = 0$ min. Even though the initial hydrogen peroxide concentrations in the first and second set of experiments were slightly different, similar hydrogen peroxide profiles are expected. From Fig. 3, the hydrogen peroxide concentrations decreased by 90% or more within 60 min for all of the hydrogen peroxide doses examined. These data also indicate that the MPUV/H₂O₂ systems dosed with approximately 10 and 60 mg/l of hydrogen peroxide were limited in terms of hydrogen peroxide after 20 min of treatment. The approximate 100 and 600 mg/l doses appeared to approach potentially limiting levels of hydrogen peroxide at 40 min of treatment, with only those levels dosed at levels of approximately 800 mg/l maintaining measurable H₂O₂ amounts after 60 min of treatment.

It is clear that the 612.5 and 98 mg/l initial hydrogen peroxide concentrations yielded the highest extent of acetone degradation. The higher concentration of hydrogen peroxide (785 mg/l) had an adverse effect on the extent and rate of acetone degradation likely because the extra hydrogen peroxide levels competed with acetone for the hydroxyl radicals produced. The scavenging effect of excess hydrogen peroxide was also observed with the 612.5 mg/l dose, as the rate of acetone removal observed with the 612.5 mg/l dose was kinetically slower than the 98 mg/l dose during the early stages of treatment. The optimum

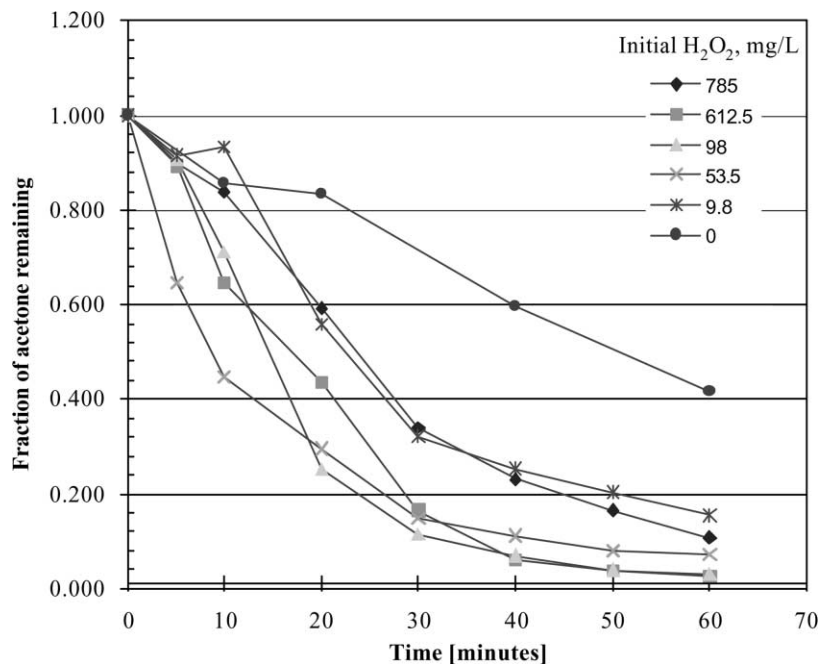


Fig. 4. Effect of the initial H_2O_2 concentration (ppm) on the decomposition of acetone at pH 7 using the 200 W MPUV lamp.

hydrogen peroxide concentration appears to be approximately 100 ppm because it had the same degree of treatment as the 612.5 mg/l dose, while using six times less hydrogen peroxide.

Closer review of Figs. 3 and 4 indicates that the hydrogen peroxide doses that were less than 90 mg/l do appear to be hydrogen peroxide limited which likely adversely impacted acetone removal by the reduced amount of hydroxyl radicals produced. The rate of acetone removal observed during these runs after 20 min of treatment appears to be similar to the rate observed with the photolysis only run (i.e. $[\text{H}_2\text{O}_2]_0 = 0$ mg/l) further indicating the lack of hydrogen peroxide present to produce hydroxyl radicals. A significant decrease in hydrogen peroxide, which is the source of the hydroxyl radicals in the UV/ H_2O_2 system will adversely impact system performance because of reduced amounts of radicals being produced. Hydrogen peroxide has a low molar absorptivity (19.6/Ms) for a primary absorber in a photochemical reaction [6]. This means that in order to generate an appreciable level of hydroxyl radicals, a relatively high concentration of H_2O_2 must be maintained within the medium. Control experiments that evaluated acetone removal due to reaction with hydrogen peroxide without the benefit of photolysis found that the reaction of acetone with hydrogen peroxide is insignificant. The addition of hydrogen peroxide when levels approached zero would have likely improved the rate of acetone removal by providing sufficient quantities of hydrogen peroxide for photolytic production of the hydroxyl radicals. In addition, this approach may have eliminated parent oxidizer scavenging during the early

stages of treatment when batch added hydrogen peroxide levels are highest. Although, this strategy was not evaluated with the MPUV/H₂O₂ system, it was tested during the peroxone runs and found to be effective in optimizing acetone degradation rate and removal for that AOP.

9. LPUV/O₃

The effect of ozone input (as % ozone in feed gas) on acetone degradation was tested and these results are presented in Fig. 5. These data clearly show that increasing the ozone concentration in the sparged stream increased the extent and rate of acetone degradation. It is noteworthy to mention that acetone was removed to levels below the analytical method detection limit in all three of the ozone doses examined. The 2.25% by weight O₃ run had the most rapid acetone degradation reaching non-detect levels within 30 min, as compared to 40 and 50 min for the 1.50 and 1.00% doses, respectively. Since ozone is also a hydroxyl radical scavenger, it is expected that very high concentrations of ozone will eventually have an adverse effect on acetone degradation; however, the levels of ozone tested did not appear to have this negative impact of acetone removal, given the gas-phase concentration of ozone sparged into the reactor.

Even though the borate buffer was used to maintain the test solutions at a pH of 7, the pH dropped very fast and was difficult to control during the 2.25% ozonated runs. The 1.50 and 1.00% ozonated systems were able to maintain neutral pH conditions throughout testing. It is recognized that acetone degrades via low molecular weight organic acids; therefore, the significant pH drop observed (7–3 in 60 min) in the 2.25% O₃ system may

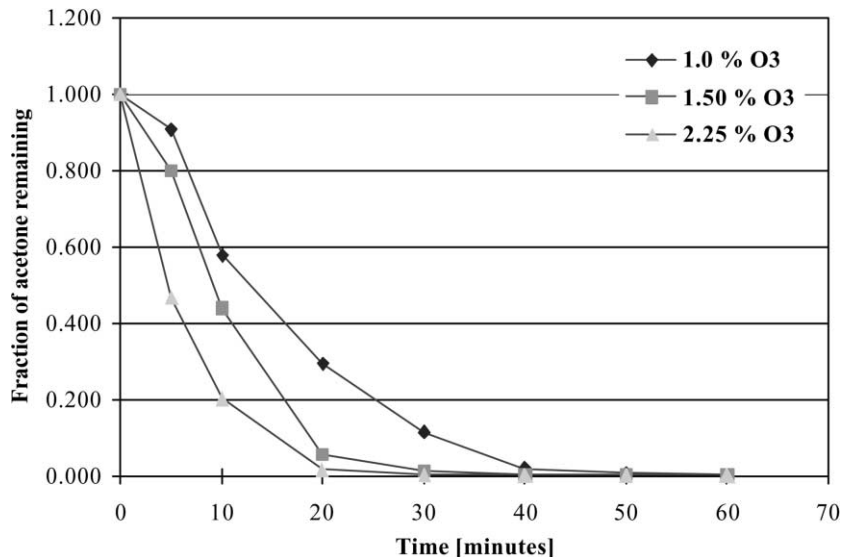


Fig. 5. Effect of the ozone concentration (wt.%) of the sparged air stream on acetone degradation (LPUV/O₃).

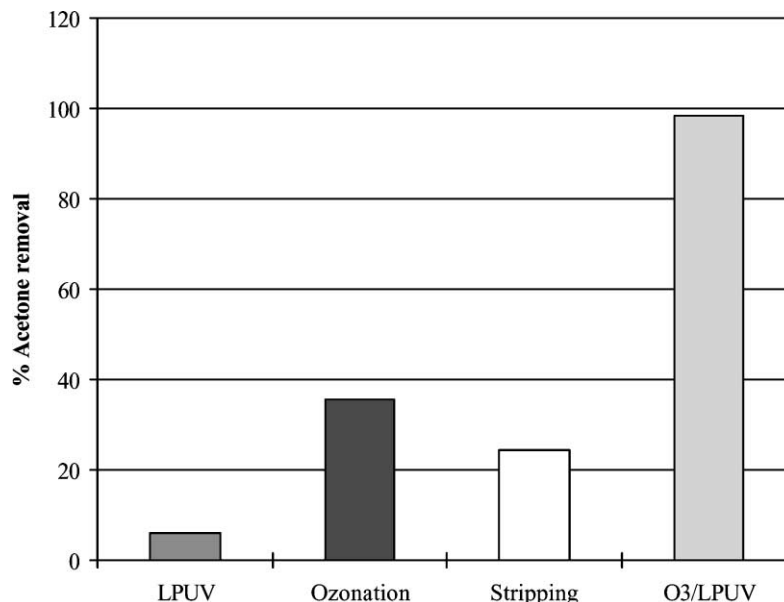


Fig. 6. Percent acetone removal efficiency obtained with photolysis, ozonation (2.25%, 2.5 SCFH), stripping (2.5 SCFH) and LPUV/O₃ (1.50%) system.

be attributable to degradation of the acetone. The likely reason that this pH drop was not observed with the other ozone doses tested is that these less aggressive ozonated systems may have not proceeded in terms of acetone degradation to the point of acid formation. Also, since this phenomenon was only observed in the experiments in which a relatively high ozone concentration was introduced into the reactor and because ozone is a weak acid, interaction between ozone and water may have also resulted in the acidification of the system.

Control experiments were performed to study the degradation of acetone via photolysis using the 12 W LPUV lamp, ozonation (2.25% O₃), and stripping (air only, 2.5 SCFH). Fig. 6 shows a comparison between the percent acetone removal obtained in the control experiments and a selected LPUV/O₃ (1.50%) system. A significant increase in acetone degradation was obtained using the AOP, demonstrating the enhancement of acetone degradation due to the reaction with hydroxyl radicals.

10. Peroxone (H₂O₂/O₃)

The experiments performed with this system studied the quantitative effect of oxidizers (H₂O₂/O₃) added using batch and/or semi-batch with respect to hydrogen peroxide dosing on the degradation of acetone. For each H₂O₂ concentration, ozonated air with an ozone concentration of 2.25% was sparged into the reactor. The results of these experiments are shown in Fig. 7. It can be seen that the fraction of acetone remaining in solution

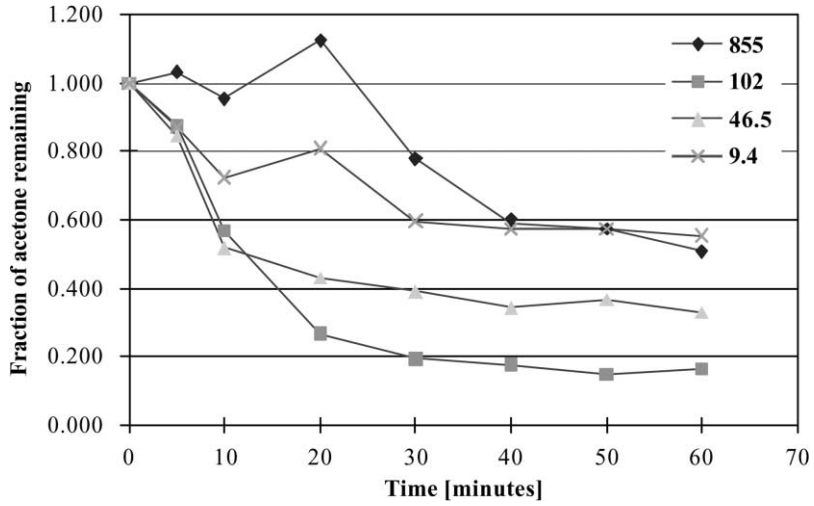


Fig. 7. Effect of initial H₂O₂ concentration (ppm) on the degradation of acetone using 2.25 wt.% concentration of O₃ in the sparged stream.

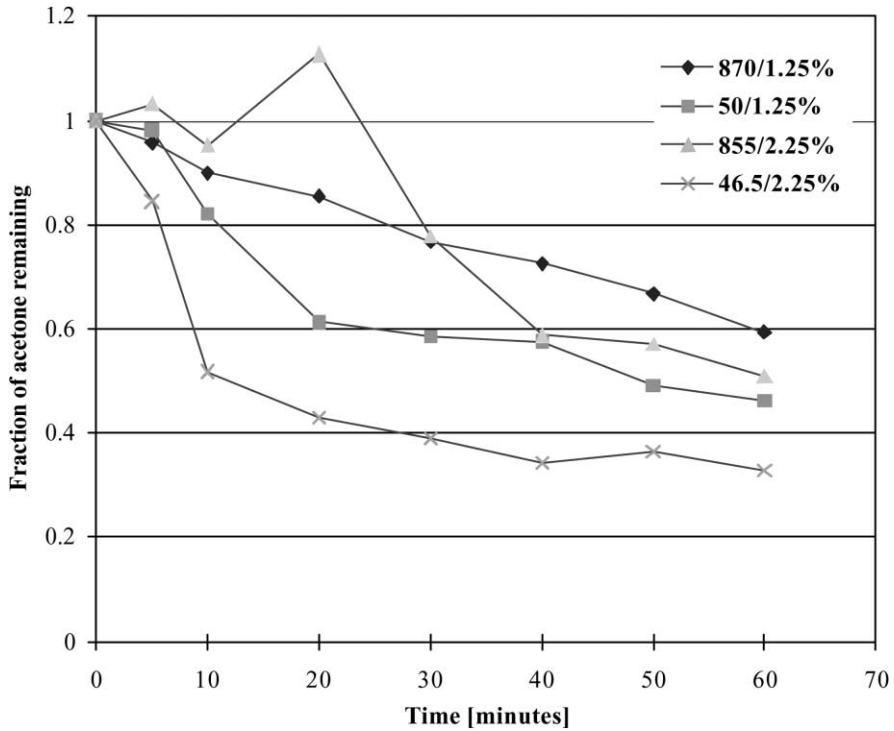


Fig. 8. Effect of concentration of ozone in the sparged air on the acetone degradation.

after treatment is much less when the hydrogen peroxide concentration was increased from 9.4–102.0 ppm. Relatively high hydrogen peroxide concentrations (855.0 ppm) had an adverse effect on acetone degradation, most likely due to the scavenging effect of the excess hydrogen peroxide toward the hydroxyl radical.

The effect of ozone concentration on the degradation of acetone was examined by reducing the ozone concentration to 1.25%. Two runs were performed using 870.0 and 50.0 ppm hydrogen peroxide concentrations and compared with the results obtained from 855.0 and 46.5 ppm doses ozonated with 2.25% O₃. These results are presented in Fig. 8. Reducing the ozone concentration in the sparged stream reduced the efficiency of the system to degrade the acetone. The curves which represent the fraction of acetone remaining in solution (Figs. 7 and 8) using hydrogen peroxide concentrations between 9.4 and 102 ppm can be divided into two parts. First, rapid acetone degradation, observed within the first 10–20 min of treatment. This is followed by a plateau of relatively slower acetone removal, where the degradation was very low. Analogous to the UV/H₂O₂ system this behavior was due to a deficiency of hydrogen peroxide based on the non-existent amounts of hydrogen peroxide analyzed within the test solutions after 30 min of treatment.

Two more experiments were performed in which hydrogen peroxide was added semi-continuously at 2 min intervals in order to maintain semi-constant hydrogen peroxide concentrations in the reactor as close as possible to 10 or 100 ppm. The ozone concentration in the sparged stream in this experiment series was 2.0% by weight. The results are shown in Fig. 9. A hydrogen peroxide concentration of 10 ppm achieved a higher percent removal of acetone than the 100 ppm dose. Acetone concentrations below the detection limit were obtained during the 60 min reaction period using the 10 ppm hydrogen peroxide dose, but

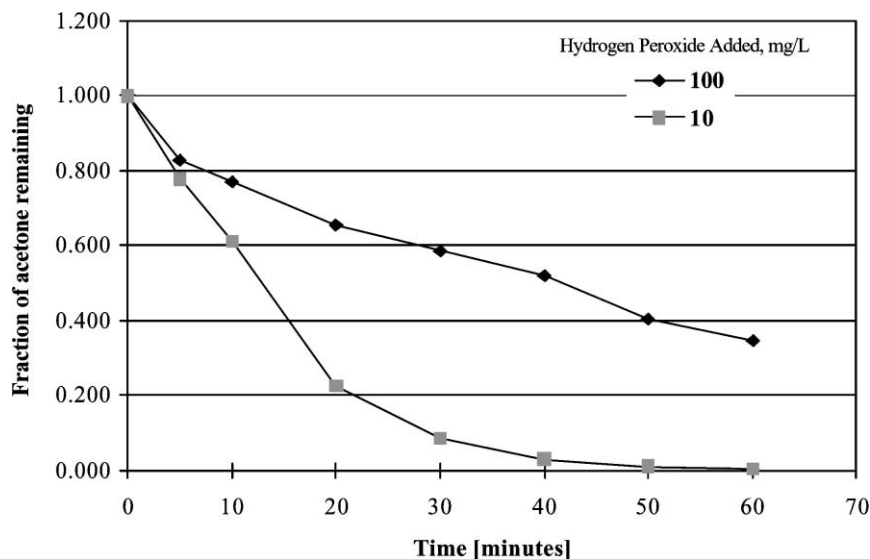


Fig. 9. Effect of H₂O₂ concentration (added semi-continuously) on the acetone degradation using a sparged stream with a 2.0% ozone concentration.

not the 100 ppm, indicating scavenging reactions at the higher dose had an adverse impact on system performance. The data suggest that an instantaneous hydrogen peroxide concentration of 100 ppm had a scavenging effect which adversely affected the initial rate of acetone degradation. The second-order rate constant for the reaction of acetone with the hydroxyl radical ($1.3 \times 10^8/\text{M s}$) [24] is approximately five times that of hydrogen peroxide ($2.7 \times 10^7/\text{M s}$) [9]. Since the hydrogen peroxide concentration (100 ppm) was 20 times that of acetone, this scavenging effect is predicted by the reaction rate constants. Thus for the $\text{H}_2\text{O}_2/\text{O}_3$ system, the optimum concentration of oxidizers is close to 10 ppm hydrogen peroxide added semi-continuously and 2.0% by weight ozone in the sparged stream.

11. Kinetics of acetone degradation

Other researchers have noted that the reaction of acetone with the hydroxyl radical is pseudo-first order with respect to acetone [24]. Therefore, the first-order model was evaluated for its applicability for modeling the degradation of acetone achieved within the various AOP systems tested during this study. The results of this evaluation are shown in Table 2 which lists the first-order rate constants calculated for each run and the respective correlation of fit (r^2) constants. The correlation of fit constants for the regressions of the data associated with all AOP runs performed in this study were all greater than 95%. This indicates a good statistical fit and that the first-order model appears to be an appropriate model for tracking acetone concentrations during AOP treatment. The LPUV/ O_3 systems yielded the highest rate constants of all the AOPs tested, followed by the semi-batch dosed hydrogen peroxide (peroxone) system with a 10 ppm H_2O_2 dose, and the MPUV/ H_2O_2 with a 100 ppm H_2O_2 dose. The highest rate constant was associated with the 2.25% ozone LPUV/ O_3 system, which had a value of 0.204 min^{-1} . As expected, all of the rate constants calculated correlated nicely with the observations made during review of the acetone removal data for all of the AOP systems.

Table 2
Pseudo-first-order rate constants for acetone degradation for each oxidizer concentration examined

	k (min^{-1})	r^2
UV/ H_2O_2 (initial H_2O_2 , ppm)		
785.0	0.0386	0.991
612.5	0.0666	0.980
98.0	0.0641	0.976
53.5	0.0446	0.959
9.8	0.0338	0.975
UV/ O_3 (O_3 , %)		
1.00	0.071	0.953
1.50	0.149	0.976
2.25	0.204	0.986
$\text{H}_2\text{O}_2/\text{O}_3$ (H_2O_2 , ppm)		
100.0	0.016	0.985
10.0	0.093	0.991

12. Conclusions

The LPUV/O₃ process was the most efficient for acetone degradation of the three AOPs studied. This process removed over 99.0% of the acetone in less than 30 min. Increasing the ozone concentration in the sparged gas increased the rate of acetone degradation.

In the MPUV/H₂O₂ system, the scavenging effect of the hydrogen peroxide at high concentrations has to be taken into account. Initial hydrogen peroxide concentrations that were batch added in excess of 700 ppm had an adverse effect on acetone removal, most likely due to the scavenging reaction of hydrogen peroxide with the hydroxyl radical. An optimum batch added hydrogen peroxide concentration appears to be in the range of a 100–600 ppm. However, little difference was observed between the 100 and 600 ppm doses; therefore, for economic reasons the 100 ppm batch added hydrogen peroxide dose appears more attractive.

The studies performed on the H₂O₂/O₃ process demonstrated that there is an optimum concentration of H₂O₂ and O₃ which enhances the formation of the hydroxyl radical. It was observed that increasing the concentration of hydrogen peroxide using a constant concentration of ozone in the sparged gas improved the overall degradation of acetone up to a certain extent. Analogous to the MPUV/H₂O₂ system, excessive H₂O₂ doses such as those greater than 100 ppm adversely impact acetone removal.

A 10 ppm semi-continuously added hydrogen peroxide dose combined with 2% ozone sparging yielded the highest rate and extent of acetone degradation for the peroxone systems tested during this study. This system removed greater than 99% of the acetone within 60 min. The performance of the peroxone system, in terms of acetone degradation, were encouraging given the lack of operational history of this promising AOP as a treatment process. This process is reported to have slower overall reaction kinetics for the degradation of many organic contaminants compared to UV-based processes. However, this research demonstrated that its performance could be comparable to these processes if the optimum operating conditions are determined. The dark reaction capabilities and low oxidizer requirements of the peroxone system, as compared to the more traditional UV-based AOPs, make this system a potentially cost competitive option.

Acknowledgements

This work was performed within the Hazardous Waste Research Center of the USAE Engineering Research and Development Center-Waterways Experiment Station (WES) located in Vicksburg, MS. The authors gratefully acknowledge that funding for this research was provided by the Installation Restoration Research Program of the US Army Corps of which is managed by Dr. M. John Cullinane, WES. Permission was granted by the Chief of Engineers to publish this information.

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