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TWO-PHASE OZONATION OF CHLORINATED ORGANICS

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INTRODUCTION

In the last few years the amount of research being conducted in the field of single-phase ozonation has grown extensively. However, traditional aqueous-phase ozonation systems are limited by a lack of selective oxidation potential, low ozone solubility in water, and slow intermediate decomposition rates. Furthermore, ozone may decompose before it can be utilized for pollutant destruction since ozone can be highly unstable in aqueous solutions. Naturally occurring compounds such as $NaHCO_3$ also affect ozone reactions by inhibiting the formation of OH· free radicals. To compensate for these factors, excess ozone is typically supplied to a reactor. Since ozone generation requires considerable electric power consumption (16 - 24 kWh/kg of O_3), attempts to enhance the ozone utilization rate and stability should lead to more efficient application of this process to hazardous waste treatment.

To improve the process, ozonation may be more efficiently carried out in a two-phase system consisting of an inert solvent (saturated with O_3) contacted with an aqueous phase containing pollutants. From practical considerations, the non-aqueous phase must meet the following criteria: 1) non-toxic, 2) very low vapor pressure, 3) high density (for ease of separation), 4) complete insolubility in water, 5) reusability, 6) selective pollutant extractability, 7) high oxidant solubility, and 8) extended O_3 stability. Previously published studies (1) have indicated that a number of fluorinated hydrocarbon compounds fit these criteria. For this project, FC40 (a product of 3M Co.) was chosen due to its low vapor pressure (3 mm Hg) and high specific gravity (1.9). The primary advantages of the FC40 solvent are that it is non-toxic, reusable, has an ozone solubility 10 times that of water, and that 85 % of the ozone remains in the solvent even after 2 hours. This novel two-phase process has been utilized to study the rapid destruction of pentachlorophenol (PCP), 1,3 dichlorobenzene (DCB), trichloroethylene (TCE), and organic mixtures.

METHODS

Ozonation studies were conducted using pentachlorophenol (PCP), trichloroethylene (TCE), and 1,3-dichlorobenzene (DCB) (Aldrich Chemical) as parent compounds. For all experiments, the non-aqueous solvent was FC40, obtained from 3M Co. The initial concentration ranges were varied for each compound: PCP at 10 - 100 mg/L for pH 3.5 - 11.7, TCE at 1442 mg/L for pH 4.4 - 10.0, and DCB at 26 mg/L and 78 mg/L for pH 2.1 - 11.2. The first stage of the study was to determine the partitioning coefficient for each compound studied. The next stage consisted of determining the effect of various variables on parent compound degradation (such as the ratio of O_3 to pollutant, reaction time, and initial pH).

Analysis of the parent compounds in the aqueous phase were conducted following the guidelines outlined EPA Methods 624 and 625 using a Hewlett-Packard 5890 Series II Gas Chromatograph with an attached 5971A Quadrupole Mass Selective Detector (GC/MS) equipped with NIST/EPA/MSDC 49K Mass Spectral Database. For analysis of the solvent phase, the parent compounds were extracted with methanol and analyzed by GCMS. Besides quantifying the parent compounds, selected intermediates and reaction products were also analyzed. Organics acids from PCP ozonation were monitored on HPLC

was 3 mg/L with ± 3% reproducibility. Chloride concentration in the aqueous phase was measured by an Orion combination electrode (Model 96-17B) with a reproducibility of ± 4%. In order to measure ozone concentration in the solvent phase, the modified indigo dye method was utilized (2). For quick analysis of ozone, the concentration could be determined by measuring the absorbance at $\lambda = 290$ nm with a Bausch and Lomb Spectronic 1001 spectrophotometer.

RESULTS

The major focus of this research was to quantitatively establish the feasibility of degrading chlorinated organics in a short reaction time. The major variables studied were O_3 dosage, feed pH, and reaction time. The experiments were characterized in terms of parent compound degradation, pH drop, free chloride formation, and selected intermediate identification. The only source of ozone is the solvent (FC40) phase. Feed ozone dosage is reported in terms of molar ratio of ozone to parent compound (M). Percent chloride formation is the amount of chloride measured in the aqueous phase after an ozonation run compared to the maximum amount of chloride that can be released by the parent compound. For 100% chloride formation, the compound has achieved complete dehalogenation.

A distribution coefficient, K_D, describes the extent that a compound partitions between the FC40 phase and the aqueous phase. The experimentally determined K_D at pH < pKa is 10.2 for PCP, 5 for DCB, 40 for TCE, and 0.003 for chlorendic acid. For ionizable compounds such as phenols, K_D is dependent on pH. The K_D for PCP at pH 10.3 is 0.03.

To demonstrate ozone stability in the fluorinated hydrocarbon, the solvent (in this case, FC40) was saturated with ozone and removed from the ozone source. No significant change in O_3 concentration was observed after the first five minutes, and after two hours in a closed container with no head space, the O_3 concentration remained steady at 85% ± 2% of the initial concentration. The effect of water phase on ozone decomposition was also established. At least 77% of the initial O_3 concentration remained even after 2 hours (92 mg/L O_3). It should be noted that the solvent used in this experiment had been used repeatedly in ozonation experiments (washed between experiments) for over a year, proving its reusability and capacity for long term ozone stability. Free radical scavengers (3), for example bicarbonate, are compounds which compete with other hazardous organics for the OH• during single phase ozonation. An experiment following the previous conditions was performed with the addition of 20 mM $NaHCO_3$ to the aqueous phase. The addition of sodium bicarbonate (20 mM) increased the ozone stability, with an ozone decomposition of only 10% after two hours.

To study the effect of initial pH on the degradation of PCP, experiments were conducted at pH 3-11 at an ozonation contact time of 5 minutes. Using a 10 mg/L solution of PCP, it was found that there was ~ 95% PCP degradation at initial pH 10.5 for **M** = 4.3, compared to ~ 92% PCP degradation at pH around 4. Since the partitioning coefficient is significantly lower at a higher pH, this result indicates that mass transfer is not a limiting factor in the degradation of PCP in the two-phase system, and that a higher pH is preferred for better PCP destruction. An enhanced reaction rate at a high pH is consistent with single aqueous phase ozonation results reported in the literature (4). PCP ozonation kinetics were studied at an initial pH of 3.5-4.5 and 10.3. The experiments indicate that a total of 79% degradation of PCP occurs within 30 seconds and nearly 92% total degradation occurs after 1 minute (pH=4, **M**=4.3). Faster destruction were found for PCP at a basic pH (**M**=6.66). 95% PCP degradation occurred in the first 30 seconds. Since the parent compound degradation was rapid, the order of the reaction at high pH was determined by varying the feed PCP concentration. The feed was varied from 10 - 100 mg/L while the initial pH, ozone dosage, and reaction time were held constant. First order kinetic rate constants were determined for the high and low pH reactions. These rate constants are respectively 200 min^{-1} and 6.7 min^{-1}. Calculations prove the reactions to be first order.

Within 1 minute, the majority of the bound chloride for PCP was converted to free chloride. All of the free chloride (Cl^-) remained in the aqueous phase, since Cl^- has no affinity for the FC40 phase. Approximately 70% of the bound chloride in the system was converted to free after 1 minute. The remaining 20 - 30 % of the chloride may have been bound within intermediate compounds instead of being converted to free chloride. 90% dechlorination of PCP occurs after 15 minutes in the two-phase batch reactor (**M**=6.66, pH 10.3). Bicarbonate is a hydroxyl radical scavenger and it has been shown that it can alter pollutant decomposition in a single-phase aqueous system (5). The addition of 20 mM $NaHCO_3$ decreased PCP degradation in the two-phase system by only 3% after 5 minutes reaction time (**M**=4.3, pH 10.3).

In an attempt to identify some intermediate organic acids formed during PCP ozonation, HPLC analysis was used on the ozonated products. One intermediate was shown to be oxalic acid. Studies by Stowell showed that oxalic acid is a product formed from single phase ozonation of 2-chlorophenol (6). From a calibration of oxalic acid on the HPLC, the maximum concentration of acid produced by ozonation of a 100 mg/L solution of PCP (**M** = 6.66, 60 minutes, pH 10.3) was determined to be 30 mg/L. Assuming that all the PCP is degraded to oxalic acid only (no CO_2), it would theoretically yield 101 mg/L acid. In order to simulate a continuous reaction system, one study was conducted by continuously bubbling O_3 into the reactor. The ozonation of 100 mg/L PCP (pH 11.7) yielded complete dehalogenation for a 5 minute ozonation (100% chloride formation) and 70 mg/L oxalic acid formation.

For comparison purposes, a single aqueous phase ozonation system was operated with 100 mg/L PCP initially at pH 10.3. Ozone was bubbled directly into the aqueous phase (400 ml) at a rate of 56.5 mg/min with no solvent present. PCP degradation and chloride formation were shown to occur at a slower rate than in the two-phase system. A value of 0.154 min^{-1} was determined as the first order rate constant ($R^2 = 0.96$) for PCP degradation. This value is 3 orders of magnitude lower than the rate constant in the two-phase system at the same pH (10.3).

PCP not only degrades faster in the two-phase system, but also the O_3 dosage requirement is lower. For 400 mL of solution of 100 mg/L PCP it would require at least 14 minutes reaction time (1200 mg O3) to achieve 90% PCP degradation, whereas over 95% PCP degradation can be acquired for the same volume in less than 5 minutes (48 mg O_3 if equal volumes solvent and water) with the two-phase system. These calculations lead to 25 times more ozone requirement in the traditional single-phase system. This value is significant because ozone generation requires substantial electrical power which increases operating costs.

The effect of molar ratio was found to be negligible for the degradation of both 1,3-dichlorobenzene (DCB) and trichloroethylene (TCE) so long as O_3 was in excess. To determine the effect of time on DCB degradation, individual runs were conducted with a feed solution of 77.3 mg/L and the reactions were quenched at 1, 5, and 10 minutes. Results showed that degradation occurred mainly in the first minute, and then appeared to cease after the first minute. Approximately 35 % of the DCB had been degraded and 30 % of the chloride was released, and these values remained relatively constant for the rest of the reaction, even after 120 minutes. To determine why the reaction slowed after the first minute, the experiments were repeated and the ozone concentration in the FC40 was quantified using the modified indigo dye method. The ozone concentration dropped significantly within the first five minutes. With a low ozone concentration, the ozone might not be in excess, and may have become a limiting reactant.

To study the effect of ozonation time on TCE, several semi-batch experiments were conducted in the 1 L reactor vessel. For the experiments, 500 mL of FC40 was saturated with ozone. Next the ozone was turned off and 300 mL of water buffered to pH 10.3 with 0.05 M KH_2PO_4added to the vessel. Finally 0.732 mg of TCE was pipetted into the vessel and the ozone was turned on again. A steady-state ozone concentration of 30 mg/L was measured in the solvent phase by the modified indigo dye method. If the solution were in equilibrium, these conditions would result in an aqueous TCE concentration of 36 mg/L and a solvent phase concentration of 1442 mg/L. For a reaction time of 110 minutes, complete mineralization of TCE was achieved. The plot of the natural log of the percent chloride released versus time proved that the mineralization reaction was first order with an apparent rate constant of 0.036 min^{-1}. In order to rapidly dehalogenate TCE, other researchers have utilized UV light (7,8). As a comparison to literature, Sundstrom reported a first order rate constant of 0.0903 min^{-1} for the degradation of TCE in a H_2O_2/UV system (8). This indicates that TCE degradation by two-phase ozonation is 3.5 times faster than H_2O_2/UV.

Previously, studies had been conducted with only one parent compound present initially. Therefore, experiments were conducted with a mixture of compounds to study the effect that the presence of other organics might have on the degradation of each compound. The mixture examined contained 21.0 mg/L pentachlorophenol, 38.6 mg/L 1,3-dichlorobenzene, and 29.3 mg/L trichloroethylene. Pollutant degradation was determined by analyzing free chloride released, PCP concentration in the aqueous phase, and DCB concentration in the solvent phase. The chloride results from a batch reaction with pHi 10.3 (unbuffered) and equal volumes of solvent and water show that ~ 65% total dehalogenation occurs within 10 minutes. Within one minute, the pH dropped to 6.2, thus indicating significant organic degradation. The K_D values were taken into account when calculating compound concentrations. PCP degradation occurred similarly as it did in a system containing only PCP with ~ 95% degradation in 5 minutes, but DCB degraded faster than in a DCB only system with 70% degradation within 1 minute. This behavior might be explained by an increase in the production of OH• that are formed as a result of PCP degradation, however, increased PCP concentration did not increase DCB or TCE degradation.

A two-phase system with a continuous supply of O_3 was operated with the same mixture solution. It was found that the total chloride released is greater than it is for a batch reaction with as much as 78% dechlorination after 30 minutes. Although at 5 minutes there is a comparable amount of Cl^- released (approx. 65%) for both the batch and semibatch systems, at 10 minutes, where there is no increase in dechlorination for the batch system (probably due to O_3 requirements), there is an increase with the continuous ozone supply.

CONCLUSIONS

Overall, the two-phase ozonation system showed superior performance over single-phase systems in several areas: higher ozone solubility and stability, lower ozone generation requirements, faster pollutant destruction rates, and the potential for selective oxidation. Also, the solvent was reused repeatedly for over a year, proving its reusability. The solubility of ozone in FC40 is ten times higher than in water. Where O_3 decomposes completely within 40 minutes in water (pH 6), ozone in FC40 has decomposed only 10 % within the same amount of time. A comparison between single and two-phase ozonation systems with PCP showed that ~ 25 times more ozone must be used for a single phase system to achieve at minimum 90% PCP degradation.

In terms of pollutant degradation, the first order reaction rate constants for PCP and TCE were orders of magnitude larger in the two-phase system than in single phase systems. The presence of a free radical scavenger (sodium bicarbonate) in the aqueous phase did not inhibit the degradation of PCP. Actually, 20 mM $NaHCO_3$ decreased the rate of ozone decomposition by a factor of ~ 10. Complete dechlorination of PCP was still achieved after only 5 minutes when bicarbonate was present.

DCB and TCE were shown to degraded faster when reacted in a solution of PCP, DCB and TCE than in a single-pollutant system. It was also shown that using a continuous supply of ozone to the two-phase system increased the amount of free chloride released for the mixture solution.

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