

COMPARISON OF KINETICS FOR REMOVAL OF BTEX COMPOUNDS AND CHLORINATED SOLVENTS USING ADVANCED OXIDATION PROCESSES

ROBERT W. PETERS, Ph.D., P.E.

Professor of Environmental Engineering
Department of Civil, Construction, and Environmental Engineering
University of Alabama at Birmingham
1075 13th Street South
Birmingham, Alabama

M.P. SHARMA, Ph.D.

Professor of Chemical Engineering
Department of Chemical and Petroleum Engineering
University of Wyoming
Laramie, Wyoming

YUSUF GBADEBO ADEWUYI, Ph.D.

Professor of Chemical Engineering
Department of Mechanical and Chemical Engineering
North Carolina Agricultural and Technical State University
1601 East Market Street, 326 McNair Hall
Greensboro, North Carolina

Abstract

This paper addresses the process interactions from combining integrated processes (such as advanced oxidation processes (AOPs), biological operations, air stripping, etc.). AOPs considered include: Fenton's reagent, ultraviolet light, titanium dioxide, ozone (O₃), hydrogen peroxide (H₂O₂), sonication/acoustic cavitation, among others. A critical review of the technical literature has been performed, and the data has been analyzed in terms of the processes being additive, synergistic, or antagonistic. Predictions based on the individual unit operations are made and compared against the behavior of the combined unit operations. The data reported in this paper focus primarily on treatment of petroleum hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylene) and chlorinated solvents. The kinetic data included in this study are obtained both from the technical literature and from research investigations of authors. The results of this study are discussed in this paper. Our first order kinetic rate constants are comparable with other researchers, although our values seem to be slightly higher than the previously reported values. Our air stripping values are significantly higher than the volatilization rate constants previously reported; this is due to the earlier study conducting volatilization studies under quiescent conditions.

Introduction

Description of Advanced Oxidation Processes

Acoustic cavitation (commonly termed sonication) involves the application of sound waves being transmitted through a liquid as a wave of alternating cavitation cycles. Compression cycles exert a positive pressure on the liquid, pushing molecules together, while expansion cycles exert a negative pressure, pulling molecules away from each other. The chemical effects of sonication are a result of acoustic cavitation. During rarefaction, molecules are torn apart forming tiny microbubbles that grow to a critical size during the alternating cavitation cycles, and then implode releasing a large amount of energy. Temperatures on the order of 5,000°K and pressures up to 500 to 1,000 atmospheres have been observed in microbubble implosions, while the bulk solution stays near ambient. The collapsing bubble interface results in the formation of hydroxyl and hydrogen radicals. These radicals destroy chlorinated organic and petroleum hydrocarbon compounds very effectively.

The performance can be further enhanced through the addition of advanced oxidants (e.g., ozone (O₃), hydrogen peroxide (H₂O₂), etc.), and incorporation of recent advancements in the acoustic cavitation field [1]. The destruction of organic pollutants can occur via several mechanisms. The organic pollutant inside the cavity and in the interfacial region can undergo pyrolysis reactions (or combustion reactions if oxygen is present) during the implosion. Free radicals (e.g., •OH, •H) formed due to thermolysis of water molecules may react with the organic in the interfacial region or in the solution near the interface. Three primary pathways have been identified for compound degradation, including: (1) hydroxyl radical oxidation, (2) direct pyrolytic degradation, and (3) supercritical water reactions. In aqueous solution, water vapor present in the microbubble is homolytically split during bubble collapse to yield •H and •OH radicals, while chemical substrates present either within or near the gas-liquid interface of the collapsing microbubble are subject to direct attack by •OH. Volatile compounds such as benzene, toluene, ethyl benzene, xylene, and MTBE readily partition into the vapor of the growing cavitation microbubbles and then undergo direct pyrolysis during transient collapse.

Vapor stripping (air sparging) operations have as their goal to transfer the volatile contaminants from the liquid phase (i.e., groundwater) to the vapor phase (i.e., air). The combination of sonication and aeration/ozonation/hydrogen peroxide results in enhanced organic destruction and better liquid/vapor contact (i.e., better mixing) to facilitate the transfer of the degraded or partially degraded products into the gas phase. The addition of ozone (made through electric discharge of oxygen) into the liquid phase coupled with application of sonication considerably enhances the formation of hydroxyl radicals resulting in enhanced destruction of chlorinated organic compounds in solution. Hydroxyl radicals (•OH) are highly reactive non-specific reactants capable of oxidizing a wide variety of contaminants to carbon dioxide, hydrochloric acid (if chlorinated organics

are present), and water. After mass transfer from the liquid phase into the gas phase, the water is pumped to a packer in the dual extraction well, resulting in the water (stripped of the volatile organic compounds (VOCs)) being returned into the subsurface, while the VOC-enriched vapor phase is passed through the second well and is sent to an above-ground vapor treatment system (that could involve capture on activated carbon/regeneration using ultrasonics, or thermal oxidation).

This research paper considered the following advanced oxidation treatment systems:

- Ultraviolet (UV) light;
- Hydrogen peroxide (H_2O_2)/UV light;
- Sonication;
- Sonication/UV light;
- Ozonation;
- Ozonation/ H_2O_2 ; and
- Fenton's Reagent.

Previous Studies with Evidence of Process Synergism

The photooxidation of *p*-xylene and *o*-nitrotoluene were studied by Ghaly [2] in a closed bench-scale unit using hydrogen peroxide or hydrogen peroxide/ Fe^{+2} as a photocatalyst. Results of the photo-Fenton process (UV/ H_2O_2 / Fe^{+2}) were compared with the UV/ H_2O_2 process; the results indicated that the photo-Fenton process resulted in a higher efficiency degradation of the selected compounds and reduced energy consumption. The degradation reactions were 1st-order; the value of the reaction rate constant k was $\sim 5x$ higher for the photo-Fenton process than that in the case of the UV/ H_2O_2 system. The quantity of both H_2O_2 and Fe^{+2} must be properly selected the pH properly adjusted to optimize the process. For their particular system studied, the optimum reaction conditions were: 0.03 mole H_2O_2 /L using the UV/ H_2O_2 system and 0.01 mole H_2O_2 /L, 1.0 mmole Fe^{+2} /L at pH ~ 3 for the photo-Fenton process.

The ozonation and peroxone oxidation of toluene in aqueous solutions was studied by Kuo and Chen [3]. They investigated the kinetics of the aqueous-phase oxidation of toluene by ozone and ozone-hydrogen peroxide mixtures at 25°C. The oxidation kinetics were 1st-order with respect to ozone concentration; the reaction order in toluene varied with pH and the presence or absence of H_2O_2 . The peroxone oxidation was half-order with respect to H_2O_2 in distilled water (initial pH of 5.4) and other solutions of higher pH. In acidic solutions with an initial pH ≤ 3 , the overall kinetics was 2nd-order; the direct oxidation of toluene by ozone molecules was predominant in determining the slow rate of reaction. The reaction became very fast and enhanced with the addition of H_2O_2 , if present, in alkaline solutions with an initial pH of 10 or higher. Under those conditions, the reaction was controlled by hydroxyl radical reactions and was independent of the toluene concentration.

RESULTS AND DISCUSSION

Previous Studies Involving Combinations of Advanced Oxidation Studies

Figure 1 presents the results on the removal of atrazine from solution [4] using UV irradiation, ozonation, and combined UV/ozonation, while **Figure 2** presents analogous results for removal of carbofuran [5] using UV irradiation, Fenton's reagent, and combined UV/Fenton's treatment. **Figure 1** indicates that the removal of atrazine from solution is better than being additive, that much better performance is observed than predicted, indicating the process performed synergistically. Similar behavior is observed for the case of carbofuran. Beltran *et al.* [4] showed that the degradation efficiencies of atrazine by advanced oxidation treatment methods were in the following order: $UV < O_3 < UV/H_2O_2 < UV/O_3$. Similarly, Benitez *et al.* [5] observed that the degradation efficiencies of carbofuran were in the following order: $UV < O_3 < \text{Fenton's reagent} < UV/H_2O_2 < UV/\text{Fenton}$. Note that the integrated processes always had the best removal efficiencies of the target compounds.

Figures 3 and 4 present the results for removal of carbon tetrachloride (CCl_4) and trichloroethane (TCA) from solution using combined sonication and air stripping operations [6, 7]; the prediction from the additivity of the 1st-order rate constants is shown by the curve in the figure; the actual observed data is shown as the individual data points. Once again, the combination of the two treatment processes (sonication and air stripping) is seen to operate in a synergistic fashion.

Tables 1 and 2 compare the 1st-order rate constants using sonication, air sparging, and their combination for removal of benzene, toluene, ethyl benzene, and *o*-xylene from solution [1]. Once again, the combination of these treatment processes is considerably better than the individual processes, and operates in a synergistic fashion, as evidenced by the observed 1st-order rate constants being higher than the predicted values.

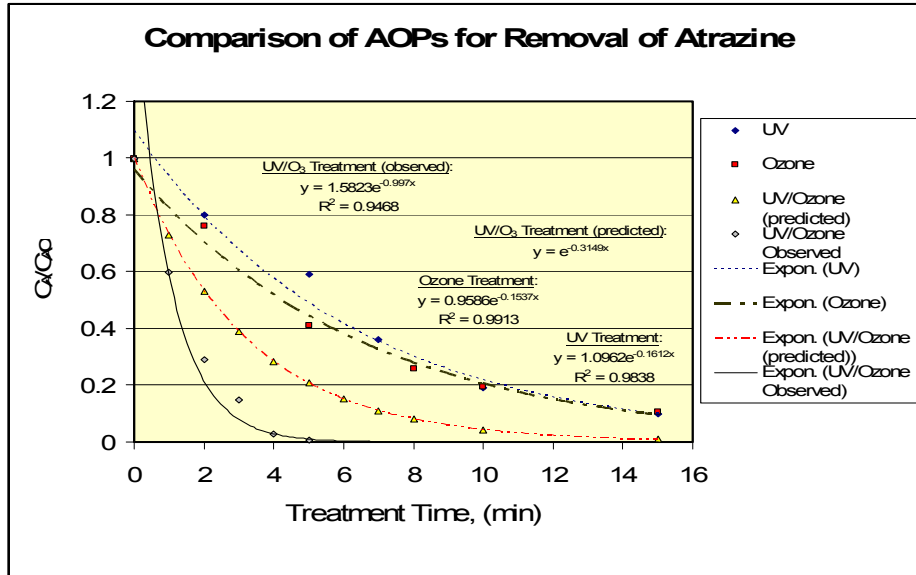


Figure 1. Comparison of AOPs for removal of atrazine from solution, adapted from [2].

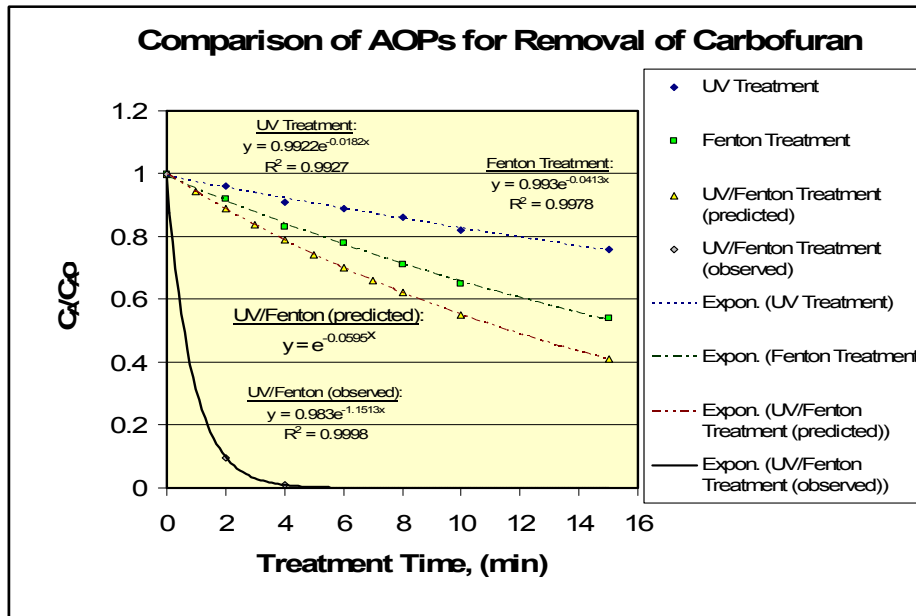


Figure 2. Comparison of AOPs for removal of carbofuran from solution, adapted from [3].

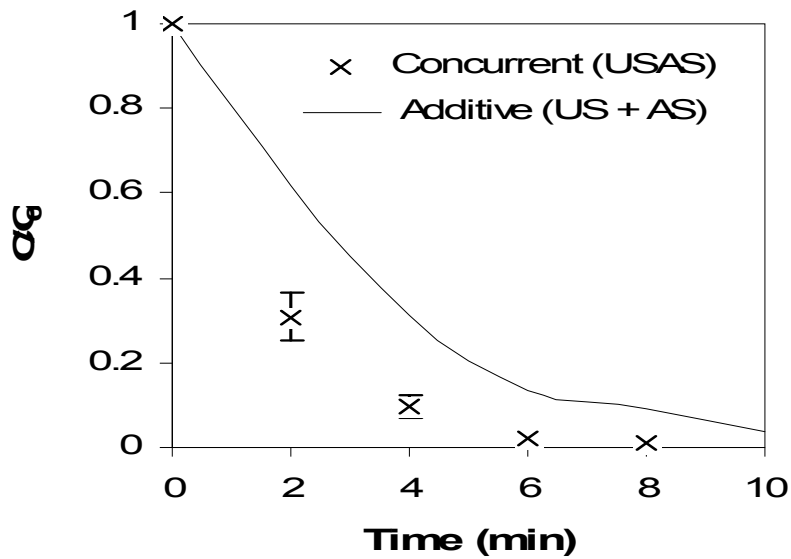


Figure 3. Removal of CCl₄ from artificial groundwater by combined ultrasound and air stripping: Ultrasonic power intensity = 35 W/cm² and air flow rate = 500-mL/min.

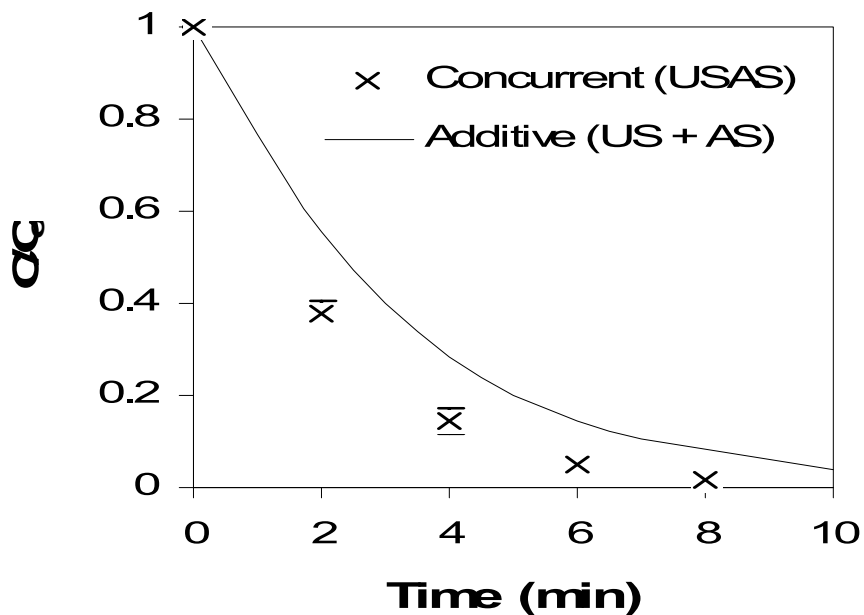


Figure 4. Removal of TCA from artificial groundwater by combined ultrasound and air stripping: Ultrasonic power intensity = 35 W/cm² and air flow rate = 500-mL/min.

Table 1. Summary of 1st-order rate constants using various treatment processes for removal of benzene, toluene, ethyl benzene, and *o*-xylene from solution [1].

Contaminant	Treatment Process	1st-Order Rate Constant, (min⁻¹)
Benzene	Sonication alone	0.0608
	Air sparging alone	0.1347
	Combined sonication + air sparging (predicted)	0.1955
	Combined sonication + air sparging (observed)	0.2166
Toluene	Sonication alone	0.0635
	Air sparging alone	0.1381
	Combined sonication + air sparging (predicted)	0.2016
	Combined sonication + air sparging (observed)	0.2443
Ethyl benzene	Sonication alone	0.0702
	Air sparging alone	0.1655
	Combined sonication + air sparging (predicted)	0.2357
	Combined sonication + air sparging (observed)	0.3684
<i>o</i> -Xylene	Sonication alone	0.0497
	Air sparging alone	0.1385
	Combined sonication + air sparging (predicted)	0.1882
	Combined sonication + air sparging (observed)	0.2132

Table 2. 1st-Order Kinetic Rate Constants Obtained by Other Researchers.

Contaminant	Treatment Process	1 st -Order Rate Constant, (min ⁻¹)	Reference Citation
Benzene	Sonication with a Near Field Acoustic Processor for applied power density of 0.6–3.6 W/mL	0.0027 – 0.0374	Thoma <i>et al.</i> , 1998
Benzene	Sonolysis	0.025	Wu <i>et al.</i> , 2004
Benzene	Volatilization @ 75-mm depth	0.000656	Peng <i>et al.</i> , 1994
Toluene	Sonication with a Near Field Acoustic Processor for applied power density of 0.6–3.6 W/mL	0.0039 – 0.0276	Thoma <i>et al.</i> , 1998
Toluene	Volatilization @ 75-mm depth	0.000692	Peng <i>et al.</i> , 1994
1-dodecanol	KOH alcohol polyethoxylation	0.00018 – 0.00348	Santacesaria <i>et al.</i> , 1992

Summary and Conclusions

For the research investigations studied, integrated processes generally perform in a synergistic manner, rather than giving the performance of the individual processes simply being additive. For example, a synergistic effect is observed in the photo-Fenton process which was attributed to the generation of hydroxyl radicals ($\bullet\text{OH}$) in several reactions and to the catalytic behavior of the Fenton's reaction in the presence of UV radiation. Thus, for the oxidant concentrations employed in the Benitez study [5], the efficiency of the photo-Fenton process was even higher than that of the conventional ozonation and the UV/O₃ system. As shown in the analyses presented in this paper, the rate constant of the 1st-order combined treatment system was 3.167x and 19.35x greater than predicted rate constant (the sum of the individual unit processes rate constants) for the removal of atrazine and carbofuran, respectively. For the removal of CCl₄ and TCA [6, 7], the observed rate constant was 1.777x and 1.653x times greater than the predicted value (the sum of the 1st-order rate constants for sonication and air stripping), respectively. Similarly, for treatment of benzene, toluene, ethyl benzene, and *o*-xylene, the observed rate constant [1] was 1.11x, 1.21x, 1.56x, and 1.13x times greater, respectively, than the predicted value (the sum of the 1st-order rate constants for sonication and air stripping). Sonication by itself is not a highly effective process, while combined processes (e.g., sonication + air sparging, sonication + H₂O₂, sonication + UV, etc.) are synergistic in nature, providing much greater treatment effectiveness than the efficiencies predicted by the sum of the 1st-order rate constants. The improvement in rate constants resulting from integrated processes can be an order-of-magnitude or more high than those of single processes alone (such as sonication or air sparging).

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