

COMBINING ADVANCED OXIDATION PROCESSES: ASSESSMENT OF PROCESS ADDITIVITY, SYNERGISM, AND ANTAGONISM

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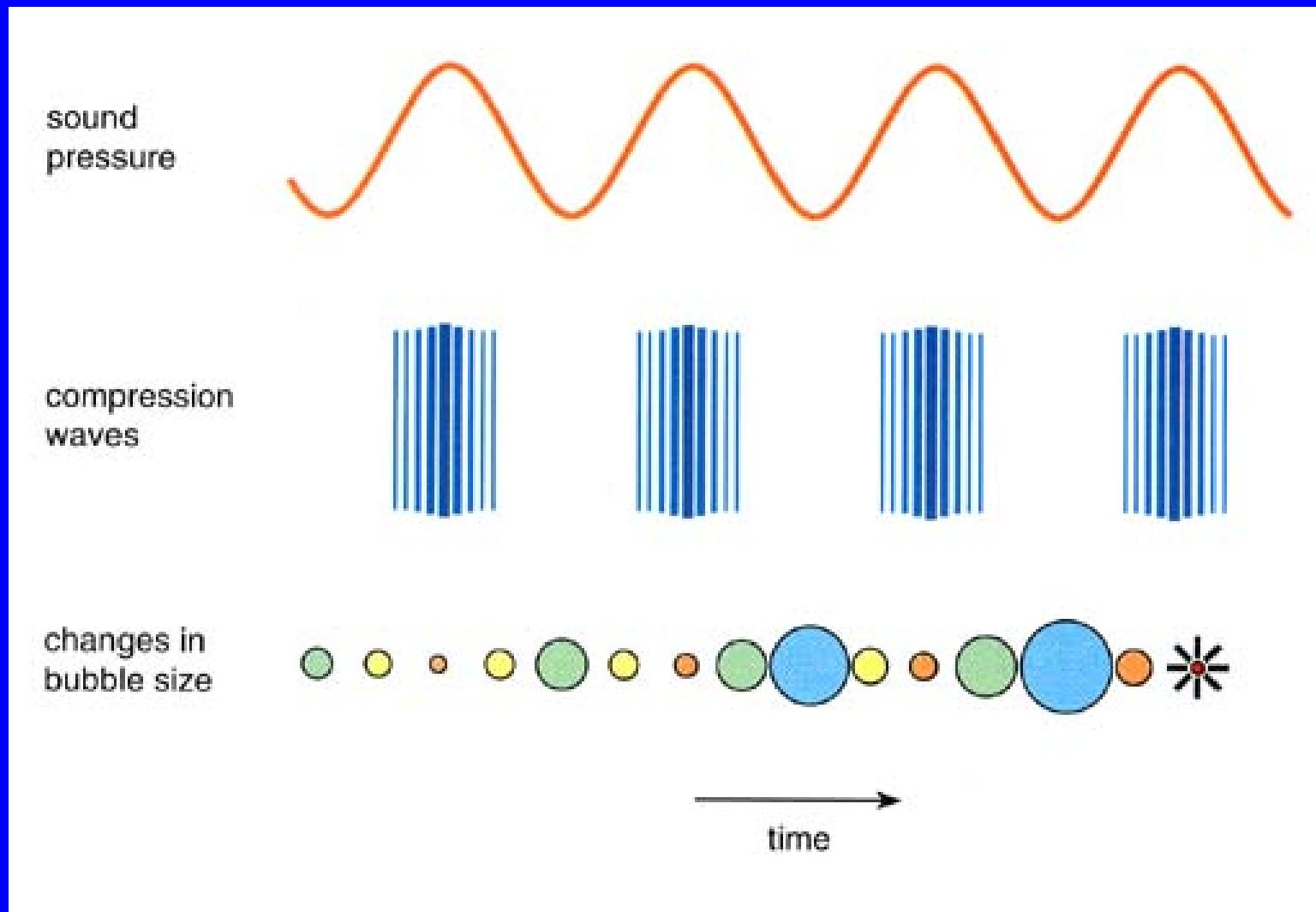
Description of Sonication Technology

- Contaminated water is subjected to sound waves.
- Sound waves travel through the liquid generating alternative compression and expansion cycles.
- Compression cycles push molecules together while expansion cycles pull molecules apart.
- During alternative expansion (rarefaction cycles) the negative pressure overcomes the intermolecular attraction forces and the liquid is “broken” creating microbubbles.

Description of Sonication Technology (cont'd)

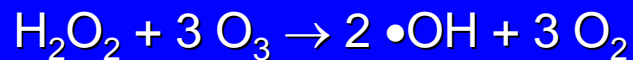
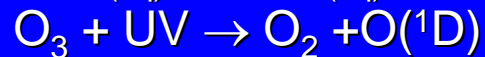
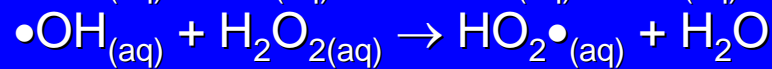
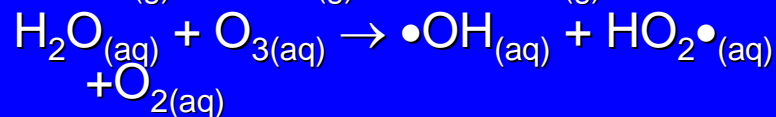
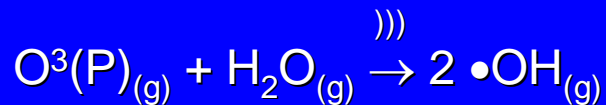
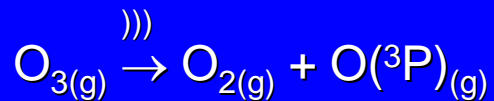
- These microbubbles absorb the energy from continuously applied sound waves and grow in size reaching a critical size, and then implode releasing large amounts of localized energy.
- Localized temperature of up to $\sim 5000^{\circ}\text{K}$ and pressure of up to 1000 atm have been determined at the collapsing microbubble interface while the bulk solution stays near ambient conditions.

Formation of Microbubbles During Sonication

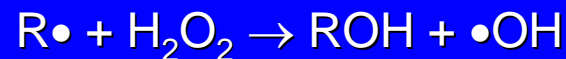
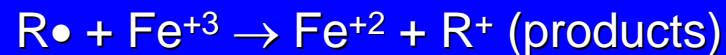
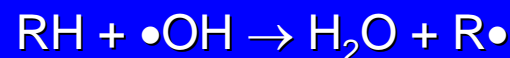
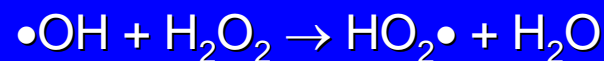
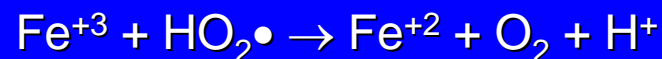
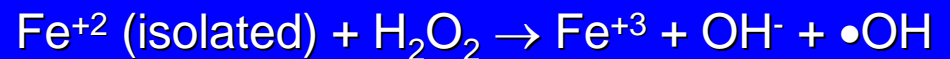
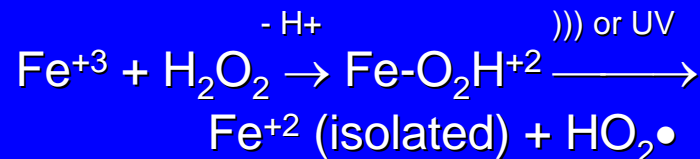
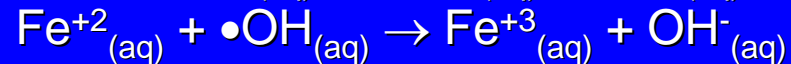
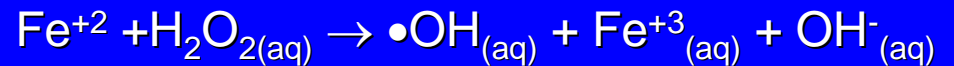


Sonophotochemical Oxidation Chemical Reactions

US-O₃-H₂O₂-UV Systems:



US-UV-Fenton Systems:



EXAMPLE: COMPARISON OF NITROBENZENE KINETICS USING INDIVIDUAL AND COMBINATIVE US-O₃ SYSTEMS

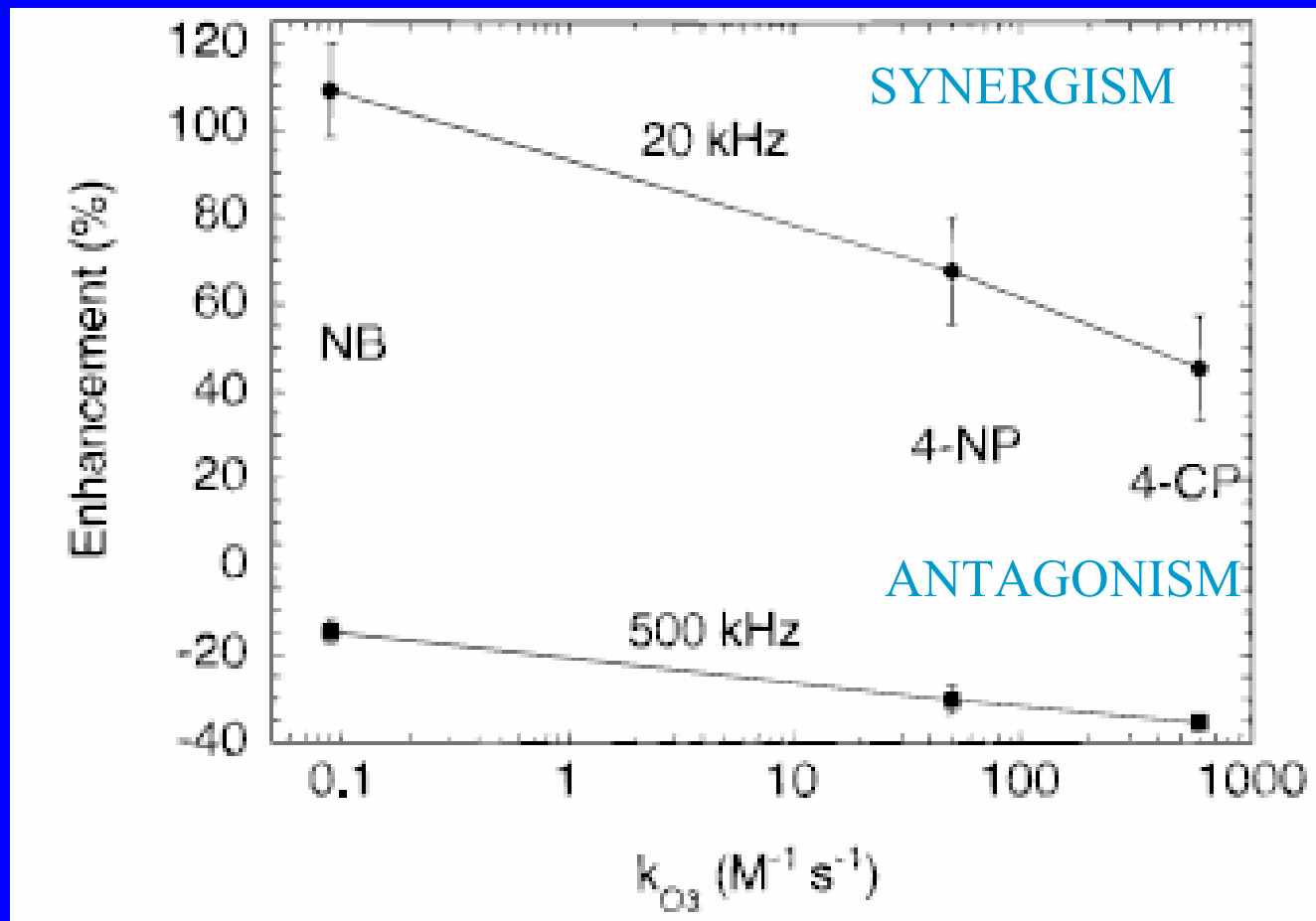
| Oxidation <u>System</u> | <u>Typical First-Order Rate Constant, min⁻¹ at 25 ± 5°C</u> | |
|--|--|--|
| | <u>20 kHz (56.1 W)</u> SYNERGISM | <u>500 kHz (48.3 W)</u> ANTAGONISM |
| k _{US/O₂} | 3.2 × 10 ⁻³ ± 8.4 × 10 ⁻⁵ | 1.3 × 10 ⁻² ± 1.1 × 10 ⁻⁴ |
| k _{O₃} | 3.9 × 10 ⁻² ± 1.1 × 10 ⁻³ | 1.6 × 10 ⁻² ± 6.1 × 10 ⁻⁴ |
| k _{US/O₃} | 4.6 × 10 ⁻² ± 4.1 × 10 ⁻³ | -4.2 × 10 ⁻³ ± 8.9 × 10 ⁻⁴ |
| k _{total(US + O₃)} | 8.8 × 10 ⁻² ± 3.9 × 10 ⁻³ | 2.5 × 10 ⁻² ± 6.5 × 10 ⁻⁴ |

where k_{total} is overall pseudo-first-order rate constant in the combined system and k_{US/O₃} = residual kinetic effect in the combined process over the individual processes

$$-\frac{dS}{dt} = k_{US}[S] + k_{O_3}[S] + k_{US/O_3}[S]$$

Weavers et al., Environ. Sci. Technol., 1998, 32: 2727-2733

Enhancement of the Combined System Compared to the Linear Combination of the Separate Sonolysis and Ozonolysis Experiments



ENHANCEMENT

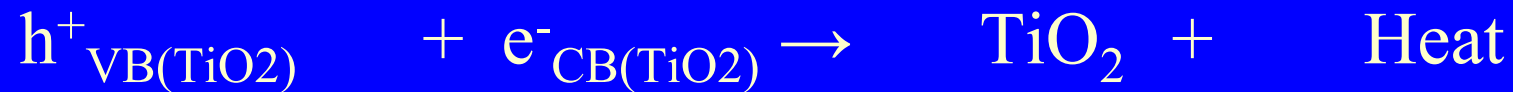
$$E = \frac{k_{US/O_3}}{k_{US} + k_{O_3}} \times 100$$

NB = Nitrobenzene

4-NP = Nitrophenol

4-CP = 4-Chlorophenol

SONOPHOTOCATALYTIC OXIDATION



TiO₂ - UV - O₂ - H₂O₂ - O₃ - S₂O₈ - HSO₅⁻ Reaction Systems

$$\text{Ultrasonic Synergy} = \frac{k_{US+UV+TiO_2} - (k_{US+TiO_2} + k_{UV+TiO_2})}{k_{US+UV+TiO_2}}$$

$$\text{Additive Rate Enhancement: } k_{obsd} = k_{sono} + k_{photocat}$$

EXAMPLE: COMPARISON OF MTBE OXIDATION KINETICS USING COMBINATIVE SONOPHOTOCATALYTIC SYSTEMS

$C_0 = 1.0 \times 10^{-3}$ M; 0.1g TiO_2 , UV: 254 nm Hg, 70.4W; US: 20 kHz, 165 W; 30°C

| <u>Oxidation System</u> | <u>Typical First-Order Rate Constant, s^{-1}</u> |
|--|--|
| US | $2.74 \pm 0.08 \times 10^{-5}$ |
| US- TiO_2 | $3.14 \pm 0.09 \times 10^{-5}$ |
| UV- TiO_2 | $9.8 \pm 0.4 \times 10^{-5}$ |
| US-UV- TiO_2 | $12.3 \pm 0.3 \times 10^{-5}$ |
| UV- TiO_2 - H_2O_2 | $13.2 \pm 0.2 \times 10^{-5}$ |
| US- TiO_2 - H_2O_2 | $3.71 \pm 0.09 \times 10^{-5}$ |
| US-UV- TiO_2 - H_2O_2 | $21.0 \pm 2 \times 10^{-5}$ |

Selli et al. Appl. Catal B 2004, 52, 205-212; Ultrason. Sonochem. 2005, 12, 395-400

EXAMPLE: COMPARISON OF NITROBENZENE KINETICS USING INDIVIDUAL AND COMBINATIVE US-O₃ SYSTEMS

| Oxidation System | Typical First-Order Rate Constant, min ⁻¹ at 25 ± 5°C | |
|--|--|--|
| | <u>20 kHz ((56.1 W)</u> SYNERGISM | <u>500 kHz (48.3 W)</u> ANTAGONISM |
| k _{US/O₂} | 3.2 × 10 ⁻³ ± 8.4 × 10 ⁻⁵ | 1.3 × 10 ⁻² ± 1.1 × 10 ⁻⁴ |
| k _{O₃} | 3.9 × 10 ⁻² ± 1.1 × 10 ⁻³ | 1.6 × 10 ⁻² ± 6.1 × 10 ⁻⁴ |
| k _{US/O₃} | 4.6 × 10 ⁻² ± 4.1 × 10 ⁻³ | -4.2 × 10 ⁻³ ± 8.9 × 10 ⁻⁴ |
| k _{total(US + O₃)} | 8.8 × 10 ⁻² ± 3.9 × 10 ⁻³ | 2.5 × 10 ⁻² ± 6.5 × 10 ⁻⁴ |

where k_{total} is overall pseudo-first-order rate constant in the combined system and k_{US/O₃} = residual kinetic effect in the combined process over the individual processes

$$-\frac{dS}{dt} = k_{US}[S] + k_{O_3}[S] + k_{US/O_3}[S]$$

Weavers *et al.*, *Environ. Sci. Technol.*, 1998, 32: 2727-2733.

Example: Comparison of Nitrobenzene Kinetics Using Individual and Combinative US-O₃ Systems

| Oxidation System | Typical 1 st -Order Rate Constant (min ⁻¹) at 25±5°C | |
|---------------------|---|--|
| | <u>20 kHz (56.1 W)</u> Synergism | <u>500 kHz (48.3 W)</u> Antagonism |
| k_{US/O_2} | $3.2 \times 10^{-3} \pm 8.4 \times 10^{-5}$ | $1.3 \times 10^{-2} \pm 1.1 \times 10^{-4}$ |
| k_{O_3} | $3.9 \times 10^{-2} \pm 1.1 \times 10^{-3}$ | $1.6 \times 10^{-2} \pm 6.1 \times 10^{-4}$ |
| k_{US/O_3} | $4.6 \times 10^{-2} \pm 4.1 \times 10^{-3}$ | $-4.2 \times 10^{-3} \pm 8.9 \times 10^{-4}$ |
| $k_{total(US+O_3)}$ | $8.8 \times 10^{-2} \pm 3.9 \times 10^{-3}$ | $2.5 \times 10^{-2} \pm 6.5 \times 10^{-4}$ |

Nitrobenzene Kinetics Using Individual and Combinative US-O₃ Systems

- k_{total} is the overall pseudo 1st-order rate constant in the combined system.
- $k_{\text{US/O}_3}$ is the residual kinetic effect in the combined process over the individual processes:

$$-\frac{dS}{dt} = k_{\text{US}} [S] + k_{\text{O}_3} [S] + k_{\text{US/O}_3} [S]$$

Reference: Weavers *et al.*, 1998. *Environ. Sci. Technol.*, 32: 2727-2733.

Example: Comparison of MTBE Oxidation Kinetics Using Combinative Sonophotocatalytic Systems

$C_0 = 1.0 \times 10^{-3} \text{M}$; 0.1 gm TiO_2 ; UV=254 nm Hg, 70.4 W; US=20 kHz, 165 W; 30°C

| Oxidation System | Typical 1 st -Order Rate Constant, (sec ⁻¹) |
|---|--|
| US | $2.74 \pm 0.08 \times 10^{-5}$ |
| US-TiO ₂ | $3.14 \pm 0.09 \times 10^{-5}$ |
| UV-TiO ₂ | $9.8 \pm 0.4 \times 10^{-5}$ |
| US-UV-TiO ₂ | $12.3 \pm 0.3 \times 10^{-5}$ |
| UV-TiO ₂ -H ₂ O ₂ | $13.2 \pm 0.2 \times 10^{-5}$ |
| US-TiO ₂ -H ₂ O ₂ | $3.71 \pm 0.09 \times 10^{-5}$ |
| US-UV-TiO ₂ -H ₂ O ₂ | $21.0 \pm 2.0 \times 10^{-5}$ |

Reference: Selli *et al.*, 2004. *Appl. Catal. B*, 52: 205-212;
Selli *et al.*, 2005. *Ultrason. Sonochem.*, 12: 395-400.

AOP Mechanisms

- Three primary pathways have been identified for compound degradation, including:
 1. hydroxyl radical oxidation;
 2. direct pyrolytic degradation;
 3. supercritical water reactions.
- In aqueous solution, water vapor present in the microbubble is homolytically split during bubble collapse to yield $\bullet\text{H}$ and $\bullet\text{OH}$ radicals, while chemical substrates present either within or near the gas-liquid interface of the collapsing microbubble are subject to direct attack by $\bullet\text{OH}$.

Vapor Stripping

- Vapor stripping (air sparging) transfers 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.

Combined Sonication + Vapor Stripping

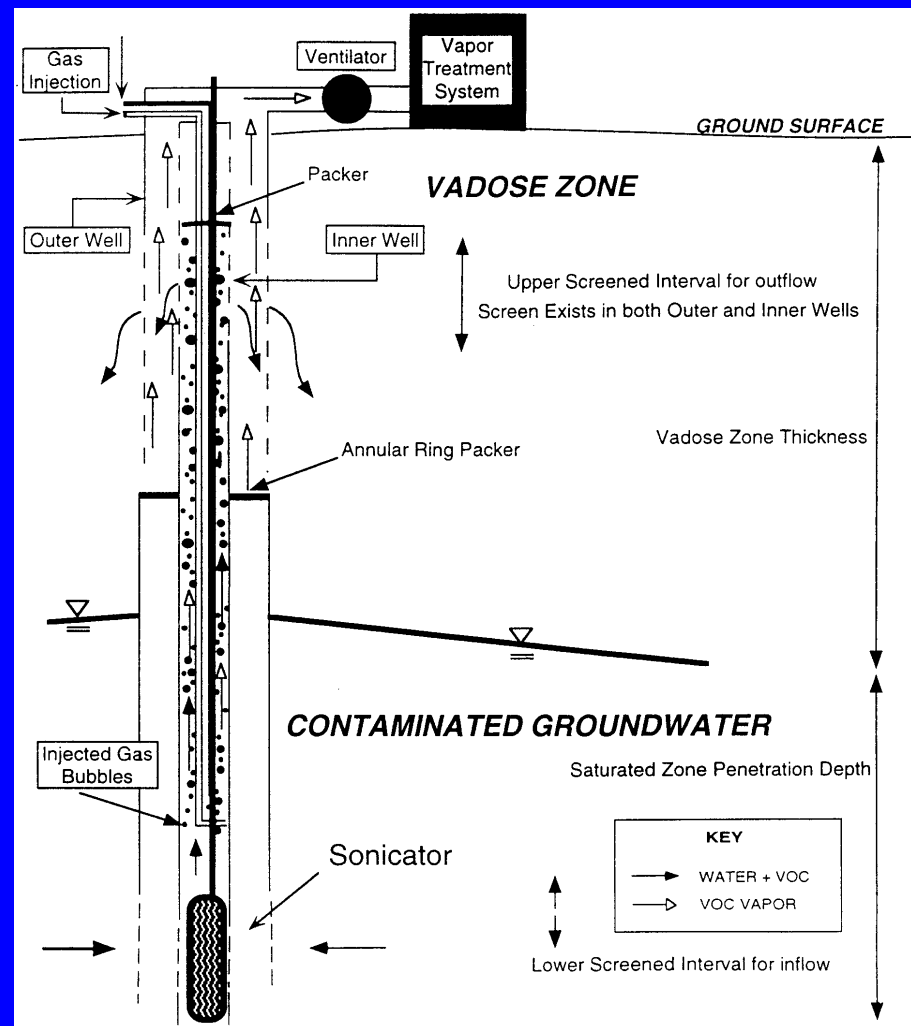
- Primary pathways for contaminant destruction/removal include:
 - hydroxyl radical oxidation;
 - direct pyrolytic degradation; and
 - Supercritical water reactions.

Process Involves:

- In-well sonication
- In-well vapor stripping
- *In-situ* biodegradation

Combined Sonication + Vapor Stripping

- Process combines in-well sonication with vapor stripping to enhance removal of semi-volatile compounds from solution.



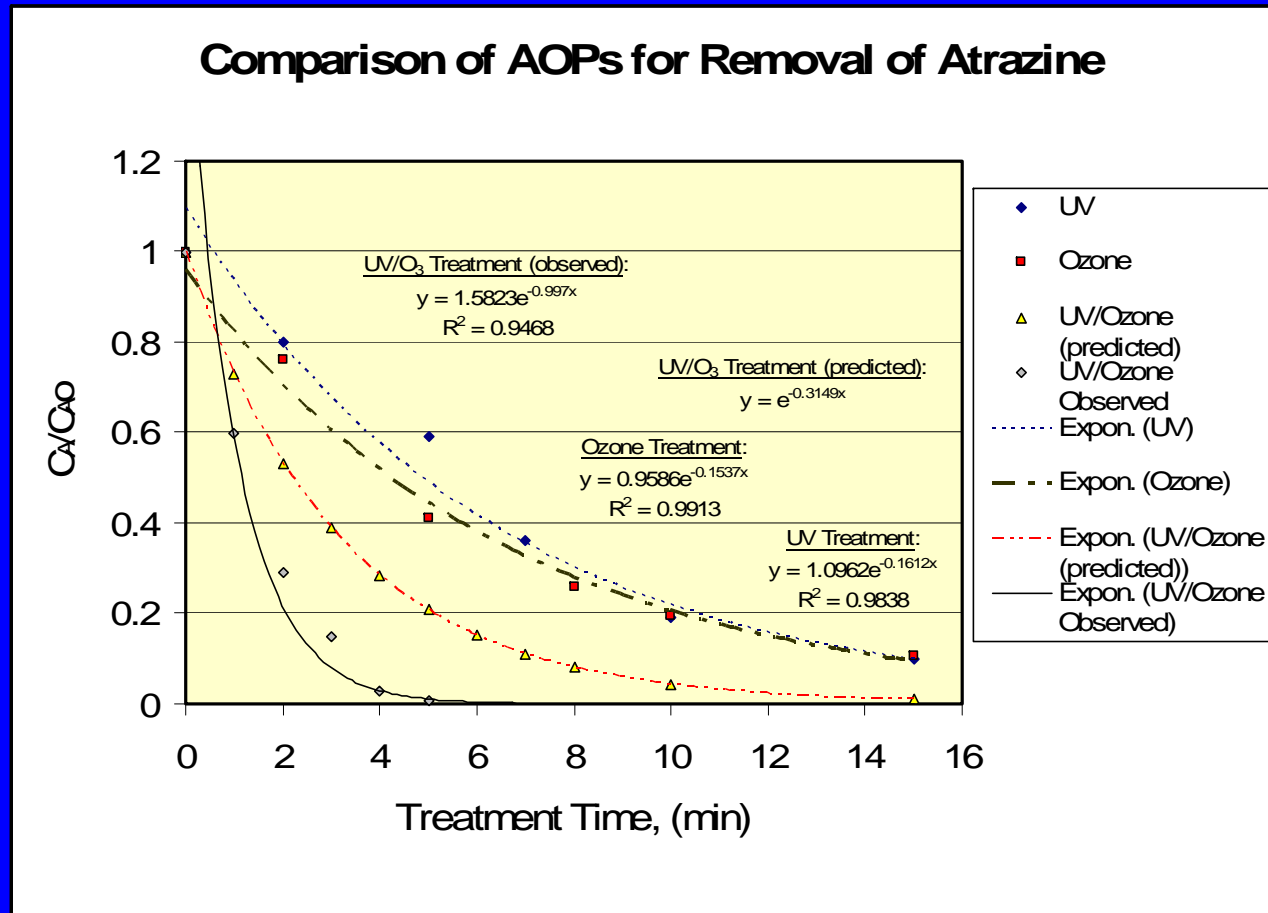
Contaminants Investigated

- Benzene
- Toluene
- Ethylbenzene
- Xylene
- Carbon tetrachloride (CCl_4)
- Trichloroethane (TCA)
- Trichloroethylene (TCE)
- Tetrachloroethylene (PCE)

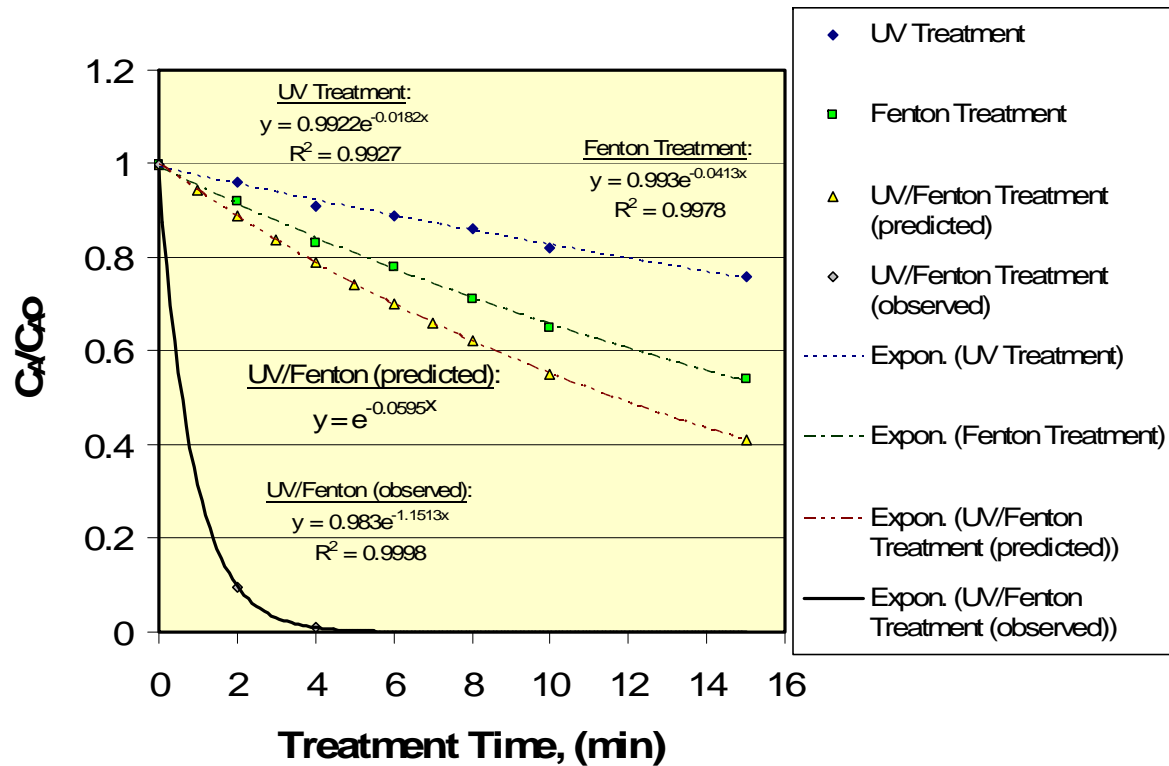
Results and Discussion

- 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.

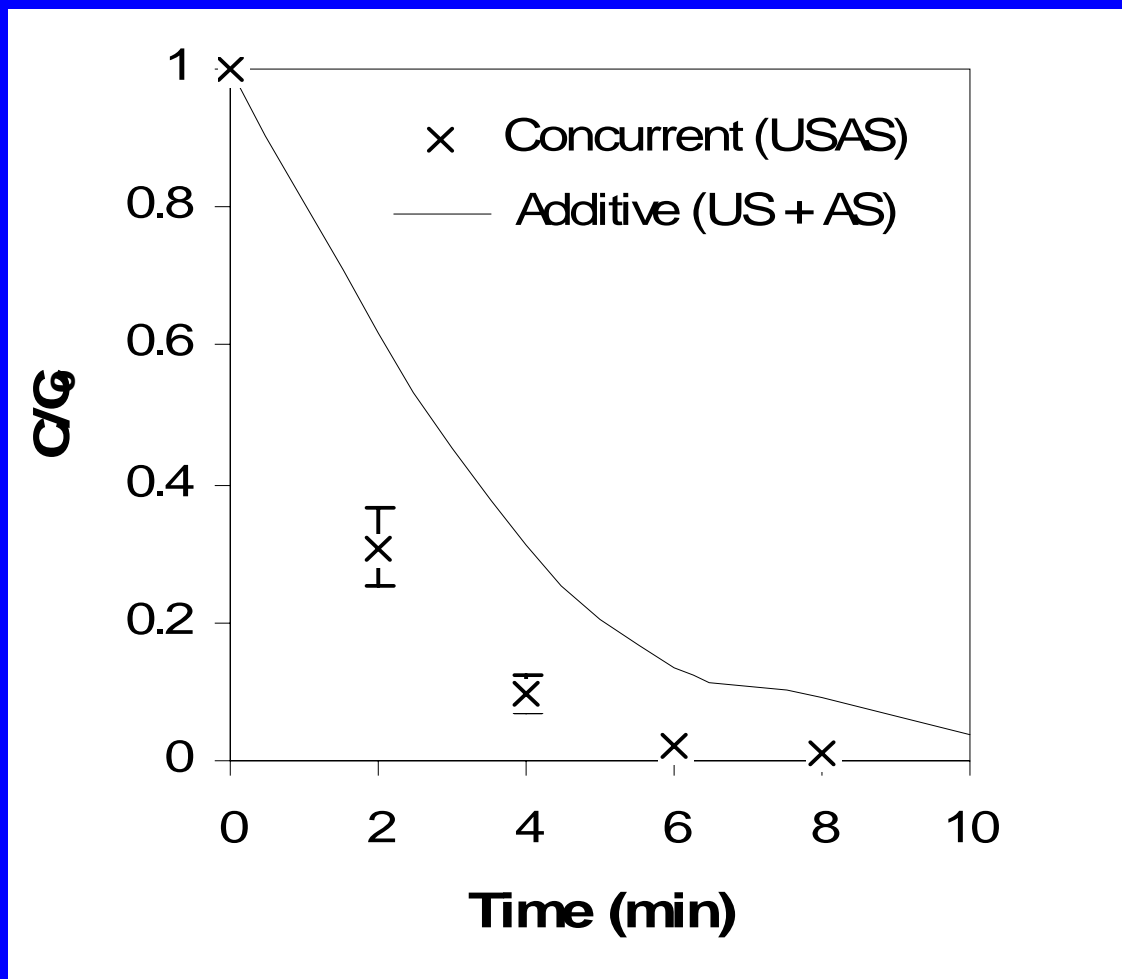
Results and Discussion



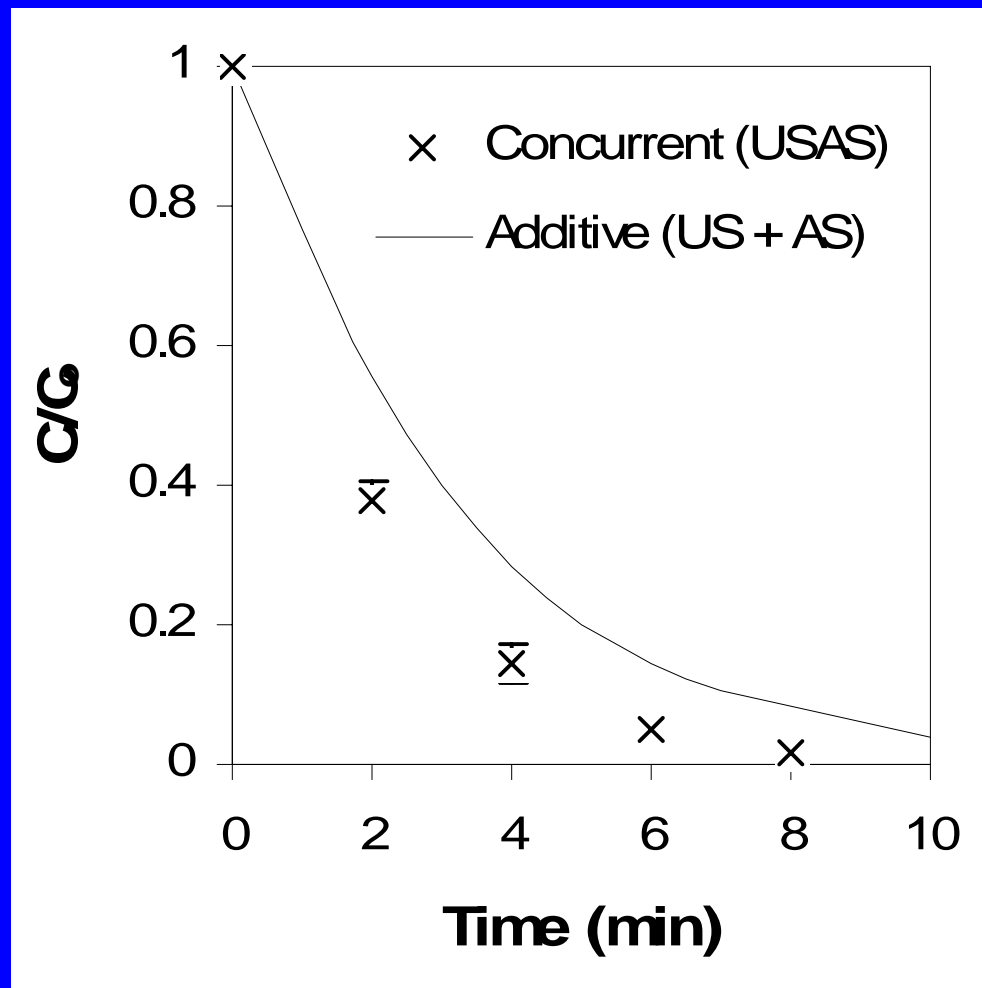
Comparison of AOPs for Removal of Carbofuran



Removal of CCl_4 from Artificial Groundwater by Combined Ultrasound and Air Stripping: Ultrasonic Power Intensity = 35 W/cm^2 and Air Flow Rate = 500-mL/min .



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.



Results

Determining Optimal Air Flow Rate for the Air Sparging System

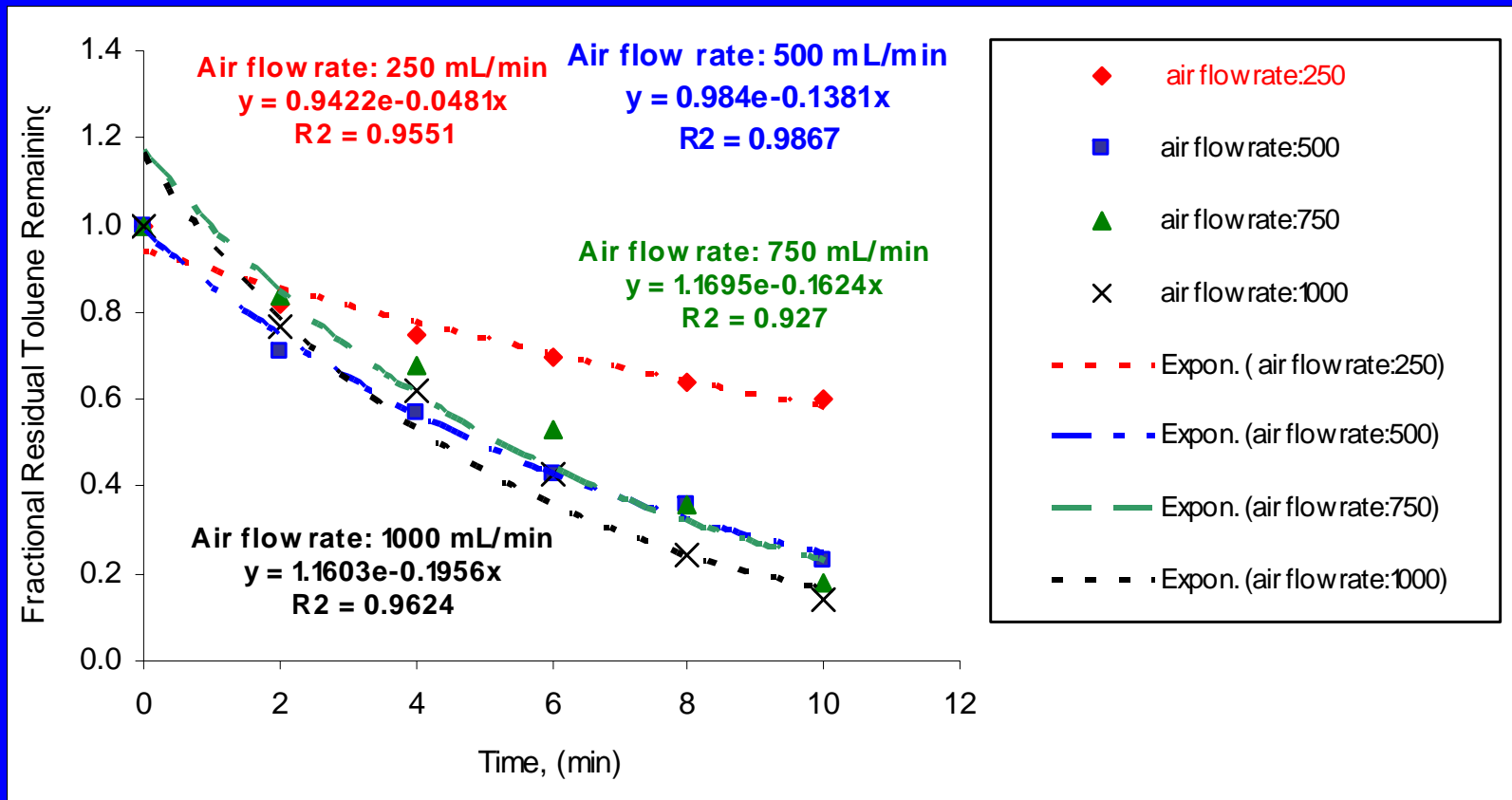


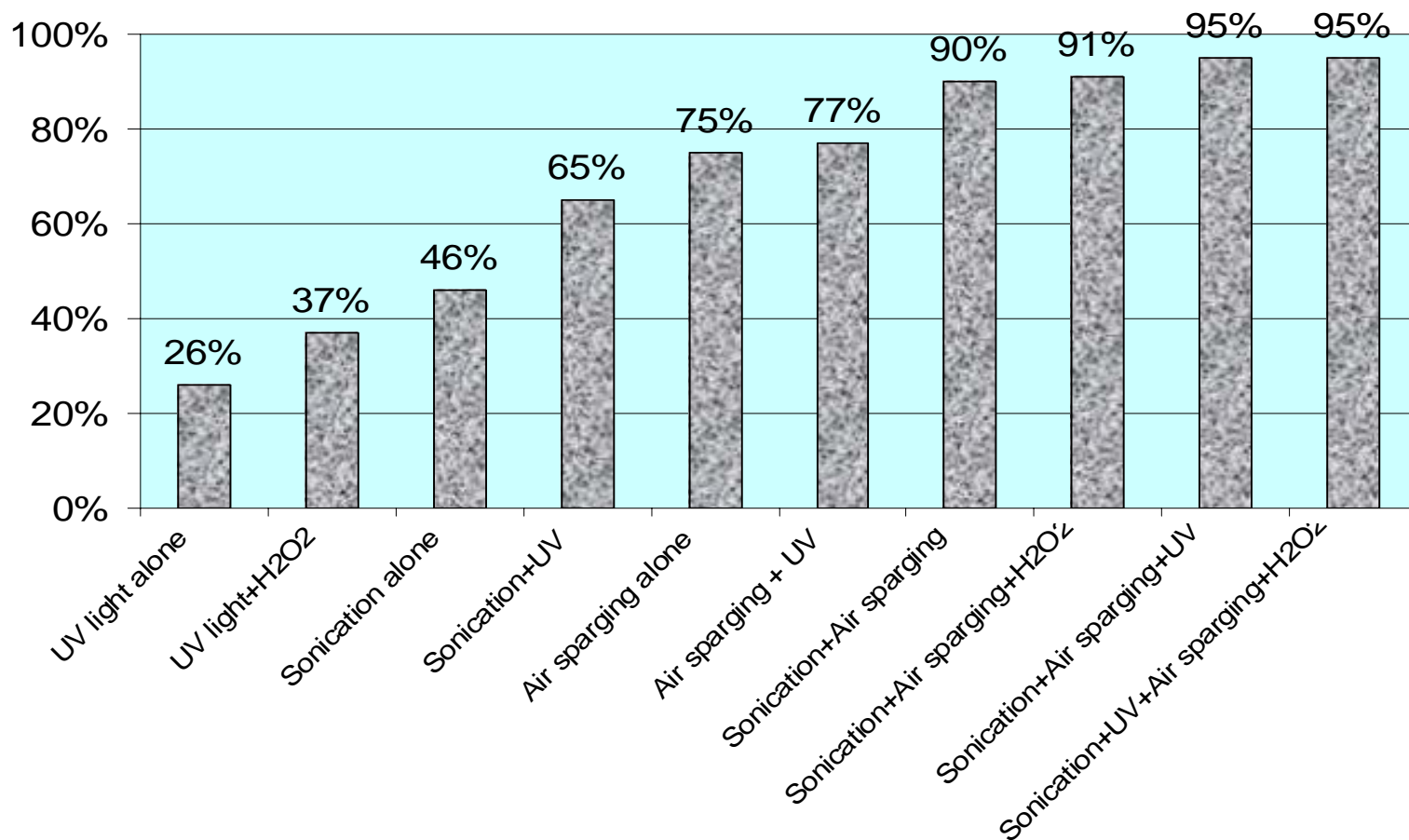
Figure 1. Comparison of Removal Efficiency of Toluene Using Air Stripping Employing Different Air Flow Rates.

AOP Systems Tested for Removal of Benzene

- UV light alone
- UV light + H₂O₂
- Sonication alone
- UV light + Sonication
- Air sparging alone
- Air sparging + Sonication
- Air sparging + UV light
- Sonication + Air sparging+ UV light
- Sonication + Air sparging + H₂O₂
- Sonication + Air sparging + UV + H₂O₂

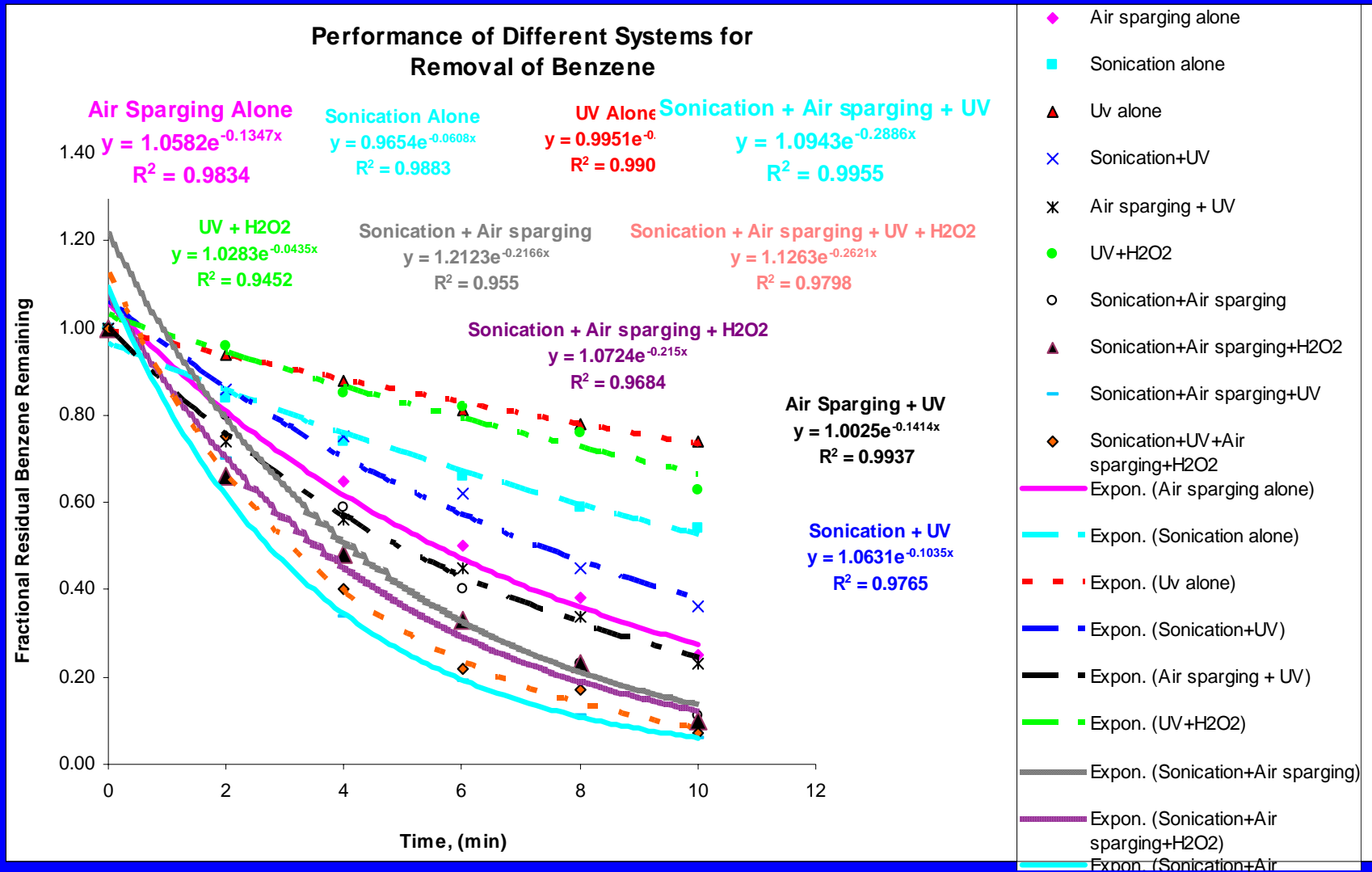
Comparison of Removals of Benzene using Various AOPs

System Comparison for Benzene Removal Efficiency
for 10 min Treatment Time



Results

System Comparison for Benzene



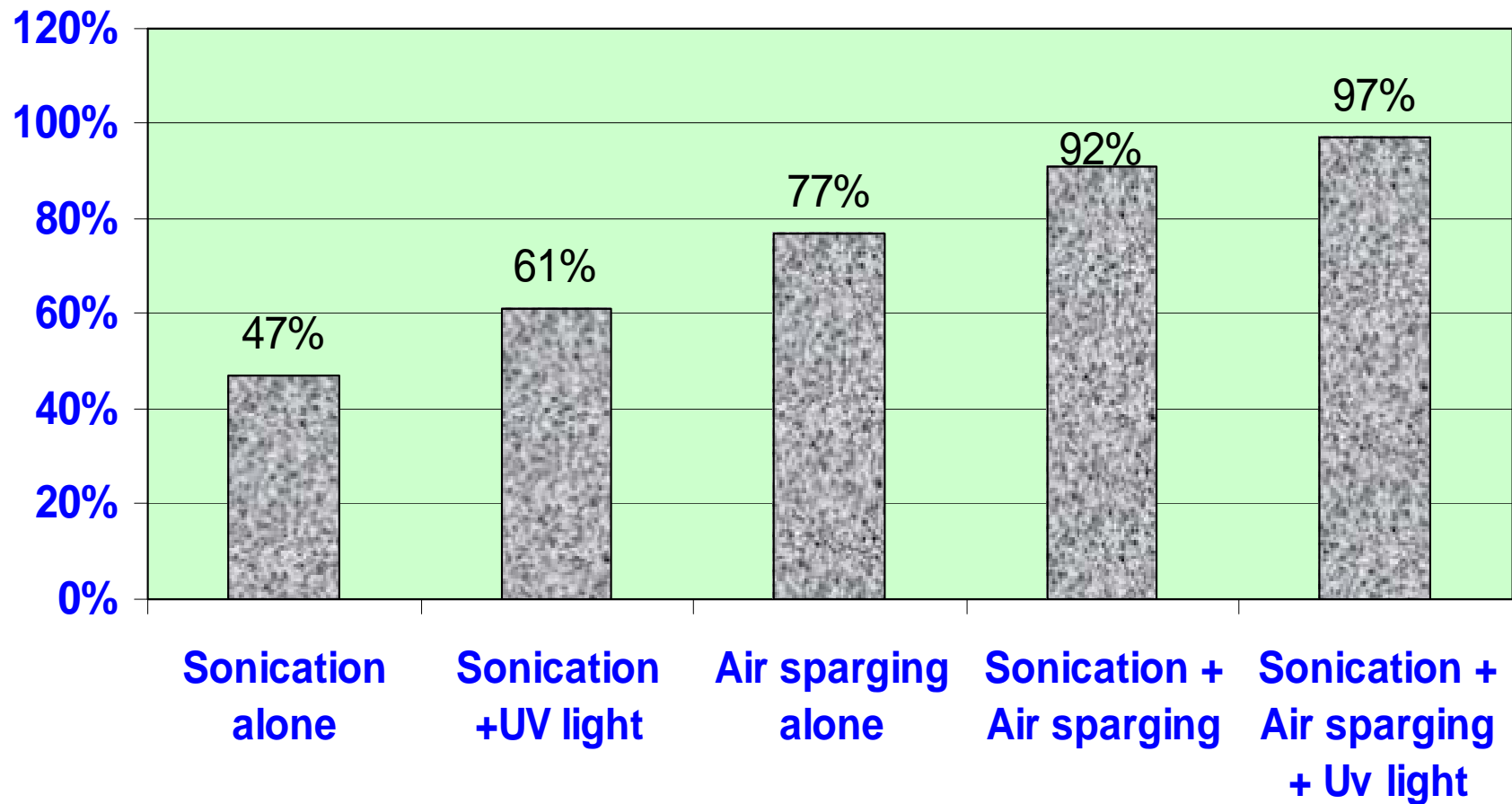
Results

Systems Tested for Toluene Removal

- Sonication alone
- Sonication +UV light
- Air sparging alone
- Sonication + Air sparging
- Sonication + Air sparging + UV light

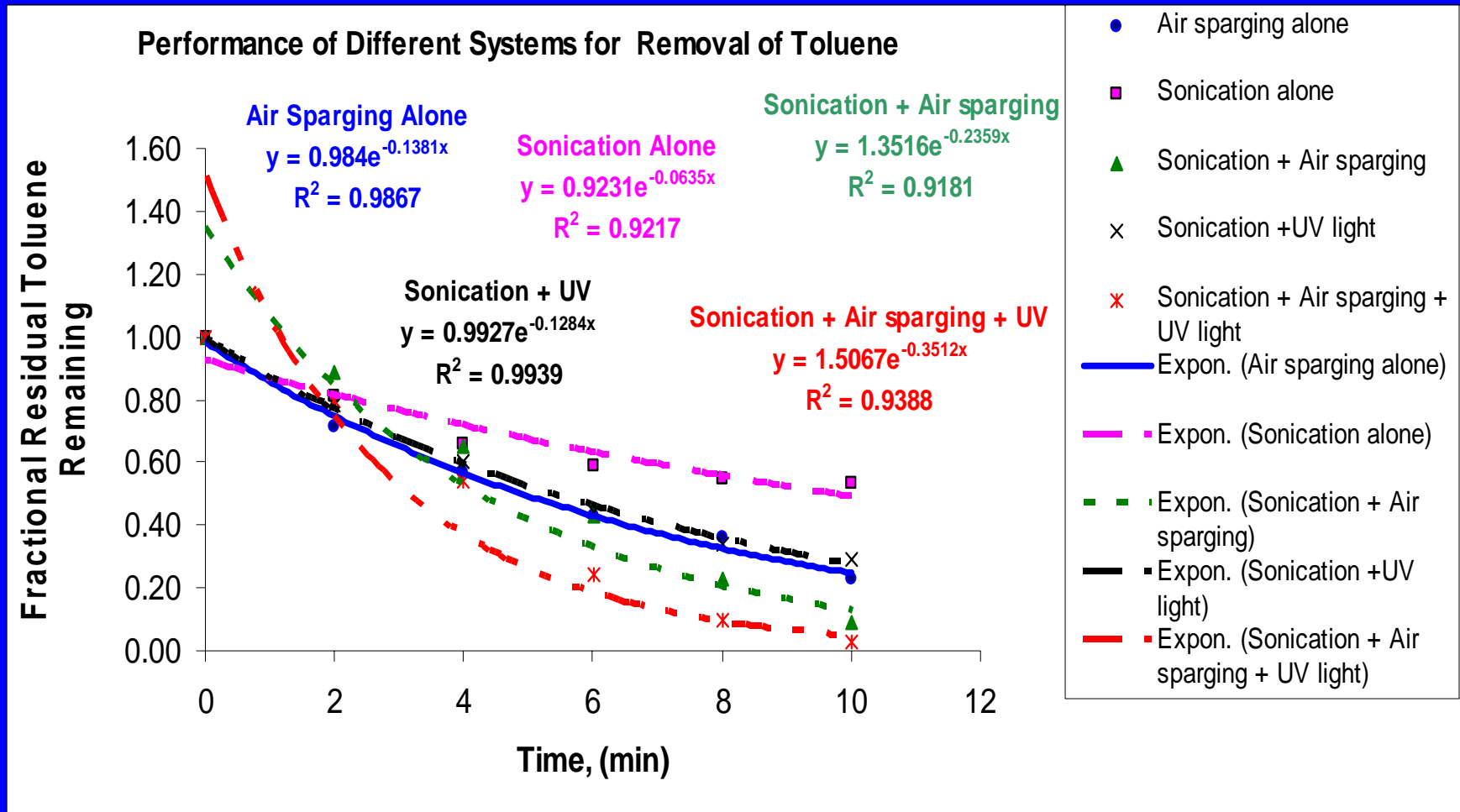
Comparison of Removals of Toluene using Various AOPs

System Comparison for Removal of Toluene for 10 min Treatment



Results

System Comparison for Toluene



Summary of 1st-Order Rate Constants for Removal of Benzene and Toluene from Solution

| Contaminant | Treatment Process | 1 st -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 |

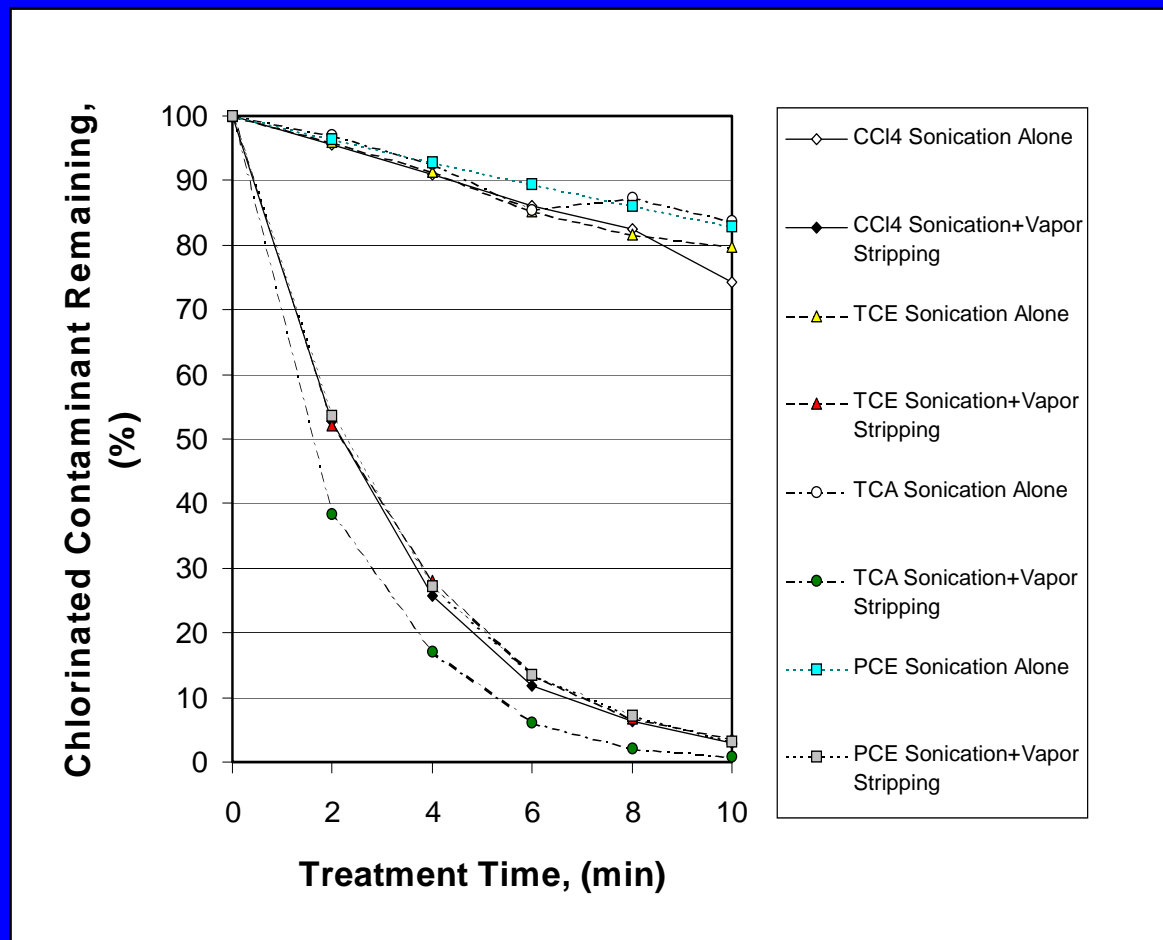
Summary of 1st-Order Rate Constants for Removal of Ethyl Benzene and *o*-Xylene from Solution

| Contaminant | Treatment Process | 1 st -Order Rate Constant, (min ⁻¹) |
|------------------|--|--|
| 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 |

Experimental Conditions – CCl₄, TCA, TCE, and PCE

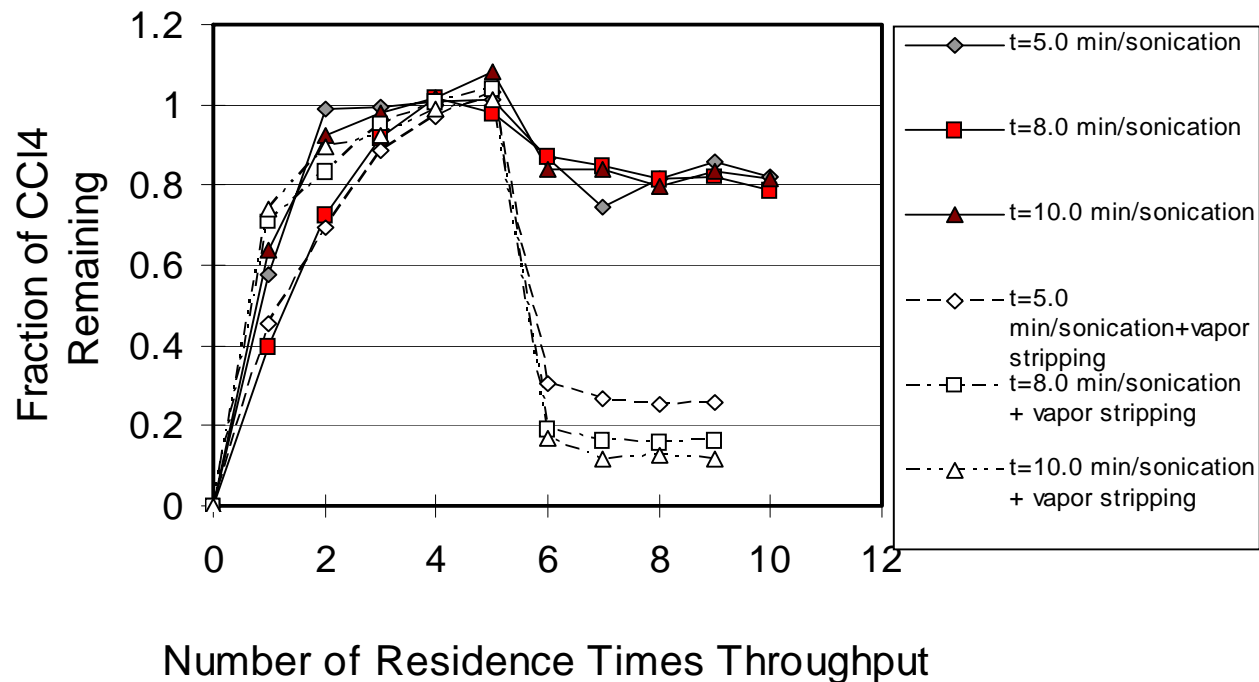
- Batch experiments were performed separately on each of the chlorinated organic contaminants (CCl₄, TCE, TCA, and PCE);
- Initial contaminant concentrations ranged from ~1 to ~100 mg/L;
- Ultrasonic frequency of 20 kHz;
- Applied power intensity was 12.3-, 25.3-, and 35.8 W/cm²;
- Air injection rates used were nominally 0- (sonication alone), 500-, 1000-, and 1500- mL/min; and
- Reactor volume of ~500-mL.

Residual chlorinated organic compound remaining after batch sonication and sonication+vapor stripping treatment.



Residual CCl_4 remaining after continuous sonication and sonication + vapor stripping treatment.

Comparison of Fraction CCl_4 Remaining Using Sonication + Vapor Stripping to Sonication Alone (20 kHz, 35.8 W/cm^2)



Residual TCA remaining after continuous sonication and sonication+vapor stripping treatment.

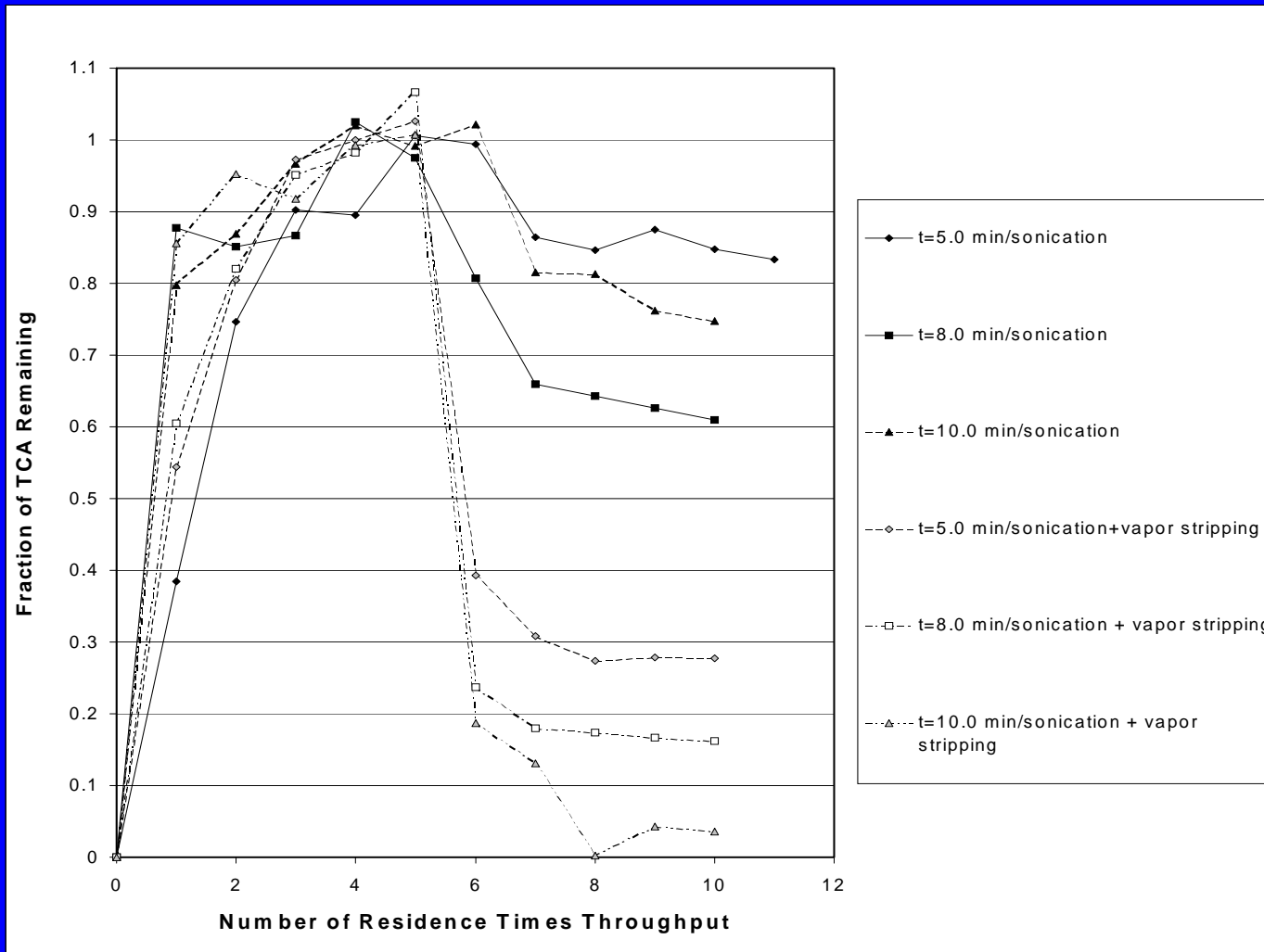


Table 2. First-Order Rate Constants (min^{-1}) Using Sonication Alone in Continuous Flow Operations.

| Compound | Power Intensity, (W/cm^2) | | |
|----------------|---|-------|-------|
| | 12.3 | 25.3 | 35.8 |
| CCl_4 | 0.028 | 0.049 | 0.062 |
| TCE | 0.019 | 0.022 | 0.024 |
| TCA | 0.020 | 0.034 | 0.049 |
| PCE | 0.019 | 0.021 | 0.022 |

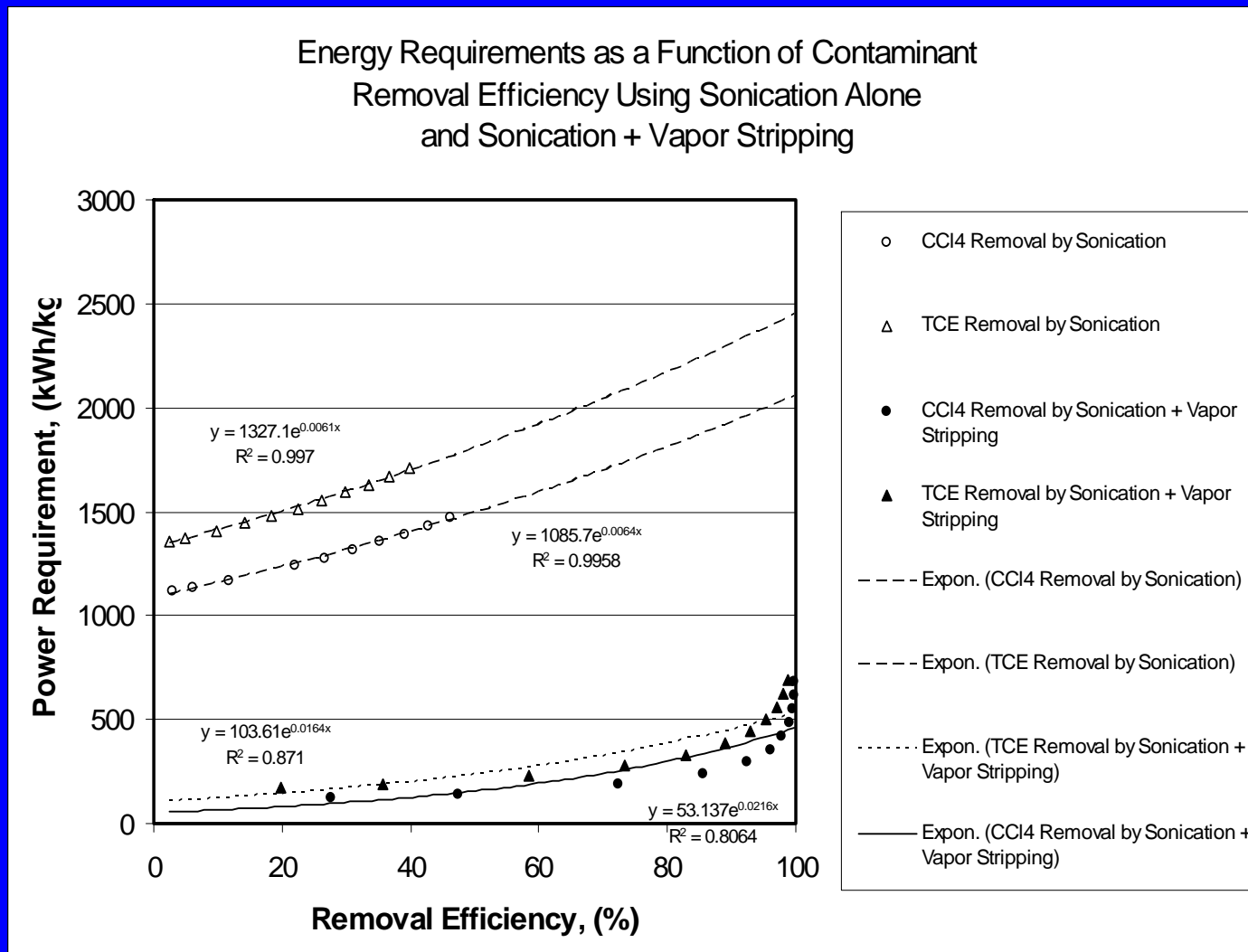
Table 3. First-Order Rate Constants (min^{-1}) Using Vapor Stripping Alone in Continuous Flow Operations.

| Compound | Air Injection Flow Rate, (mL/min) | |
|----------------|-----------------------------------|-------|
| | 500 | 1000 |
| CCl_4 | 0.286 | 0.411 |
| TCE | 0.243 | 0.401 |
| TCA | 0.228 | 0.531 |
| PCE | 0.282 | 0.454 |

Table 4. First-Order Rate Constants (min^{-1}) Using Combined Sonication/Vapor Stripping in Continuous Flow Operations.

| Compound | Air Injection Rate (mL/min) and Ultrasonic Power Intensity (W/cm^2) | | | | | |
|----------------|---|--------------|--------------|---------------|---------------|---------------|
| | 500/ 12.3 | 500/ 25.3 | 500/ 35.8 | 1000/ 12.3 | 1000/ 25.8 | 1000/ 35.8 |
| CCl_4 | 0.353 | 0.487 | 0.645 | 0.729 | 0.870 | 0.866 |
| TCE | 0.356 | 0.356 | 0.440 | 0.516 | 0.583 | 0.633 |
| TCA | 0.341 | 0.549 | 0.640 | 0.691 | 0.864 | 0.904 |
| PCE | 0.483 | 0.411 | 0.447 | 0.492 | 0.412 | 0.494 |

Energy requirements as a function of contaminant removal efficiency using sonication alone and sonication+vapor stripping.



Benefits of In-Well Sonication Technology

- Performance of remediation *in-situ*;
- Complementary treatment systems that can drastically reduce or remove SVOCs and VOCs from solution;
- Treatment unit operations are synergistic in nature;
- Ability to convert hard-to-degrade organics into more volatile organic compounds;
- Eliminates handling or disposing of waters; and
- Improves efficiency resulting in shortened clean-up times to remediate a site and greater cost-effectiveness.

Conclusions

- The innovative technology couples in-well sonication, in-well vapor stripping, and biodegradation into an integrated process.
- By partially destroying the SVOCs (e.g., opening up the benzene-ring structures), the ability to remove the resultant VOCs and biotreatment of the resultant organics is enhanced (over the case of biotreatment alone).
- The combined sonication+vapor stripping system operates in a synergistic fashion, as the rate constants are greater than the additive rate constants from sonication alone and vapor stripping alone.

Conclusions (cont'd)

- The combined system is more effective than either of the separate sonication or vapor stripping systems. For example, while sonication is capable of removing ~30% of the TCA after 10 minutes reaction time, the combined sonication/vapor stripping system can remove nearly 97% after 4 minutes treatment time, and nearly 100% removal after 10 minutes.
- The rate constants for the combined system are nearly an order of magnitude higher than those for sonication alone (and for vapor stripping alone).

Conclusions (cont'd)

- Continuous flow experiments had removals of TCA and CCl_4 ranging from 72% to 97% and 74% to 88%, respectively, for residence times of 5 to 10 minutes.
- The combined sonication+vapor stripping system operated synergistically.

Acknowledgements

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