

A Critical Evaluation of Integrated Advanced Oxidation Processes: Assessment of Process Synergism

by

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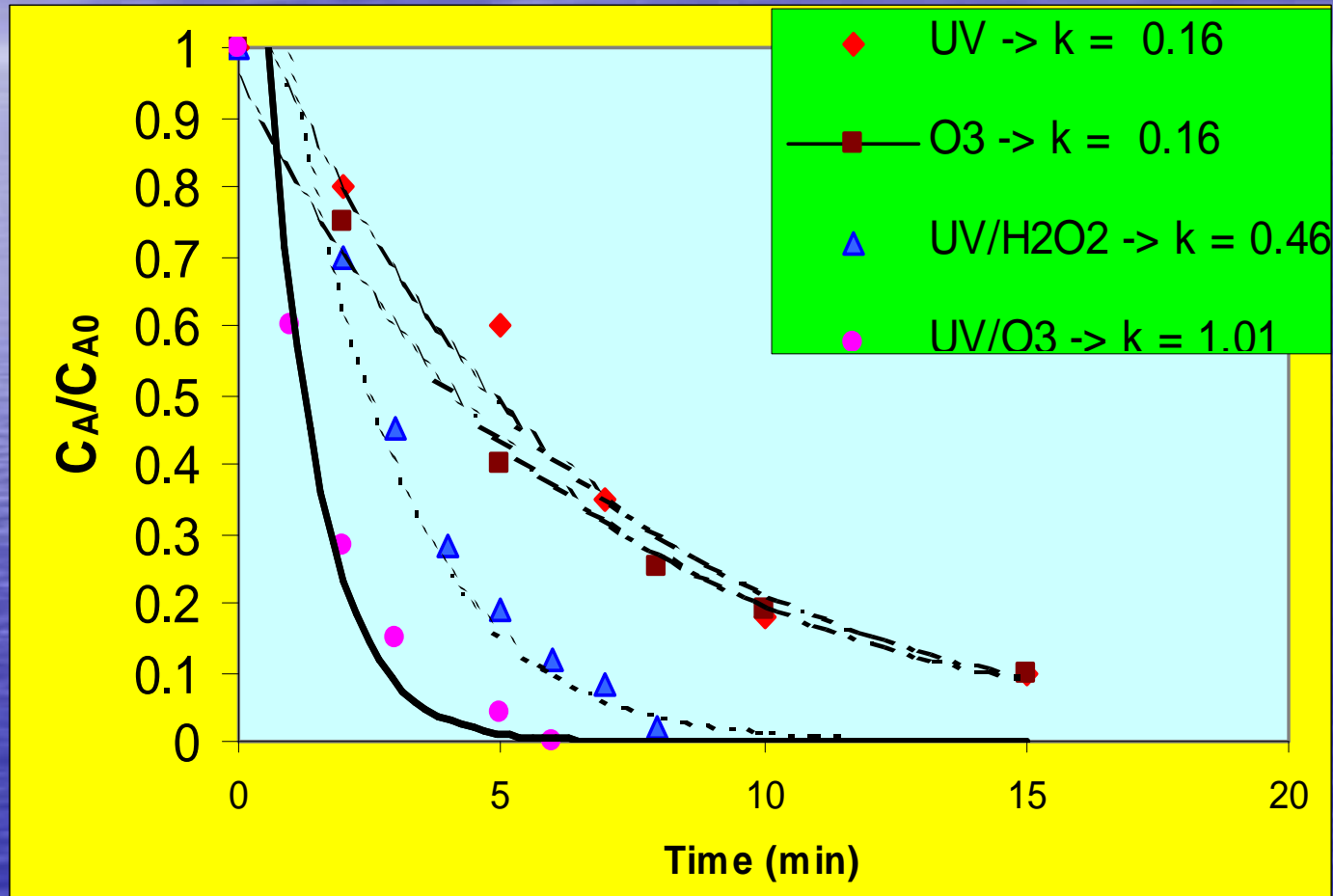
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Advanced Oxidation Processes

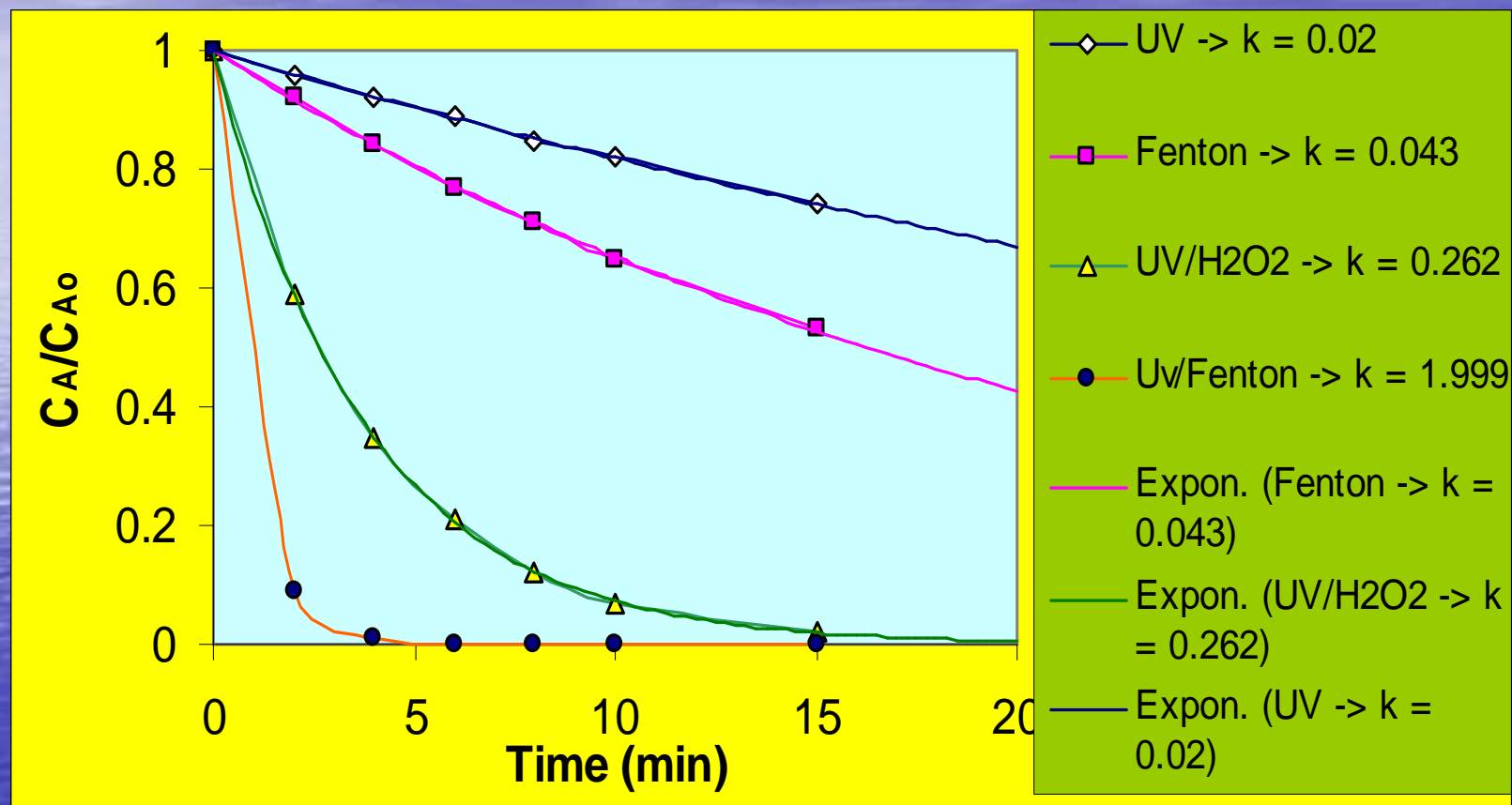
- UV light;
- H_2O_2 / UV light;
- Sonication;
- Sonication/UV light;
- Ozonation;
- Ozonation/ H_2O_2 ; and
- Fenton's Reagent.

Comparison of AOPs for Removal of Atrazine



Source: Beltran *et al.*, (1994). *Water Res.*, 28(10): 2165 – 2174.

Comparison of AOPs for Removal of Carbofuran



Source: Benitez *et al.*, (2001), *Journal of Hazardous Materials*, **B89**: 51-65.

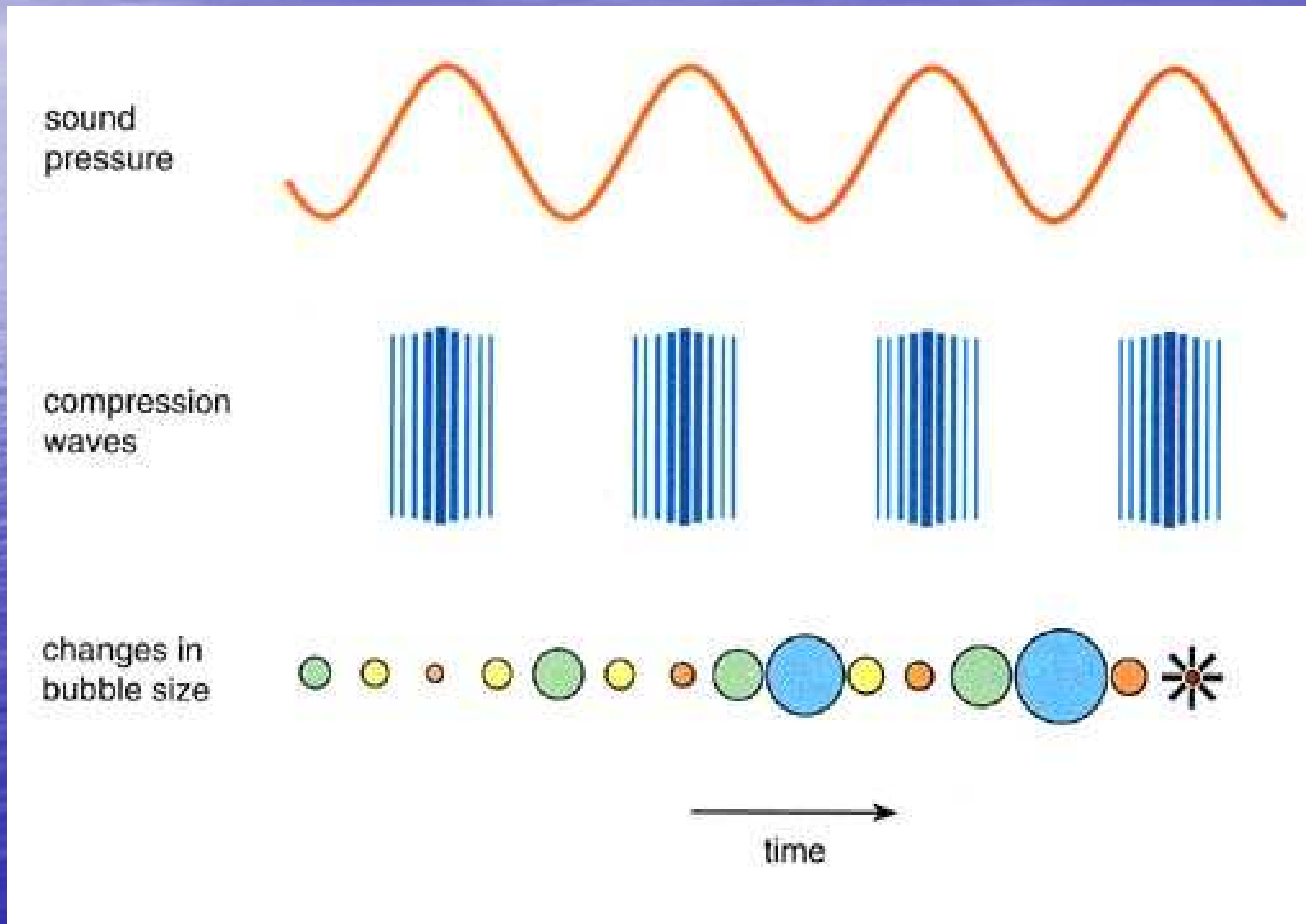
Description of Sonication Technology

- 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.

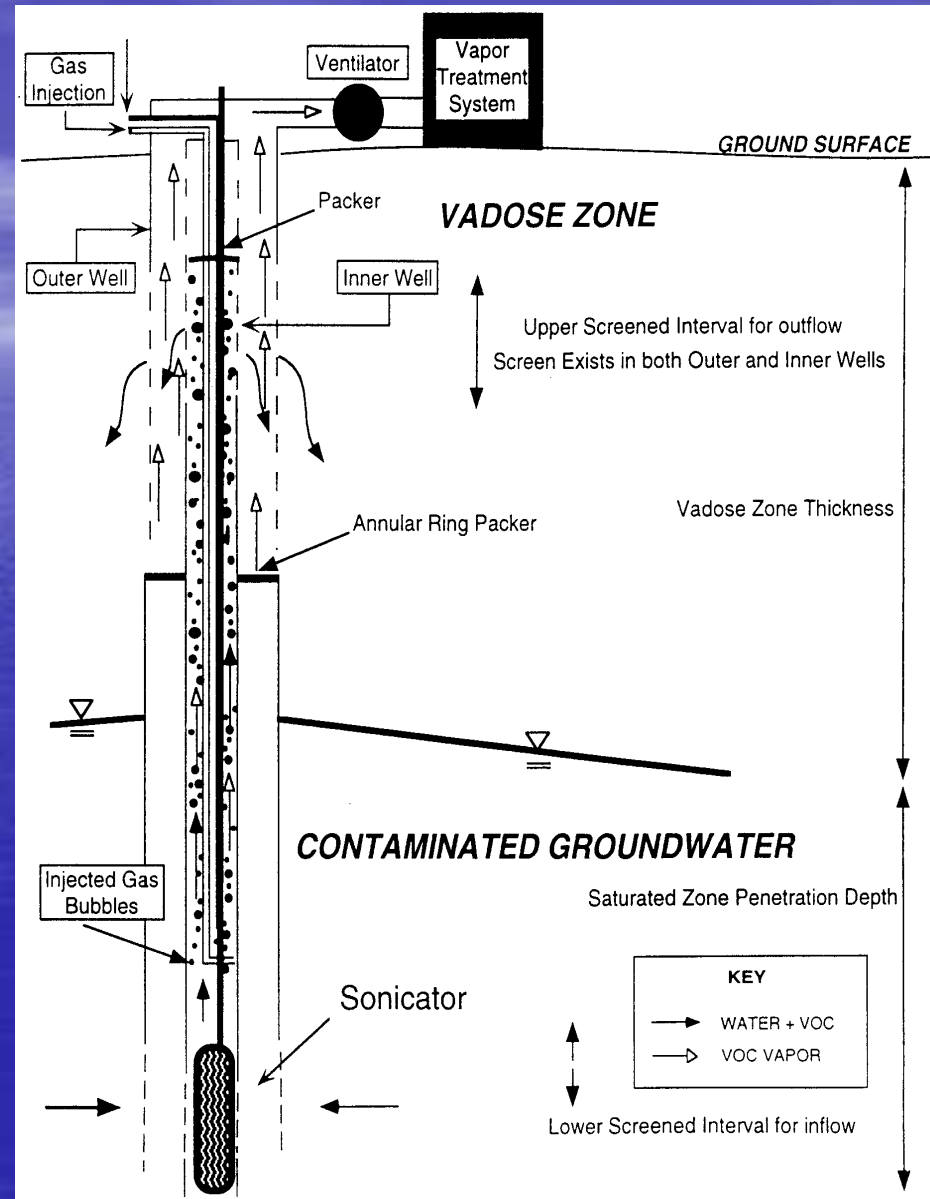
Description of Sonication Technology (cont'd)

- 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 ~ 5000 °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



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



Mechanisms Involved

- 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

Reaction Mechanism

- Pyrolysis:

The extreme localized conditions caused by microbubble implosion (i.e., acoustic cavitation) result in direct pyrolysis (incineration) of contaminants

- •H and •OH Reactions:

The extreme localized conditions generated by acoustic cavitation results in decomposition of water into hydroxyl ($\bullet\text{OH}$) and hydrogen ($\bullet\text{H}$) radicals. These extremely reactive radicals destroy organic compounds very effectively.

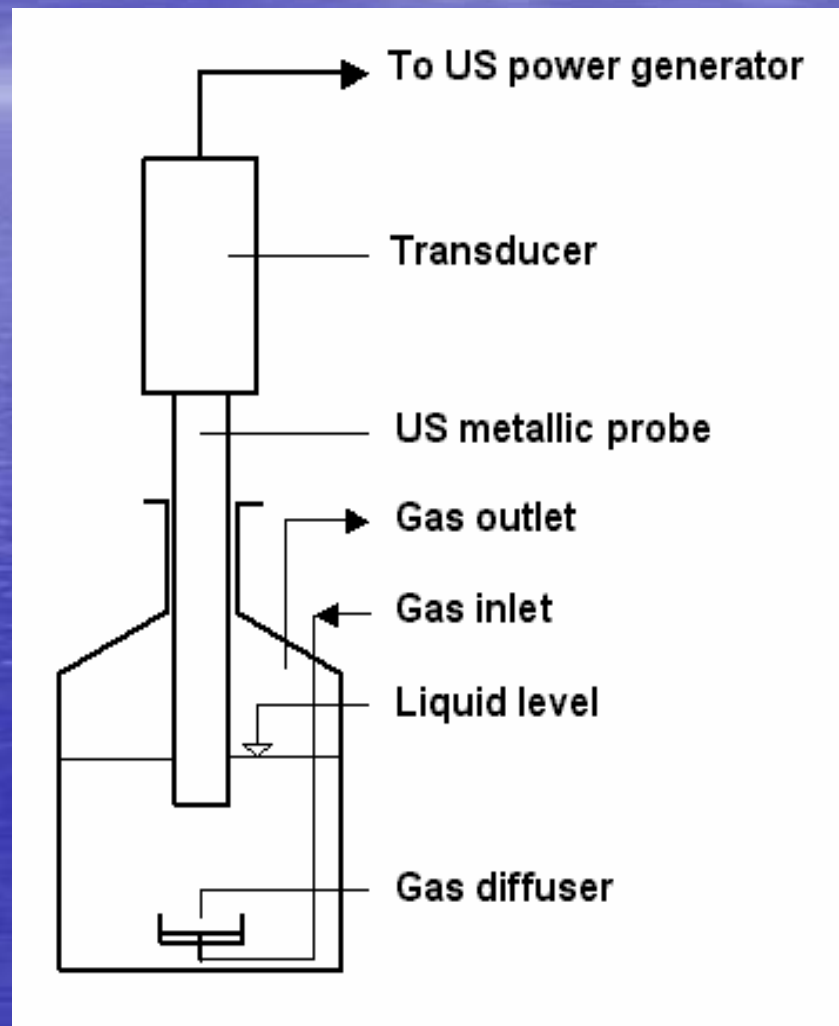
Contaminants Investigated

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

Table 1. Composition of Artificial Groundwater

Components	Concentration, (mg/L)
Ca ⁺²	25.65
CaSO ₄ (aq)	4.12
Mg ⁺²	5.69
Na ⁺	9.85
K ⁺	7.72
H ₂ CO ₃ ⁰ (aq)	22.99
HCO ₃ ⁻	3.52
SO ₄ ⁻²	33.51
Cl ⁻	57.65
Final pH ~ 5.5	

Figure 1. Ultrasonic-Air Stripping Cell



Results

Determining Optimal Air Flow Rate for the Air Sparging System

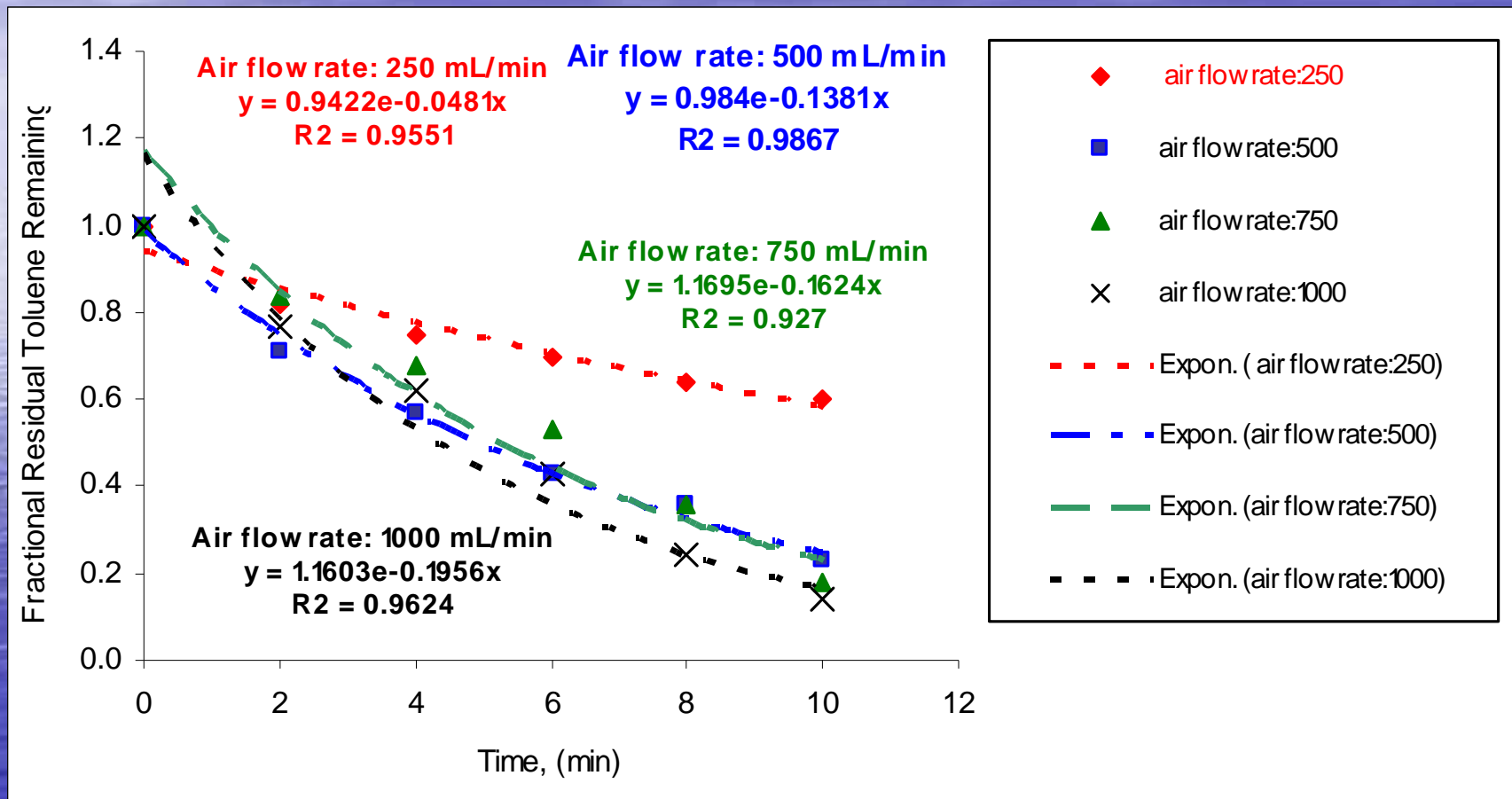
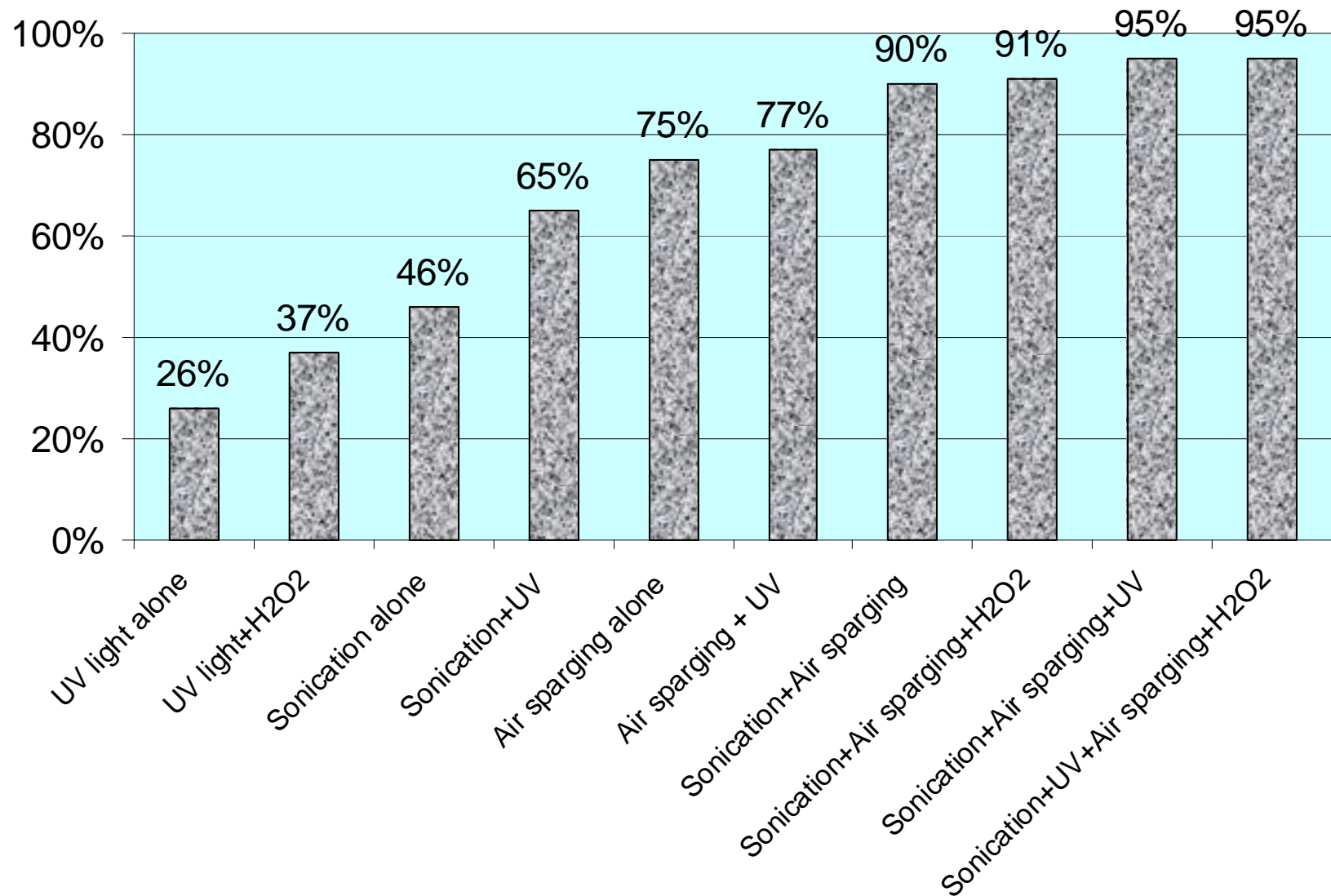


Figure 1. Comparison of Removal Efficiency of Toluene Using Air Stripping Employing Different Air Flow Rates.

AOP Systems Tested for Removal of Benzene

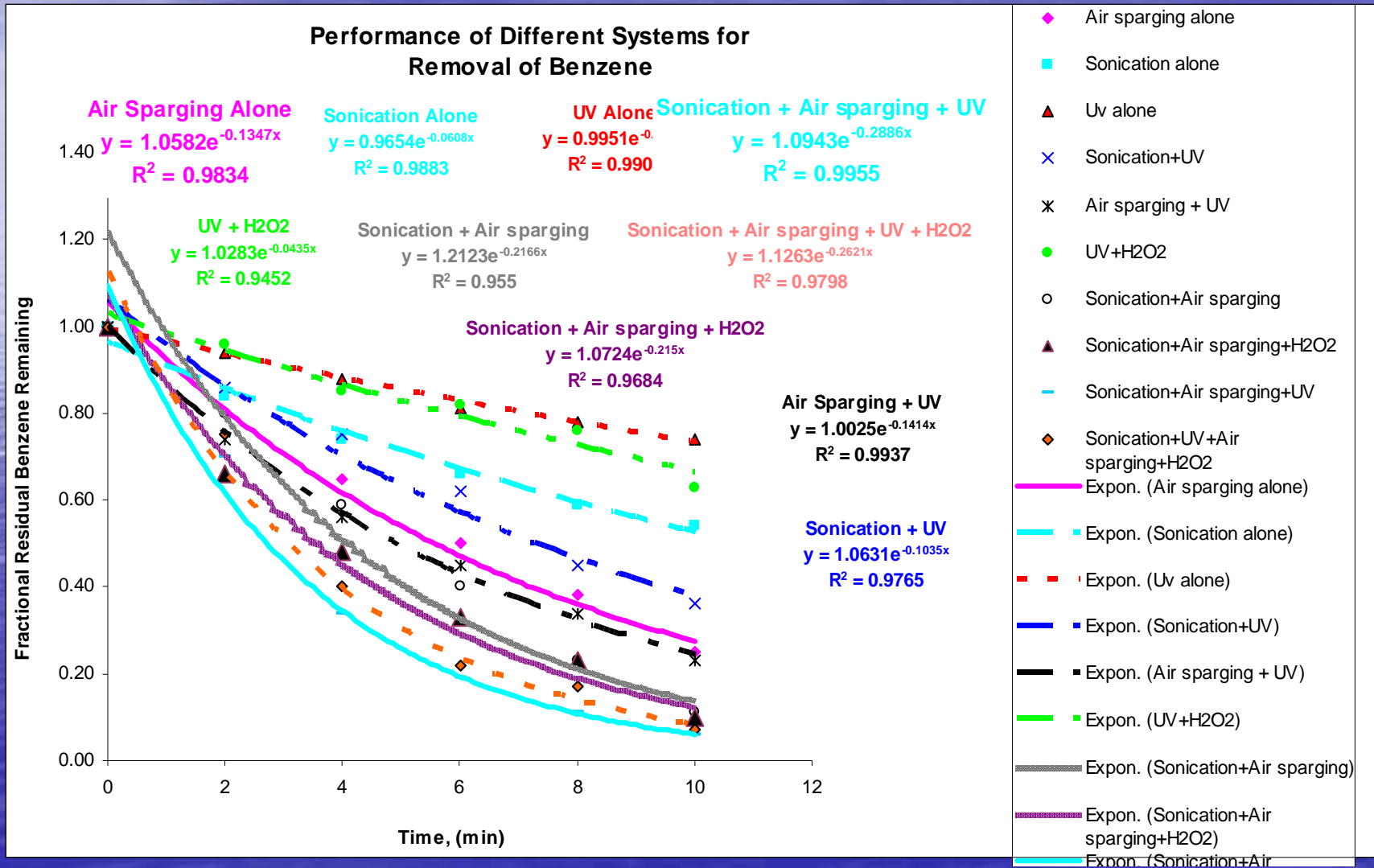
- UV light alone
 - UV light + H₂O₂
 - Sonication alone
 - UV light + Sonication
 - Air sparging alone
 - Air sparging + Sonication
- Air sparging + UV light
 - Sonication + Air sparging+ UV light
 - Sonication + Air sparging + H₂O₂
 - Sonication + Air sparging + UV + H₂O₂

System Comparison for Benzene Removal Efficiency for 10 min Treatment Time



Results

System Comparison for Benzene

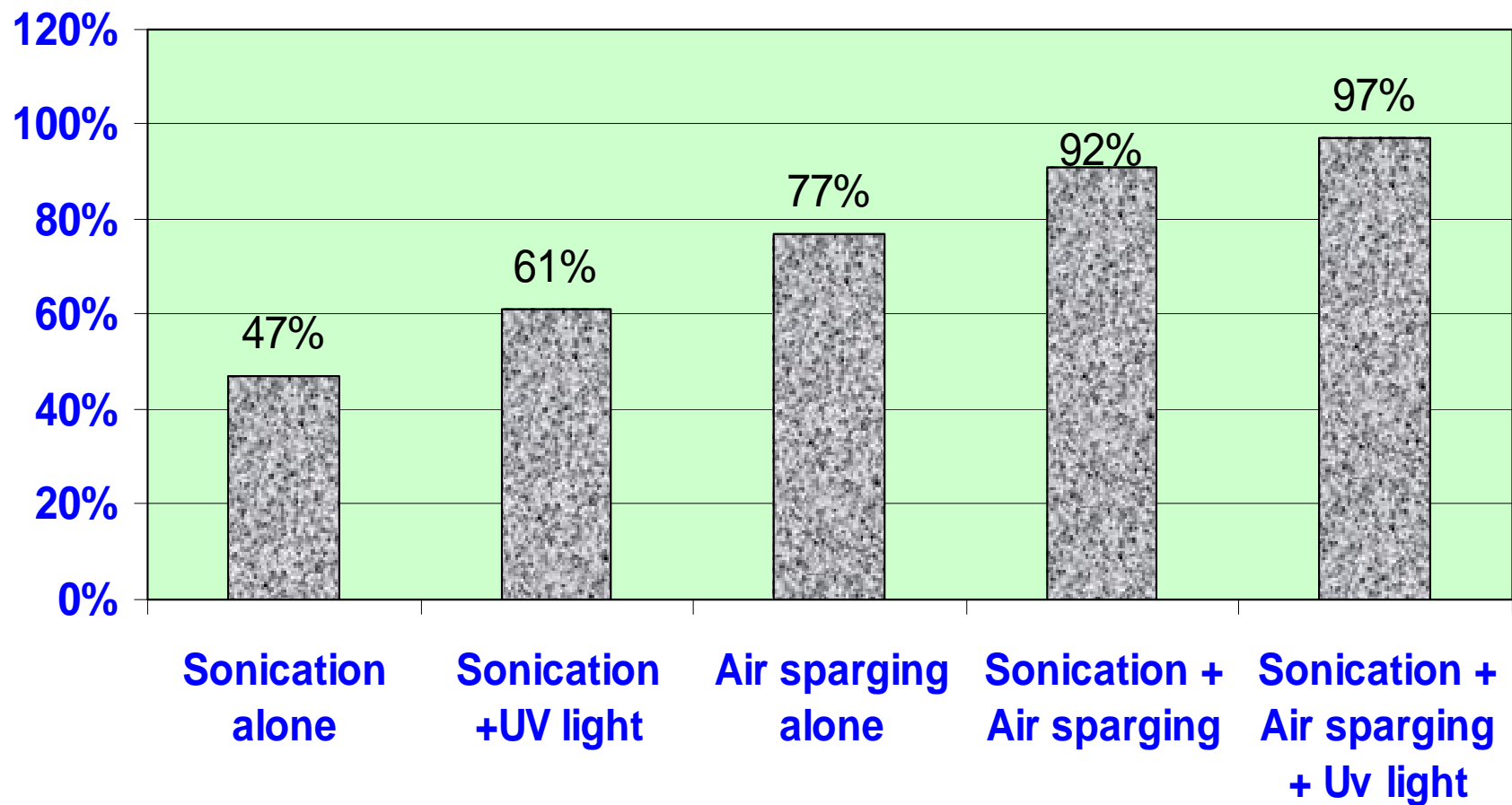


Results

Systems Tested for Toluene Removal

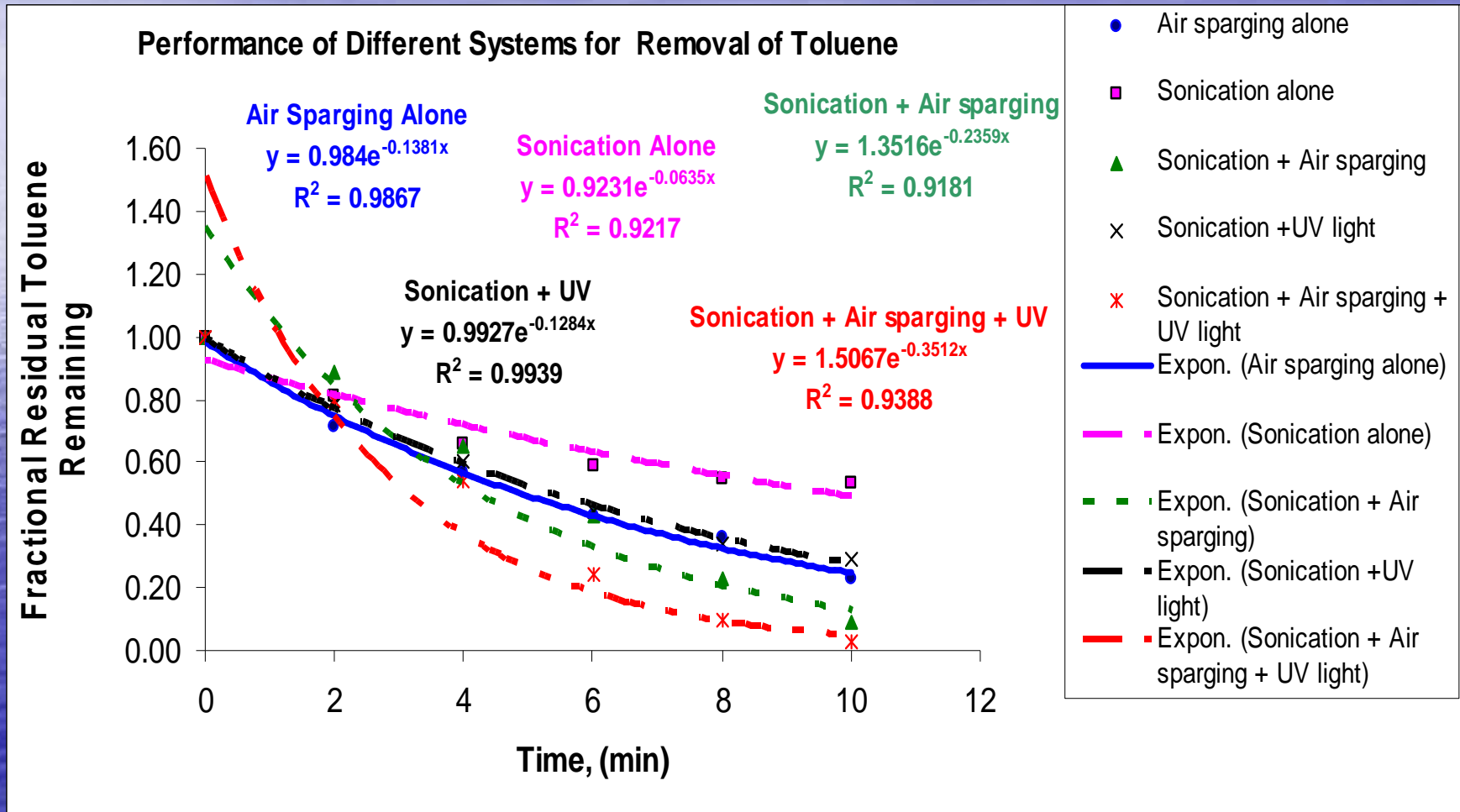
- Sonication alone
- Sonication +UV light
- Air sparging alone
- Sonication + Air sparging
- Sonication + Air sparging + UV light

System Comparison for Removal of Toluene for 10 min Treatment



Results

System Comparison for Toluene



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.

Figure 2. Removal of CCl_4 from Artificial Groundwater by Ultrasound (US) and Air Stripping (AS): Ultrasonic Power Density = 35 W/cm^2 and Air Flow Rate = 500 mL/min .

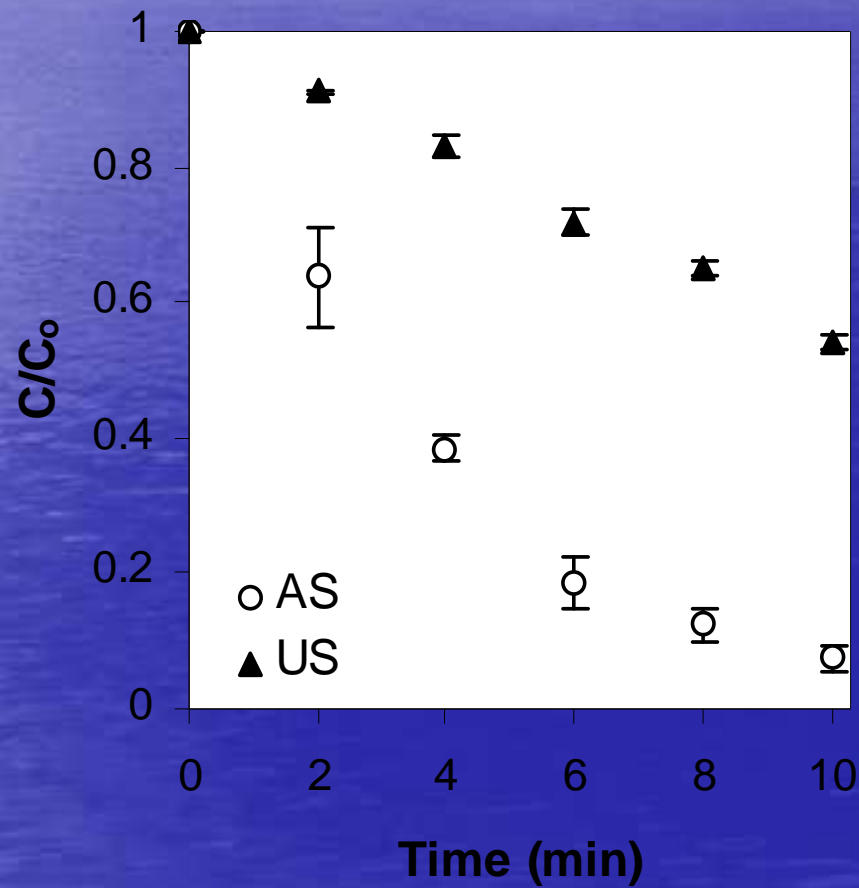


Figure 3. Removal of TCA from Artificial Groundwater by Ultrasound (US) and Air Stripping (AS): Ultrasonic Power Density = 35 W/cm² and Air Flow Rate = 500 mL/min.

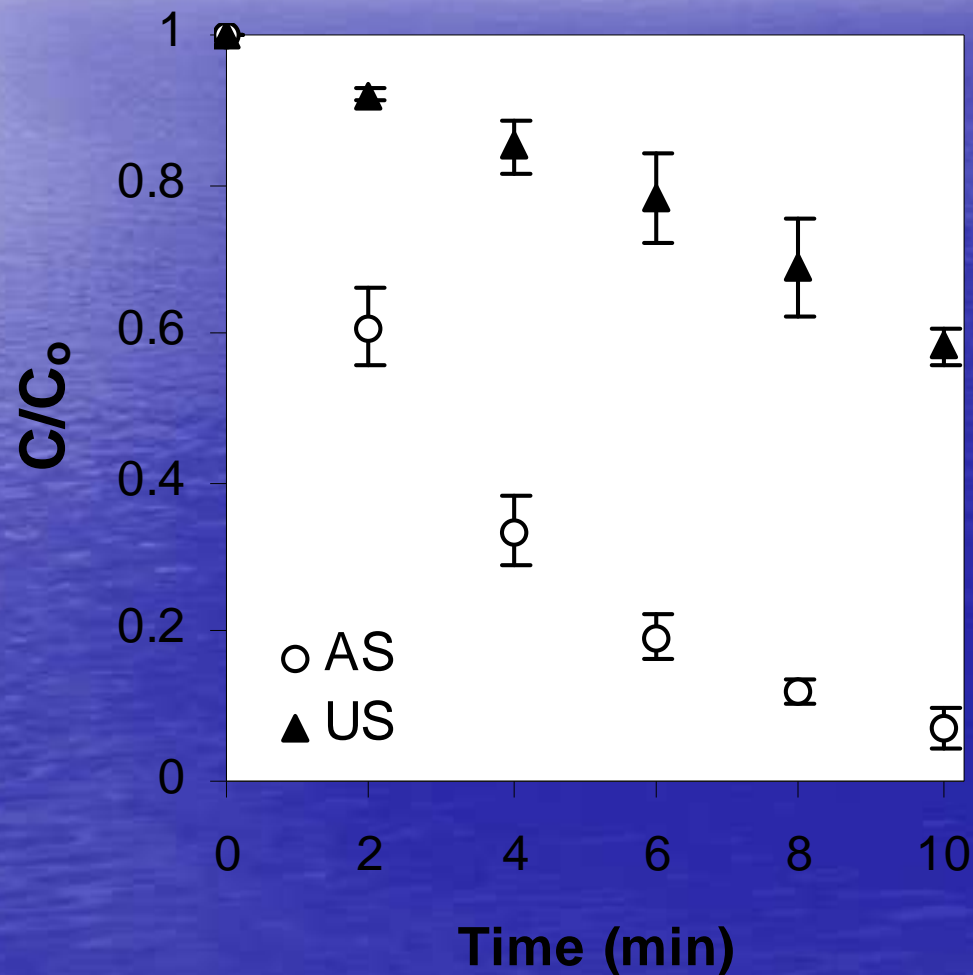


Figure 4. Removal of CCl_4 from Artificial Groundwater by Combined Ultrasound and Air Stripping: Ultrasonic Power Intensity = 35 W/cm^2 and Air Flow Rate = 500-mL/min .

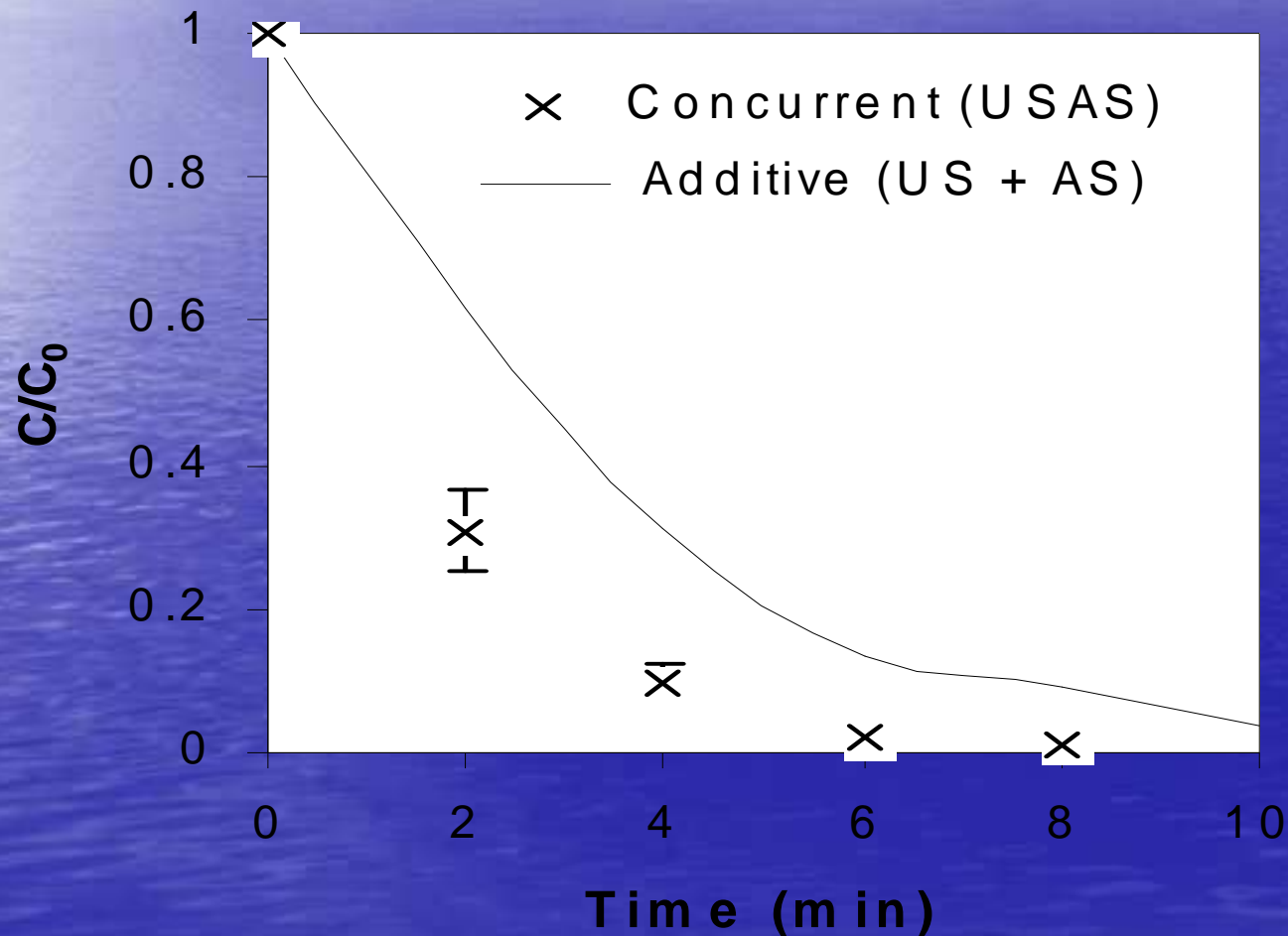


Figure 5. Removal of TCA from Artificial Groundwater by Combined Ultrasound and Air Stripping: Ultrasonic Power Intensity = 35 W/cm² and Air Flow Rate = 500-mL/min.

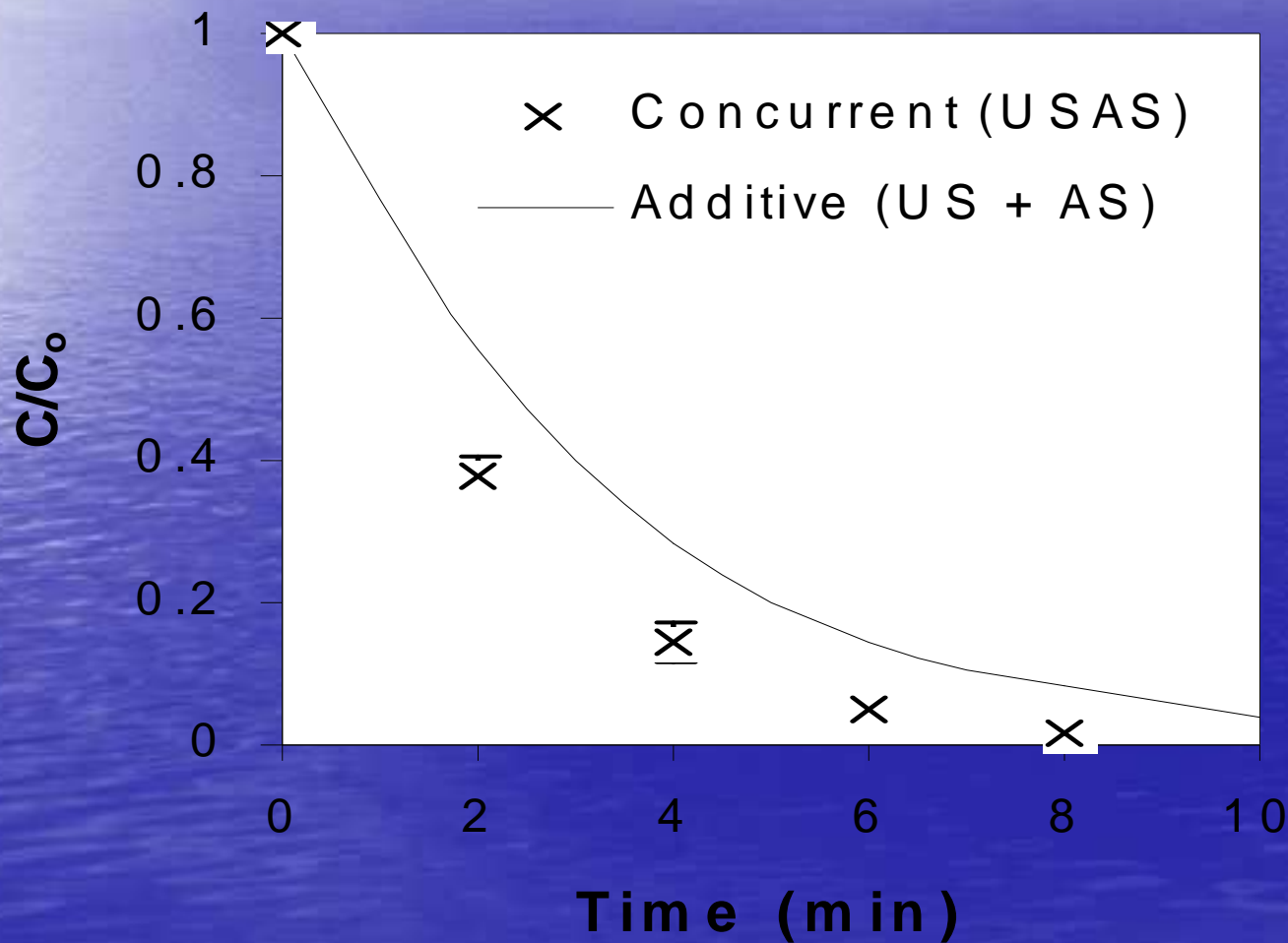


Figure 6. Residual chlorinated organic compound remaining after batch sonication and sonication+vapor stripping treatment.

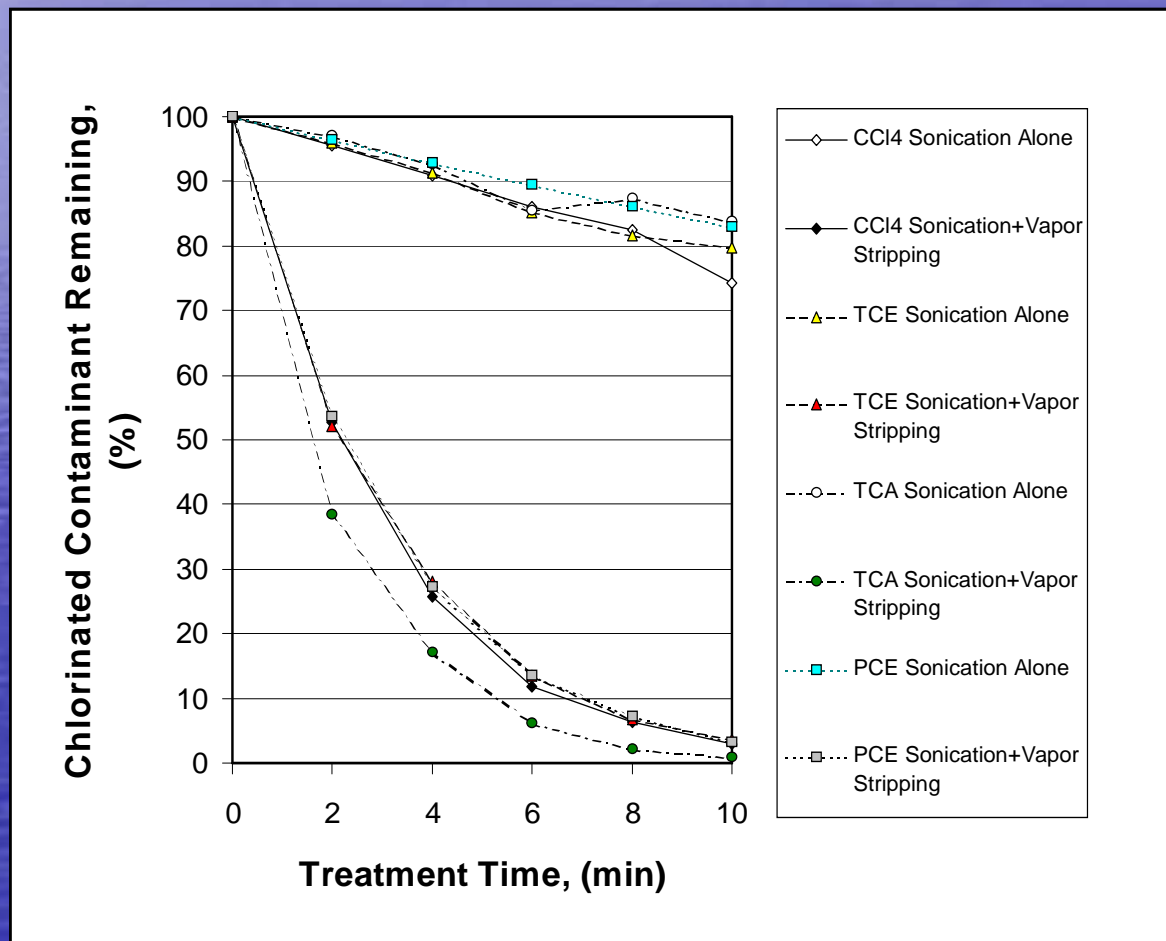


Figure 7. Residual CCl_4 remaining after continuous sonication and sonication + vapor stripping treatment.

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

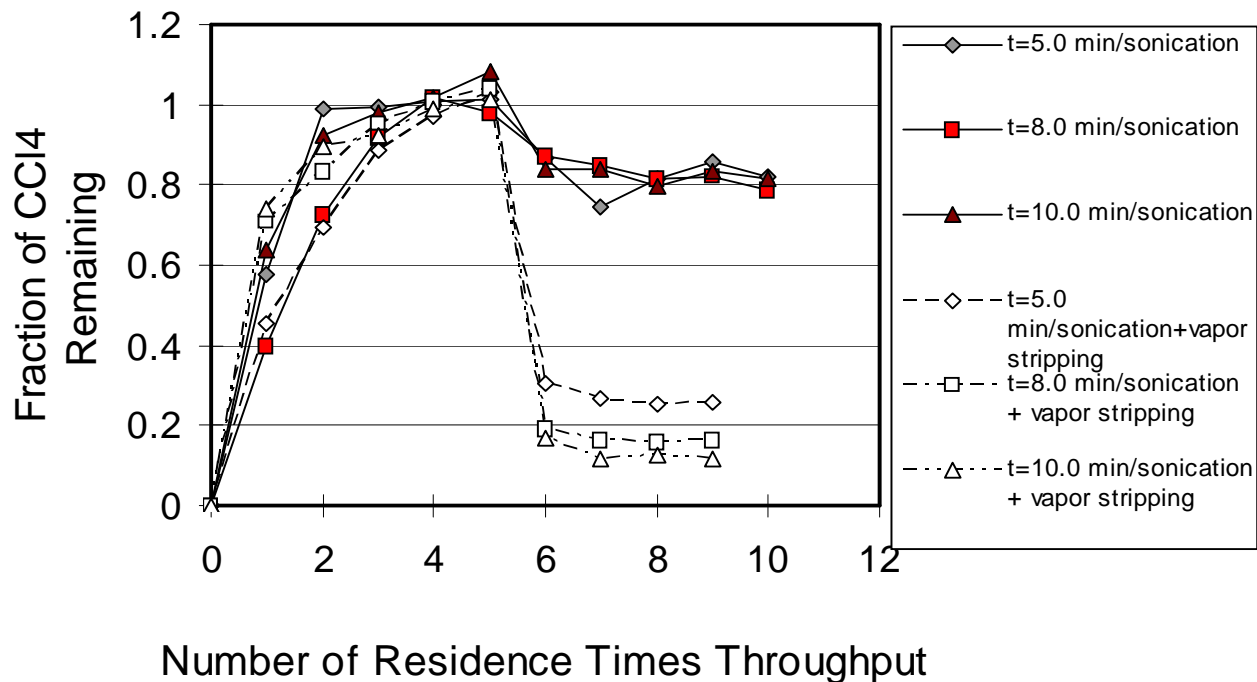


Figure 8. Residual TCA remaining after continuous sonication and sonication+vapor stripping treatment.

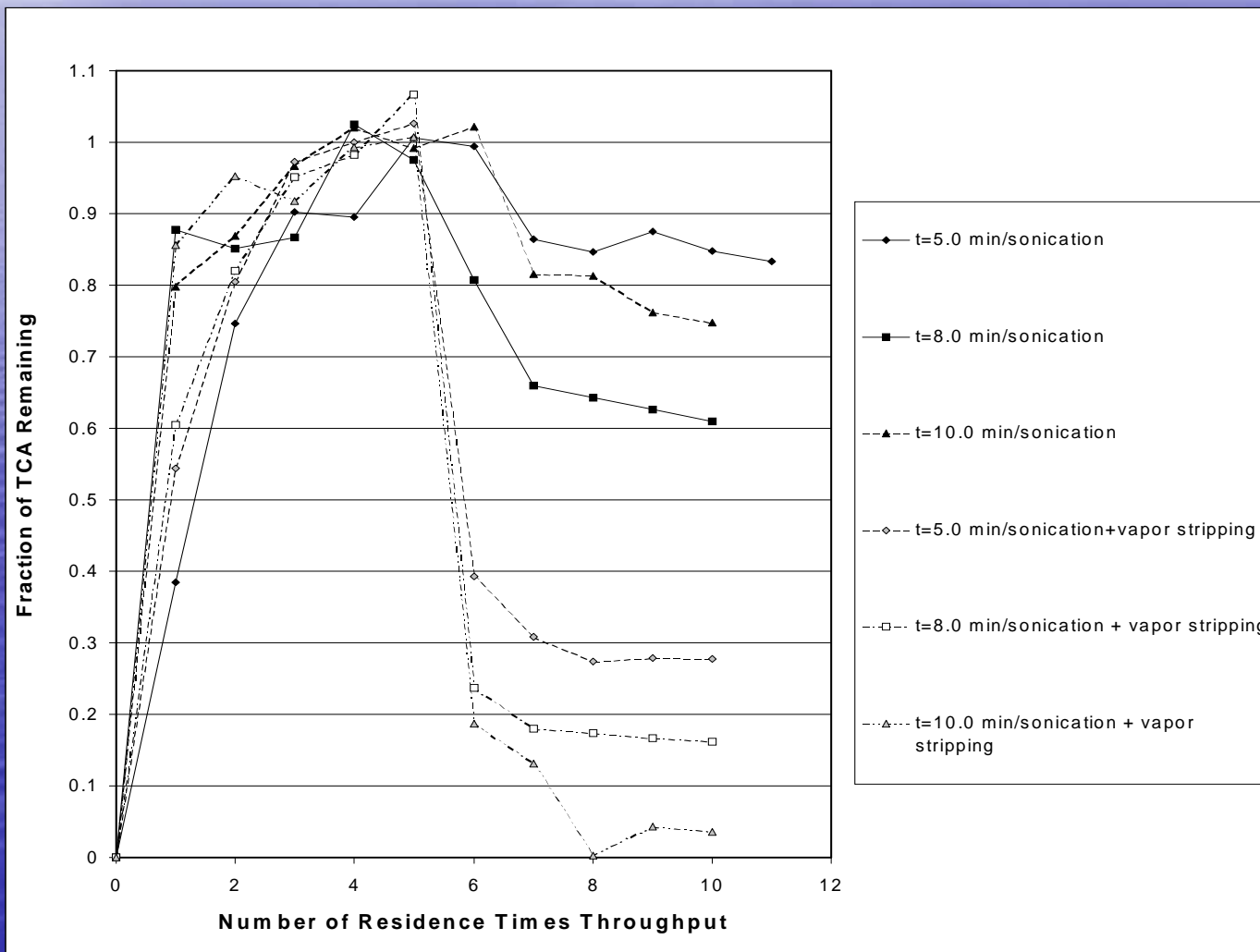


Table 2. First-Order Rate Constants (min^{-1}) Using Sonication Alone in Continuous Flow Operations.

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.

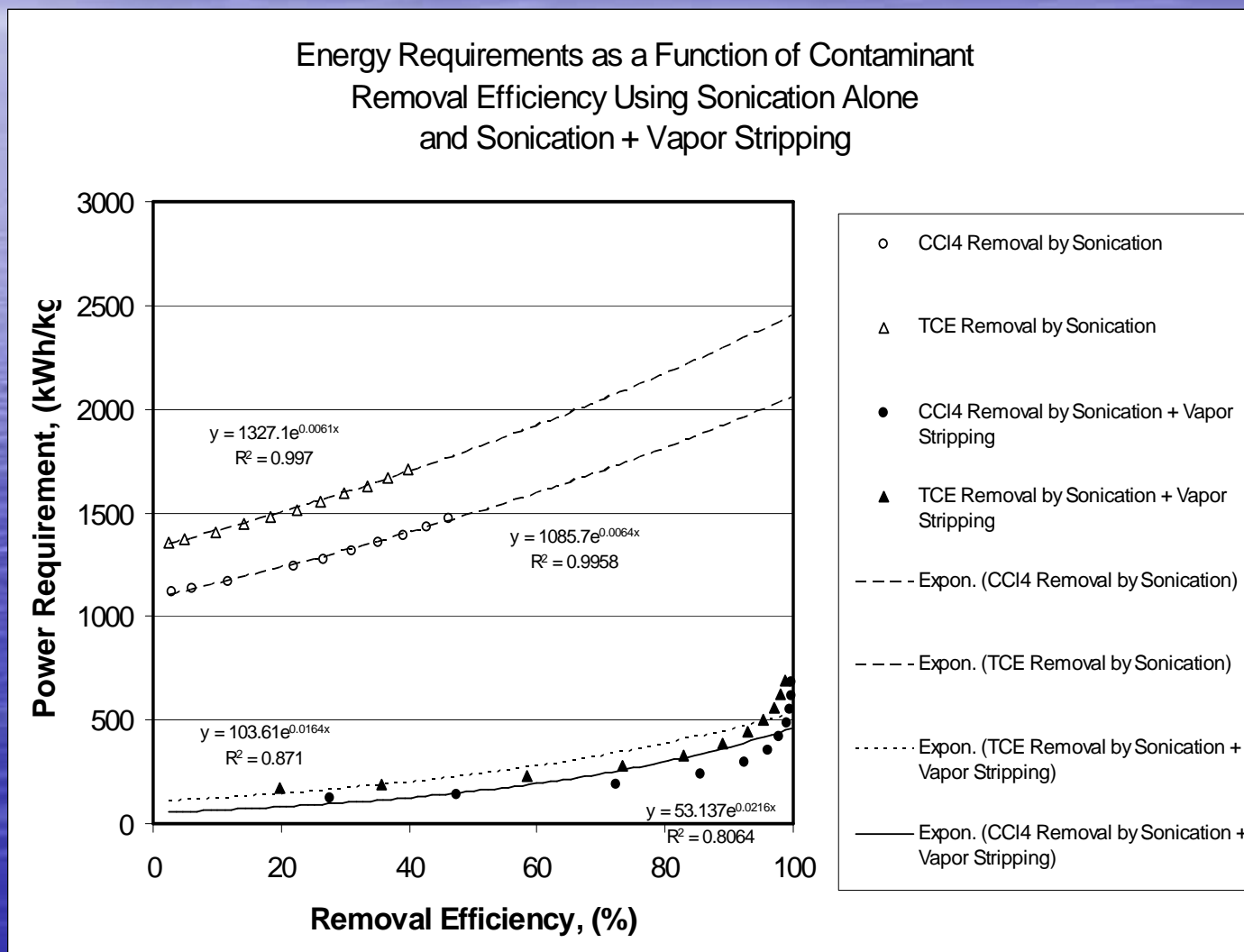
Compound	Air Injection Rate (mL/min) and Ultrasonic Power Intensity (W/cm^2)					
	500/ 12.3	500/ 25.3	500/ 35.8	1000/ 12.3	1000/ 25.8	1000/ 35.8
CCl_4	0.353	0.487	0.645	0.729	0.870	0.866
TCE	0.356	0.356	0.440	0.516	0.583	0.633
TCA	0.341	0.549	0.640	0.691	0.864	0.904
PCE	0.483	0.411	0.447	0.492	0.412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

Power Requirements

- The power requirements for a sonolytic system and the combined sonication/vapor stripping system were determined for an ultrasonic power intensity of 35.8 W/cm² treating water containing 50 mg/L of CCl₄ or TCE.
- For batch treatment, the electrical energy per unit mass is calculated using the equation:

$$EE/M = (10^6 \times P \times t) / [60 \times V \times (C_i - C_f)]$$

Figure 9. 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 $\sim 30\%$ 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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