

Scoping Study for the Adsorption of Tetraphenylborate Decomposition Products

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Scoping Study for the Adsorption of Tetraphenylborate (TPB) Decomposition Products

SUMMARY

This study examined the adsorption (K_d) of tetraphenylborate decomposition products – triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB) from a simulated waste solution. The focus areas included three adsorbents: activated carbon, silica bonded with octyldecylsilane (C18), and silica bonded with a quaternary ammonium salt (Quat). The study examined the adsorbents at two concentrations, 100 and 200 g/L in salt simulant. The following conclusions summarize the results:

- Activated Carbon exhibited significantly greater equilibrium coefficients for both diphenylborinic ($K_d = 309 \text{ mL/g}$) and phenylboronic ($K_d = 4 \text{ mL/g}$) acids in this application
- The low K_d values indicate the need for an impractical quantity of adsorbent.

INTRODUCTION

Tank 49H currently contains approximately 83,000 gallons of the initial 180,000 gallons of wash water transferred in from the In-Tank Precipitation Process Demonstration conducted in 1983. Current analyses of waste samples indicate that the tank contains about 12 g/L of the TPB decomposition intermediates (3PB, 2PB, & 1PB) in the aqueous phase.¹ Over time, these compounds generate flammable benzene as they decompose to mainly boric acid, phenol and benzene. Removal of these decomposition products would allow for safe disposal of the tank waste. High Level Waste Engineering would like to disposition the contents of Tank 49H to allow for additional tank space for the addition of new waste.² This study evaluates three sorbents for the removal of the intermediates. The evaluation includes determination of the equilibrium distribution coefficient (K_d) - the mass of absorbed intermediates relative to the final concentration of intermediates in the salt solution -- as illustrated in the following formula.

$$K_d = \left(\frac{\text{Concentration}_{\text{Initial}}}{\text{Concentration}_{\text{Final}}} - 1 \right) \times \frac{\text{Volume of Salt Solution}}{\text{Weight of Adsorbent}}$$

EXPERIMENTAL PROCEDURE

Testing examined the feasibility of the three adsorbents as filtering agents listed in Table 1 on a 5.6 M Na^+ , average hydroxide composition simulated salt solution (Table 2, FFF-3, 8/11/99). Test 1 evaluated the effects of silica bonded octyldecylsilane (C18) and silica bonded with a quaternary ammonium salt (Quat). Test 2 evaluated activated carbon. We selected non-polar C18 and activated carbon because of their ability to retain low concentrations of the TPB decomposition products. We chose Quat. sorbent for its relatively high polarity and ionization properties that may help retain the intermediates.

The Analytical Development Section analyzed the samples with High Performance Liquid Chromatography (HPLC).

Table 1: Adsorbents

Adsorbents	Particle Size	Manufacturers
Activated Carbon	4 - 12 mesh	Darco
Silica bonded octadecylsilane	40 μm	J. T. Baker
Silica bonded quaternary ammonium salt	40 μm	J. T. Baker

Table 2: Composition of Simulated Waste used in the Experiment

Analytes	Concentration (M)
Na ⁺	5.6
K ⁺	0.015
Cs ⁺	0.00014
OH ⁻	1.91
NO ₃ ⁻	2.14
NO ₂ ⁻	0.52
AlO ₂ ⁻	0.31
CO ₃ ²⁻	0.16
SO ₄ ²⁻	0.15
Cl ⁻	0.025
F ⁻	0.032
PO ₄ ³⁻	0.010
C ₂ O ₄ ²⁻	0.008
SiO ₃ ²⁻	0.004
MoO ₄ ²⁻	0.0002

Test 1

Lab personnel prepared simulated average salt solution containing 53 mg/L 3PB, 6525 mg/L 2PB, and 8021 mg/L 1PB. These concentrations fall well below the solubility limit for the compounds in the alkaline solution and researchers did not observe any second organic phase. Personnel weighed 1.0 gram and 2.0 grams of C18 and Quat each into four 30-mL polypropylene bottles. They then added 10-mL of the salt solution to each bottle. Personnel capped and taped the bottles, and placed them in a horizontal Cole/Parmer Polystate water bath shaker (controlled at 25 °C and 120 rpm) for 24 hours.

Test 2

Lab personnel prepared simulated average salt solution containing 1018.1 mg/L 3PB, 4997.7 mg/L 2PB, and 8026 mg/L 1PB. These concentrations fall well below the solubility limit for the compounds in the alkaline solution and researchers did not observe any second organic phase. Personnel weighed 1.0 gram and 2.0 grams of activated carbon (Size 4-12 mesh) into two polypropylene bottles and added 10-mL of salt

solution. Personnel capped and taped the bottles, and placed them in a horizontal Cole/Parmer Polystate water bath shaker (controlled at 25 °C and 120 rpm) for 24 hours.

Analyses

In both test sets, personnel analyzed the change in concentration(mg/L) for 3PB, 2PB, and 1PB using HPLC. Based on initial sample results, the author calculated K_d for samples taken at 1.5 and 24 hours. Sample analyses at 1.5 hours helped to determine if rapid equilibrium occurred. Generally, equilibrium occurred between analytes and sorbents within 24 hours.

RESULTS & DISCUSSION

Personnel collected samples at 1.5 hours and 24 hours from both test sets. Table 3 provides the K_d values determined in Test 1. Both adsorbents removed 3PB to levels below the detection limit of the HPLC. Thus, the K_d value for 3PB uses the concentration at the detection limit (10 mg/L) as the final concentration. However the quantities tested did not adsorb high levels of the 2PB and 1PB. The C18 and the Quat sorbent appeared to reach equilibrium within 1.5 hours since little change occurred in K_d values at 1.5 and 24 hours for 2PB and 1PB. The amount of sorbent used had little effect on the K_d values obtained for C18 and Quat. No increase in the phenol concentration occurred during the 24 hour run indicating adsorption rather than decomposition of the analytes.

Table 3: K_d Values for Test 1

1.5 Hour Sample			
Sample ID	3PB (mL/g)	2PB (mL/g)	1PB (mL/g)
1.0g C18	22	7	1
1.0g Quat	22	1	0
2.0g C18	11	15	4
2.0g Quat	11	1	0
24 Hour Sample			
1.0g C18	22	6	2
1.0g Quat	22	4	2
2.0g C18	11	6	2
2.0g Quat	11	6	2

Table 4 provides the K_d values determined from Test 2. The activated carbon adsorbed 3PB to levels below the detection limit of the HPLC; therefore the K_d value uses the detection limit as the final concentration. For the 24-hour samples, an increase of less than 10 mg/L to approximately 500 mg/L in phenol concentration accompanied the reduction of concentration of 3PB. A control sample showed no increases in phenol, suggesting that the activated carbon plays a role in the decomposition of 3PB. The activated carbon may to a lesser extent play a role in the decomposition of 2PB and 1PB. The calculated 2PB distribution value increased significantly between 1.5 and 24 hours. The 1PB analyte showed little affinity for the sorbent. The K_d values for activated carbon proved higher than the K_d values for both the C18 and Quat adsorbents.

Table 4: K_d Values for Test 2

1.5 Hour Sample			
Sample ID	3PB (mL/g)	2PB (mL/g)	1PB (mL/g)
1.0g Carbon	1129	13	3
2.0g Carbon	565	12	2
24 Hour Sample			
1.0g Carbon	1130	166	3
2.0g Carbon	565	309	4

Operations must remove a sufficient amount of the intermediates to minimize benzene formation potential in an air-based mode, and for transfer to Tank 50H. The acceptance limits for transfer to Tank 50H for benzene and sodium tetraphenylborate are 3 mg/L and 1000 mg/L.³ The rate of benzene generation from TPB and its decomposition products shall remain less than 0.02 mg/L/h at 40 °C.³ Assumed acceptable concentrations of 2PB and 1PB are 650 mg/L and 350 mg/L. To reduce 1PB to its acceptable limit would require approximately 1.8 million KG of activated carbon (See Appendix I).

At a cost of \$2/lb, the estimated carbon price for this process is \$7,936,641.44. The Effluent Treatment Facility (ETF) utilizes 10,000 KG of carbon which requires an ASME section VIII code stamped process vessel rated for 150 psi with the following dimensions; 10 ft. in diameter and 10 ft deep.⁴ This process would utilize 180 charges for such a vessel for the amount of carbon required to process the waste. Implementation would also require further studies to investigate waste disposal cost, which varies widely depending on the waste form (e.g., hazardous, mixed, LLW, and TRU).

CONCLUSION

The activated carbon adsorbed the intermediates at a higher level than the C18 and Quat. Adsorption is a viable process, however the low K_d values indicate the need for an impractical amount of adsorbent to get to the desired decontamination factors.

REFERENCES

¹ K. B. Martin, T. B. Peters, "Combined R&D Program for Tank 49H (JCO and Content Disposition)", WSRC-RP-99-01069, November 21, 1999.

² R. C. Fowler, "The Waste Stored in Tank 49", WPT-TAR-99001, January 3, 2000.

³ WSRC 1S Savannah River Site Waste Acceptance Criteria Manual, "Procedure 4.01 Acceptance Criteria for Aqueous Waste Sent to the Z Area Saltstone Production Facility", Rev. 2, June 19, 1998.

⁴ Wiggins, Arthur, CC Mail Correspondence dated 1/27/000, "Re[2]: Carbon Bed Usage at ETF".

APPENDIX I

Input

1. $K_d = 4 \text{ mL/g} = 4 \text{ L/kg}$ for 1PB, 2.0 grams of activated carbon
2. Initial 1PB concentration in the waste simulant equals 8026 mg/L.

Note: Removal of 1PB represents the limiting organic given the results of the adsorption study given in Table 4 (i.e., lowest distribution coefficient for activated carbon existed for 1PB)

Assumptions

1. Final 1PB concentration should $\leq 350 \text{ mg/L}$ based on limits to transfer waste to Tank 50H.
2. Assume 83,000 gallons of waste are in Tank 49H.

Calculation

$$K_d = \left(\frac{\text{Concentration}_{\text{Initial}}}{\text{Concentration}_{\text{Final}}} - 1 \right) \times \frac{\text{Volume of Salt Solution}}{\text{Weight of Adsorbent}}$$

$$\text{Weight of Adsorbent} = \left[\left(\frac{8026}{350} - 1 \right) * \frac{314,189.2 \text{ Liters}}{4 \text{ L/kg}} \right]$$

$$\text{Weight of Adsorbent} = 1,722,654 \text{ kg} \approx 1.8 \text{ M kg}$$

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