Coal-Based Activated Carbon for Removing Perchlorate and other Anions from Water

Final Report

Reporting period

January 1, 2001 to April 15, 2002

DOE Award Number DE-FC26-98FT40350

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Report Issued: April 15, 2002

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ABSTRACT

The focus of this recent research has been on tailoring the activated carbon in a manner that provides better perchlorate adsorption. We have focused on two approaches to tailoring the activated carbon. The first has been to thermally treat the activated carbon with a reducing gas. The second has been to preload the activated carbon with organic cations. Both of these protocols have offered considerable enhancement of perchlorate removal. We have achieved three to ten times the adsorption capacity for perchlorate, above that for commercial activated carbon.

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EXECUTIVE SUMMARY

By employing reducing gas thermal treatment, the authors were able to achieve three times the bed volumes for removing perchlorate before initial breakthrough, when compared to virgin non-tailored activated carbon. By preloading the activated carbon with an NSF approved organic cation, the authors achieved four times the bed volumes for removing perchlorate before initial breakthrough, when compared to virgin non-preloaded activated carbon. By preloading with an organic cation that is not yet NSF approved, the authors achieved more than ten times the bed volumes to breakthrough.

REDUCING GAS TREATMENTS

From previous work, we noticed that three types of carbon from Calgon Carbon Company had higher pHpzc/higher positive charges than the SAI carbon and that this helped increase the adsorption capacity of perchlorate.

A. Experimental

During this research, we tailored the SAI carbon with a reducing gas at different temperatures with various durations of time to compare the effect of tailoring on carbon's adsorption capacity for perchlorate.

The tailoring of the SAI carbon consisted of placing a sample of carbon in a TGA (Thermogravimetric Analyzer) under flowing nitrogen. The furnace was heated to the desired temperature and then the gas was switched to the tailoring gas. The samples were held for a predetermined time and then cooled to room temperature. The samples are

denoted using the carbon type, the temperature, and time. For example, SAI500-60 is a SAI carbon treated at 500°C for 60min.

We then investigated the effects of tailoring on perchlorate removal during small column tests. We also appraised these tailored carbons relative to their pore size, surface area, and surface charge. This helped us to gain an understanding as to the effect of physical and chemical characteristics of carbon on perchlorate adsorption. Pore structure analyses were conducted via Micromeritics (Norcross, GA) ASAP 2010 unit while surface charge distribution was done by a DL53 automatic titrator.

B. Results and Discussion

1. Characterization of pore structure

Table 1 lists the surface area, micropore volume (pore width <20A), and average pore width of all the samples. Figure 1 shows the pore volume distributions for these tailored carbons. At treatment temperature 500°C, there is a decrease in all three parameters that may be the result of this tailoring gas reacting with surface groups/active carbon atoms. The resultant nitrogen-containing surface functional groups may block the previously accessible pores. While for treatment at 700°C, there was an increase in all these parameters compared with 500°C. One possible cause is that this tailoring gas is acting as an activating agent at this temperature, and more micropores are created by this activating effect.

Table 1: Physical characteristics of tailored activated carbon

Sample	BET surface area (m^2/g)	Micropore volume (mL/g)	Average pore width (Å)
Virgin SAI	874.09	0.193	36.64
SAI500-30	854.25	0.182	35.83
SAI500-60	861.28	0.188	36.36
SAI500-150	864.42	0.202	36.51
SAI700-30	1084.01	0.231	36.18
SAI700-60	940.96	0.202	35.91
SAI700-150	965.13	0.197	36.51

2. Characterization of surface charge distribution and pHpzc

Automatic titrations were carried out using a DL53 titrator (Mettler Toledo) to measure the surface charge distribution of activated carbon. About 0.15 g carbon was added to 200 mL of 0.01 M NaCl solutions respectively. The surface charge distribution of samples was shown in Figure 2. The Figure indicates that the positive surface charge of all samples were increased remarkably after tailoring. In addition, for treatment time of 30 and 60 min, the carbon products had more positive charges at 700°C treatment than the 500°C treatment. When the thermal gas treatment time was 150 minutes, the temperature no longer made as great a difference in the surface charge distribution.

According to the research on pH_{pzc} during the last progress report period, slurry pH (pH of supernatant after the 0.01M NaCl solution was equilibrated for 24h with 10% carbon mass) is a fairly close representative of the carbon pHpzc value. So we use this slurry pH to represent the sample pHpzc. Table 2 is the slurry pH of tailored samples.

Table 2: Slurry pH

Sample	Slurry pH	Sample	Slurry pH
SAI500-30	9.59	SAI700-30	9.67
SAI500-60	9.86	SAI700-60	10.17
SAI500-150	9.92	SAI700-150	9.94

Compared with the slurry pH of virgin SAI carbon (8.75), after the tailoring, the pH_{pzc} increased for all tailored products.

In comparison to this, the point of zero charge (pH_{pzc}) determined by a 10% by mass slurry for the virgin material used in Redlands was determined to be 8.3, while the spent GAC had a pH_{pzc} of 5.7. In comparison the SAI GAC used in the lab had a pH_{pzc} of 7.6 for the virgin and 7.2 for GAC treated with the same number of bed volumes that the Redlands GAC saw at full-scale. A GAC with a pH_{pzc} of 5.7 would be negatively charged when water with a pH of 7.5-8 (the pH of the groundwater at Redlands) is flowing through it, and the adsorption of the negatively charged perchlorate ion would be poor.

3. Rapid small column test

Two of the tailored carbon products, SAI500-60, SAI700-60 were tested for perchlorate removal in small column tests. RSSCT columns used in this experiment were approximately 8 inches in length and had an inner diameter of 0.56 cm. Each test employed about 1.67 grams of GAC held in place by glass wool. The carbon sample was crushed and sieved to the US mesh 200*400. The actual EBCT of these columns were about 0.75 min to simulate a full-scale EBCT of 20min. Figure 3 shows the breakthrough curve for the tailored carbons. It indicates that tailoring can effectively improve the adsorption capacity for perchlorate. The bed volumes operated till the initial breakthrough was at 3500 BV for the SAI 700-60 tailored carbon; and was more than three times the capacity before breakthrough (1000 BV) that was observed for the virgin SAI carbon.

ORGANIC CATION TAILORING

Progress has also been made in the area of tailoring the GAC with organic cations. In previous research, a test was developed to screen cations to provide a way of determining which materials could provide the greatest improvements in perchlorate adsorption.

A. Experimental

The protocol used in this experiment was somewhat arbitrary, but they allowed for useful comparison amongst organic cations. This protocol called for 1.67 grams of 200 x 400 SAI GAC, 100 mL of a 4 g/L solution of the organic cation being tested (on a

dry weight basis), and recirculating the organic cation solution though the column of GAC for one day. In some cases, as listed below, the recirculation period proceeded for more than one day.

Figure 4 shows one round of tests conducted. Organic cations designated as C54a, C54b, C54c, C54d, and C54e were obtained from a Pennsylvania company. These organic cations have been NSF approved for use in drinking water; and they are commonly used in the drinking water industry. After one day of recirculating a soluion of each through a column of SAI GAC, Redlands water was then passed through the column.

B. Results and Discussion

C54a showed a breakthrough point similar to that of virgin GAC, but showed continued adsorption of perchlorate through about 2000 BV. C54b and C54e had perchlorate breakthrough at approximately 2000 BV. C54c was able to treat 2500 BV before breakthrough. C54d performed the best in this round of tests. It was able to process 3300 BV of Redlands water prior to perchlorate breakthrough. This represented 3.3 times more water processed before breakthrough than for that of the virgin GAC (in this column configuration, perchlorate breakthrough occurred at 1000 BV).

Based on this finding, C54d was run in another set of experiments. This time the same solution would be allowed to recirculate through the column for a period of 2 days and 5 days respectively. Past experiments had shown that the length of exposure to the cation could have a dramatic effect on the number of BV processed prior to perchlorate breakthrough. These results are shown in Figure 5. There was a slight improvement with longer treatments: 3800 BV for 2-day recirculation and 4000 BV for 5-day recirculation.

Another set of 1-day recirculation experiments was run with three organic cations designated as C60a, C60b, and C60c from another source and one column was run with C54d. The authors herein are not aware that the C60a, b, c organic cations have been NSF approved for drinking water use. The column run with C54d utilized HD4000, a lignite based GAC from NORIT, while the other columns employed the SAI GAC. These results are shown in Figure 6. As you can see, there is nothing to see! No perchlorate breakthrough whatsoever, up to 6300 BV for C60a, 3900 BV for C60b, 13750 BV for C60c, and 4200 BV for C54d with the HD4000. This lack of breakthrough is both a good and a bad thing. Good because the longer the columns can run before breakthrough, the more economically feasible these treatment methods become. Bad in the sense that we are completely out of water and are awaiting more water so these columns can continue. These columns are showing tremendous promise. If you recall, the GAC at Redlands treated approximately 18,000 BV for TCE removal, and the ultimate goal was to bring the perchlorate removal in line with the TCE removal. While we aren't sure that these columns will reach 18,000 BV, C60c has reached 13750 BV without breakthrough. The treatments in these columns may exceed 18,000 BV individually, or we may be able to achieve that "magic number" by coupling these methods with another organic cation or reducing gas treatment.

CONCLUSIONS

Both the thermal pretreatment with the reducing gas and the organic cation preloading enhanced perchlorate removal considerably.

Figure 1: Pore Volume Distribution of Tailored Carbons

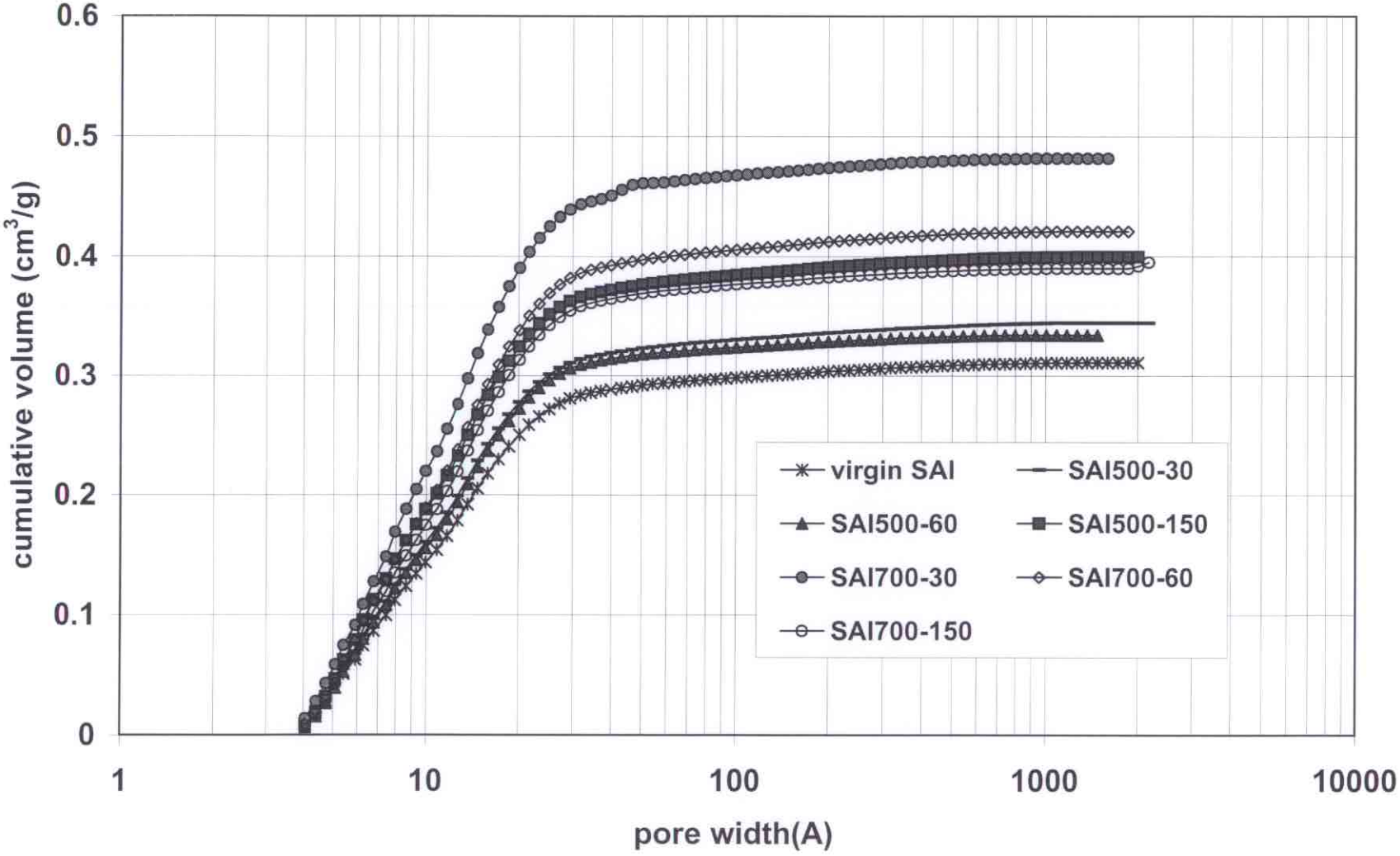

Figure 2: Surface Charge vs. pH for GAC Treated with a Reducing Gas

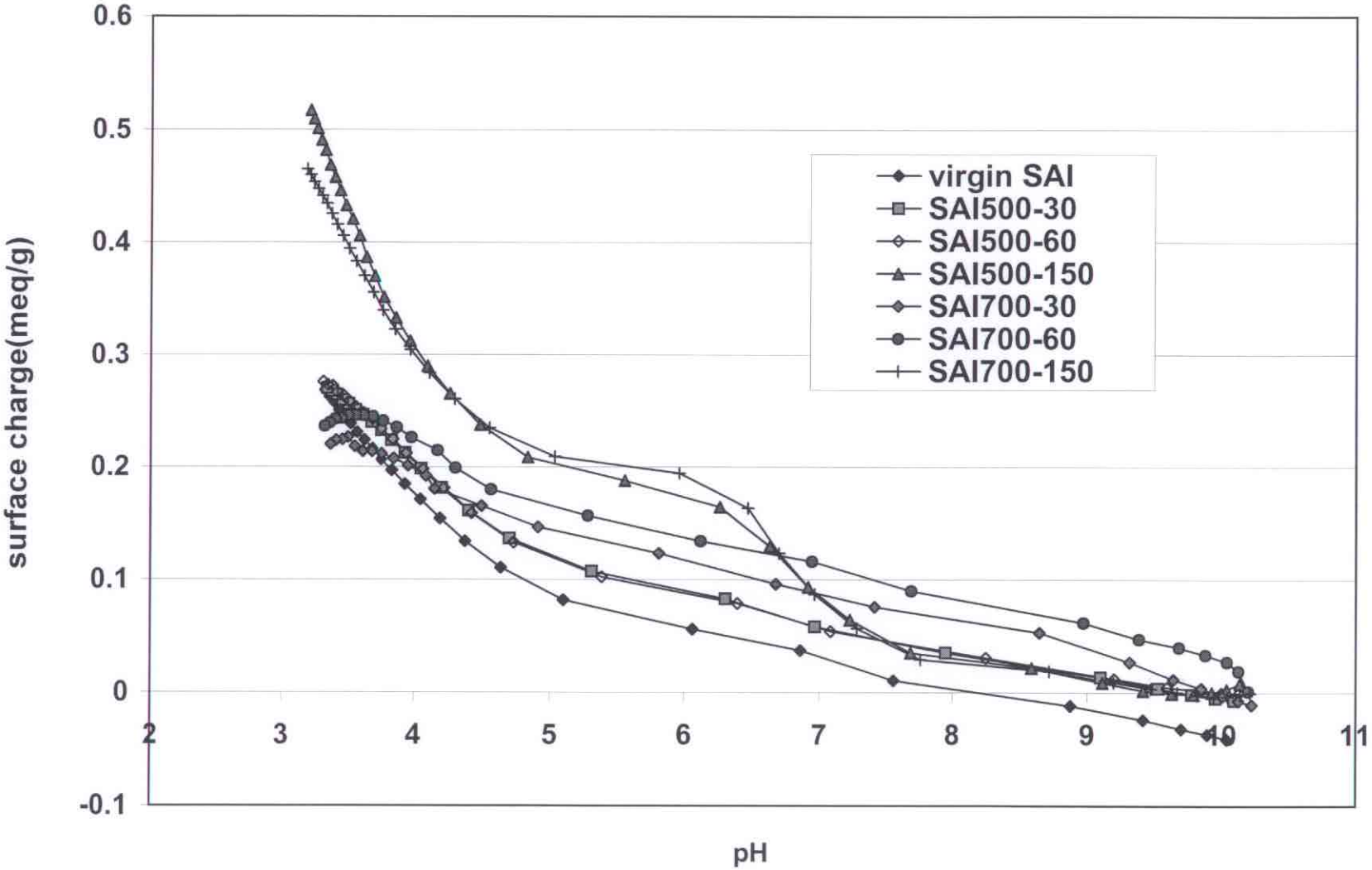

Figure 3: Perchlorate Breakthrough for GAC Treated with a Reducing Gas

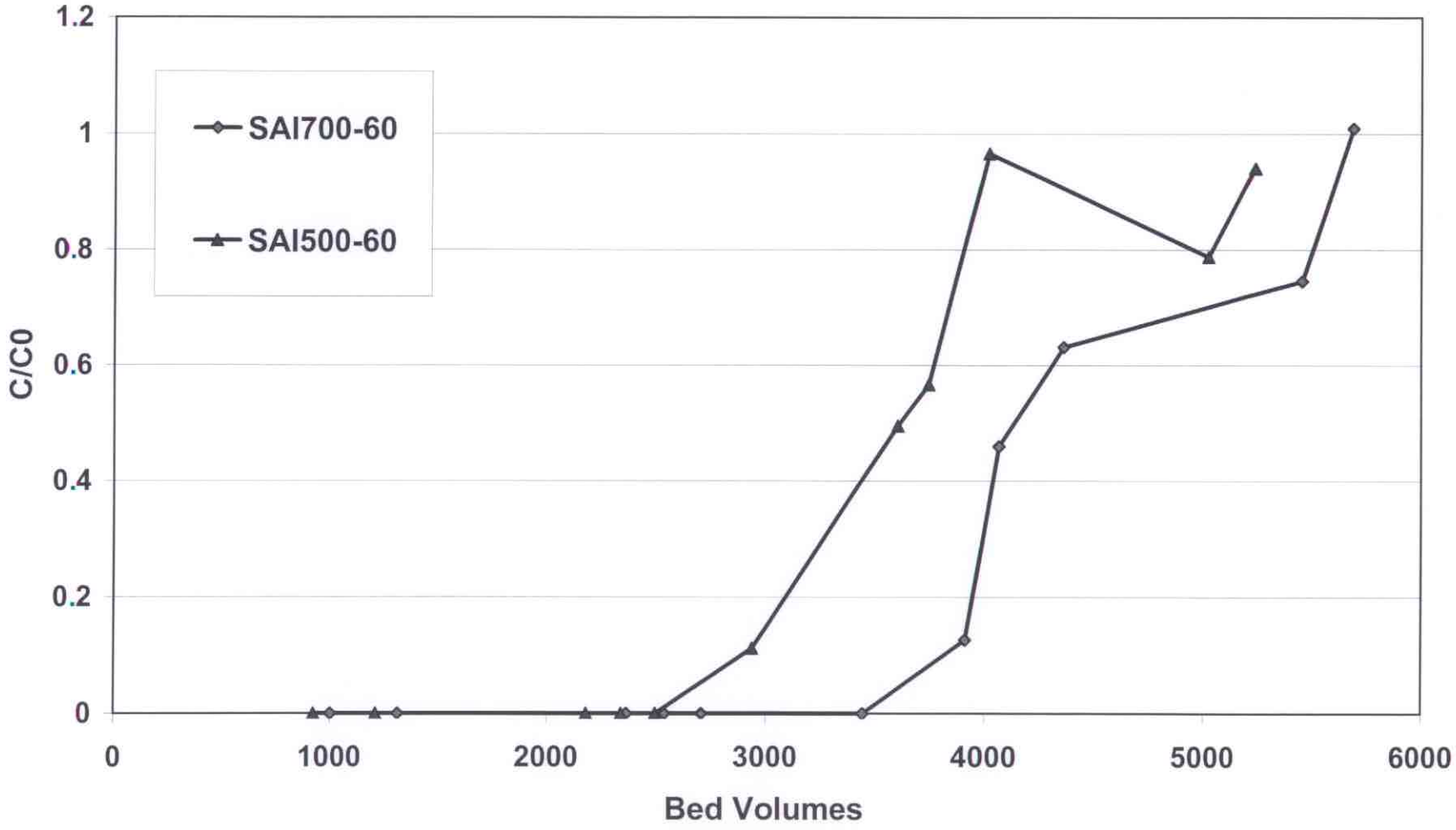

Figure 4: ClO_4^- Breakthrough with 200x400 SAI GAC Tailored with Organic Cations from e-Calgon. 1 Day Loading.

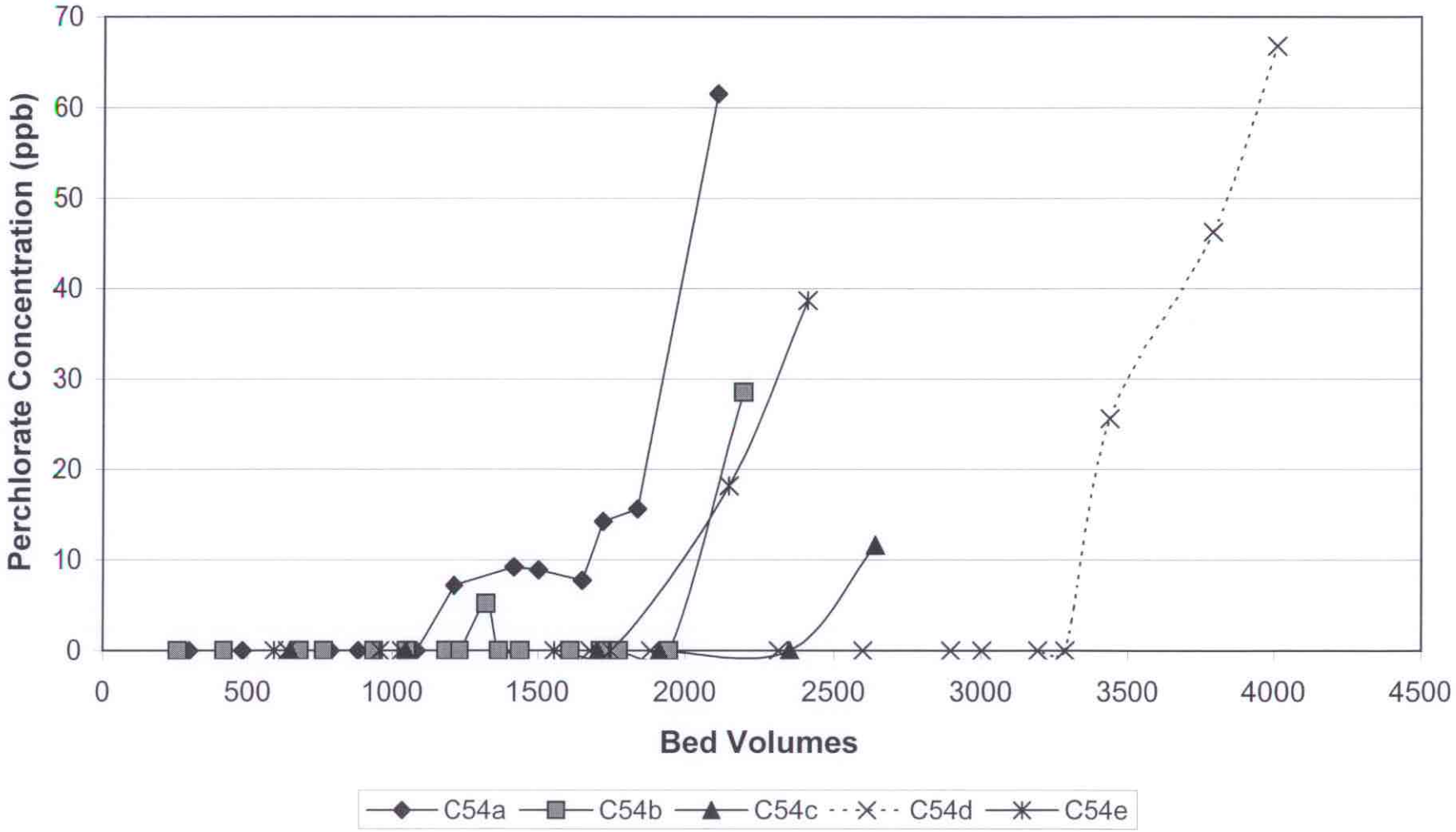

Figure 5: Adsorption of Perchlorate from Redlands Water onto 200x400 SAI GAC Pre-Treated with Organic Cation C54d with Different Pre-loading Times

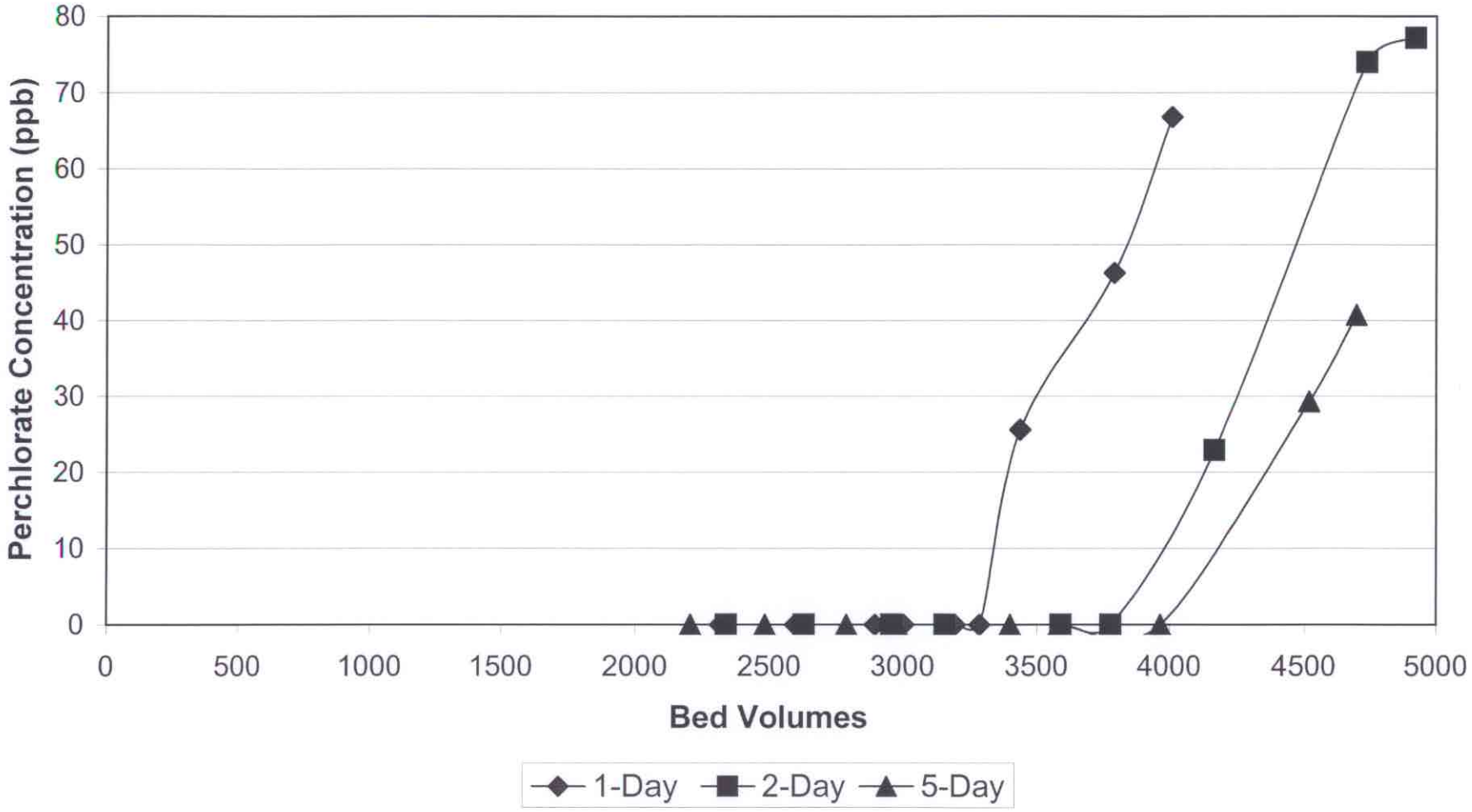

Figure 6: No Perchlorate Breakthrough to Date with SAI GAC Tailored with C60a, C60b, and C60c as well as HD4000 Tailored with C54d