PERCHLORATE REMOVAL USING TAILORED GRANULAR ACTIVATED CARBON AND CHEMICAL REGENERATION

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Abstract

Perchlorate contaminates the water supplies that serve 15 million American people, particularly in California and Nevada. The measured concentrations range from 8 ppb to as high as 3700 ppb. The Environmental Protection Agency (EPA) has reviewed the toxicology of perchlorate, and it has recommended a reference dose of 4-18 ppb in drinking water. Based on this, the California Department of Health Services (CDHS) has adopted a provisional action level of 18 ppb.

Region IX of the EPA, the CDHS, the Air Force, and others searched for perchlorate treatment methods that could be effective at the levels being found in drinking water supplies. The consensus of these entities as of 1997 was that no proven removal process was available that was effective at such low concentrations. The lack of a treatment technology prompted funds through the American Water Works Association Research Foundation (AWWARF) for conducting research on treatment methods for perchlorate removal and destruction. Jointly funded by the AWWARF and EPA, this research has capitalized on the granular activated carbon (GAC) infrastructure that is already installed at many of the water utilities that process perchlorate-contaminated water.

The rapid small-scale column test (RSSCT) has been suitably employed to evaluate GAC's perchlorate adsorption capacity. The RSSCT ensures that the experimental conditions, such as flow rate, empty bed contact time (EBCT) and carbon mass, is compatible to those in the full-scale GAC beds, by simulating the full-scale breakthrough curve in a small RSSCT column.

The RSSCT experiments showed that preloading with an iron-organic complexing solution improved GAC's perchlorate adsorption capacity. Specifically, after preloaded with a protocol that employed an iron-organic complexing solution, a bituminous SAI GAC exhibited 20-25% more capacity than its non-preloaded counterpart. This was observed when the preloaded GAC was dried at 105ºC before use. Moreover, when the preloaded GAC was maintained wet, it exhibited 40-45% more capacity than did the non-preloaded GAC. The adsorption capacity of the dry preloaded SAI GAC was 0.29 mg

ClO_4^-/g GAC; the wet preloaded GAC was 0.34 mg/g; and these compared with 0.24 mg/g that the non-preloaded GAC had achieved.

When the preloaded GAC was exhausted in its capacity to adsorb perchlorate, tests showed that a reducing solution restored 65-74% of the initial adsorption capacity that the GAC preloaded with iron-organic complexing solution had initially hosted, and this capacity could be maintained through several cycles of water service

City of Redlands, CA Experience with GAC and Perchlorate Removal

The City of Redlands hosts its Texas Street water treatment plant that has been equipped with 24 GAC contactor vessels (or 12 pairs of vessels). This GAC facility was initially installed to remove trichloroethylene (TCE-a solvent) and dibromochloropropane (DBCP-a pesticide) from a groundwater plume. Each pair of two vessels together contain 40,000 pounds of GAC, and they were designed to together provide a 40 minute empty bed contact time (EBCT) in each vessel pair at 4.3 MGD, or 30 minute EBCT at 6.5 MGD, or 20 minute EBCT at 8.6 MGD. These have been operated with two vessels in series, such that at any given time 12 vessels are in the "lead" mode, and 12 are in "follow" mode. As conventionally operated for TCE and DBCP removal, when the organic contaminants penetrated half way through the "follow" vessel, the "lead" vessel was taken out of service and regenerated. At this time, this "follow" vessel became the new "lead" vessel, and a new "follow" vessel commenced service down stream of it. On the basis of organic loading parameters, the Redlands staff have been taking a GAC vessel out for thermal reactivation after it has been in operation for 18 months while operating at roughly 4.3 MGD. Reactivation of this bituminous GAC (Westates Northwerstern LB 830)has been performed off site by U. S. Filter Westates.

The Texas Street plant has been treating water from Well 31A, which can deliver 4.3 MGD, and is one of Redland's higher-yielding wells. This groundwater originates from within the Crafton-Redlands plume area; and in addition to the TCE and DBCP, this groundwater also contains 60-138 ppb perchlorate. Once perchlorate was detected in this well, the Texas Street plant was shut down. The City of Redlands also has two other wells (30A and 32) that can deliver water through the Texas Street plant; and well 32 samples contained 20-50 ppb perchlorate. After isolating high-nitrate water tables from the upper levels of these two well screens, wells 30A and 32 are expected to deliver 2.3 MGD; and thus the projected capacity for the Texas Street plant will ultimately be 6.5 MGD. Redlands also has other groundwater and surface water sources that contain scant perchlorate. In the summer, Redland's peak day water demands of 45-50 MGD are just matched by their system-wide water treatment capacity; and water production at Texas Street will soon become crucial for meeting these summer demands.

The City of Redlands conducted testing regarding perchlorate removal by full-scale GAC vessels that commenced operation on May 5, 1997 and remained in service through a sampling event on June 3, 1997. During this month, the flow averaged 3.6 MGD through their 12 pairs of vessels, and the flow was 4.3 MGD on June 3, which corresponded to a 40-minute EBCT through two vessels in series. During May 5- June 3, there had been 93 MG of water that had processed through the Texas Street GAC beds, and there had been 730 skid-bed volumes (i.e. the volume of both beds in a skid together) processed through vessels 1A and 1B together. During most of the operations time, groundwater originated from Redland's Well 31A, which was analyzed to contain 62-138 ppb perchlorate.

On June 3, 1997, water was sampled from Vessels 1A and 1B at eight port locations, with resultant perchlorate concentrations as shown in Table 1. This table highlights that the GAC confined its perchlorate mass transfer zone within 15-20 minutes. The data also shows that when these GAC vessels were operating in the above-described mode, they could have processed roughly 1280 skid-bed volumes of groundwater before 18 ppb perchlorate would have broken through. This would correspond to six weeks of operation until change-out of a given single bed, with a 40 minute empty bed contact time (EBCT) through each of the beds.

Table 1: Perchlorate Removal through City of Redlands GAC Vessels on June 3, 1997, following Start-up on May 5, 1997

Sample Port	ClO_4^-, ppb	Skid-Bed Volumes Processed above This Sample Port*
Vessel 1A		
1/8 port	101	5840
2/8 port	97	2920
3/8 port	87	1950
4/8 port	39	1460
Vessel 1B		
5/8 port	5	1170
6/8 port	<4	980
7/8 port	<4	840
8/8 port	<4	730

*Skid-bed volumes based on 93 MG total water processed, May 5-June 3, 1997; and 1.1 times as much flow rate through Vessels 1A&B than was averaged through all.

This six weeks of operation between change-outs, as required by perchlorate loading, would be short relative to the 18 months between change outs as required relative to organic loading requirements. None-the-less, the authors emphasize that this currently available commercial GAC was indeed effective at removing perchlorate. It just was not effective for very long, nor for as low a cost as for other conventional water treatment operations that are designed to remove other contaminants. The intent of the research herein has been to build on this finite adsorptive capacity, move beyond what has previously been available commercially, and to tailor a GAC and interim chemical regeneration protocol that would translate an effective but expensive technology into an effective and inexpensive technology.

Penn State Testing

On the foundation afforded by this limited perchlorate adsorption capacity, our Penn State research has explored means of (a) enhancing the adsorption capacity of tailored GACs, while also (b) chemically regenerating the GAC with an anionic reducing compound, so that the GAC could sustain an acceptable overall adsorption capacity between thermal reactivation cycles. To this end, Penn State bench scale tests have employed rapid small scale column tests (RSSCT's) to process Redlands water from Well 31A. By this protocol, we have appraise what perchlorate-removal enhancement could be anticipated by pre-loading a bituminous GAC with iron-organic complexing solution. The RSSCT tests have aimed at modeling full-scale performance when a bed has a 20 minute EBCT, 3.14 gpm/ft^2 loading, 10 foot depth, and #8 x 30 GAC mesh size. The RSSCT beds have hosted a 3.56 min EBCT, 0.9 gpm/ft^2 loading, 0.49-0.59 foot depth, and #60 x 80 mesh size.

The objective of this research has been to extend the service life of GAC beds so that the GAC would be able to serve for perchlorate removal as long as it serves for the removal of organic compounds. To achieve this goal, the author has employed an iron-organic complex preloading protocol to improve GAC's perchlorate adsorption capacity, and also an *in-situ* chemical regeneration protocol to restore the capacity of perchlorate-spent GAC. Rapid small-scale column tests (RSSCT) were conducted to simulate full-scale performance.

RSSCT Simulation:

A comparison of the full-scale breakthrough curve and those of the RSSCT columns is shown in Figure 1. As indicated, the proportional-RSSCT columns that used SAI GAC offered a fairly good simulation of full-scale breakthrough. This similarity indicated that the intraparticle diffusivity of perchlorate is a linear function of particle size. It is also noted that the simulated proportional breakthrough curves were sharper than the full-scale breakthrough curve. This greater sharpness results when one uses a Re_{min}, instead of the Reynolds number of the full-scale bed in RSSCT columns, and this represents an unavoidable, and perhaps somewhat inconsequential limitation of the RSSCT simulation method**.**

Other proportional-RSSCT columns that employed Westates GAC and Hydrodarco GAC had the same steep slope as the column that employed SAI GAC. Perchlorate broke through the Hydrodarco GAC sooner than for SAI, and perchlorate broke through Westates GAC later than through SAI GAC. In contrast, the constant-RSSCT column did not show any similarity to the full-scale breakthrough curve and instead exhibited breakthrough far sooner than for the full-scale GAC. Therefore, the proportional-RSSCT was selected as the most representative simulation of the full-scale adsorption behavior.

Performance of Non-Preloaded GACs

The limited adsorption capacity of commercially-available GAC is also shown in the Figure 1 data. As shown, perchlorate started to break through when the adsorption beds had processed 1,200 to 1,800 bed volumes (BV) of water, and full breakthrough occurs within 2,000-2,500 BV when the beds operated with the full-scale equivalent of a 20 minute EBCT and employed bituminous GACs. The Westates bituminous GAC initiated 10% breakthrough at 1,800 BV, while the SAI bituminous GAC initiated 10% breakthrough at 1,200 BV, and the full-scale reactivated ATP carbon initiated 10% breakthrough at 1,500 BV.

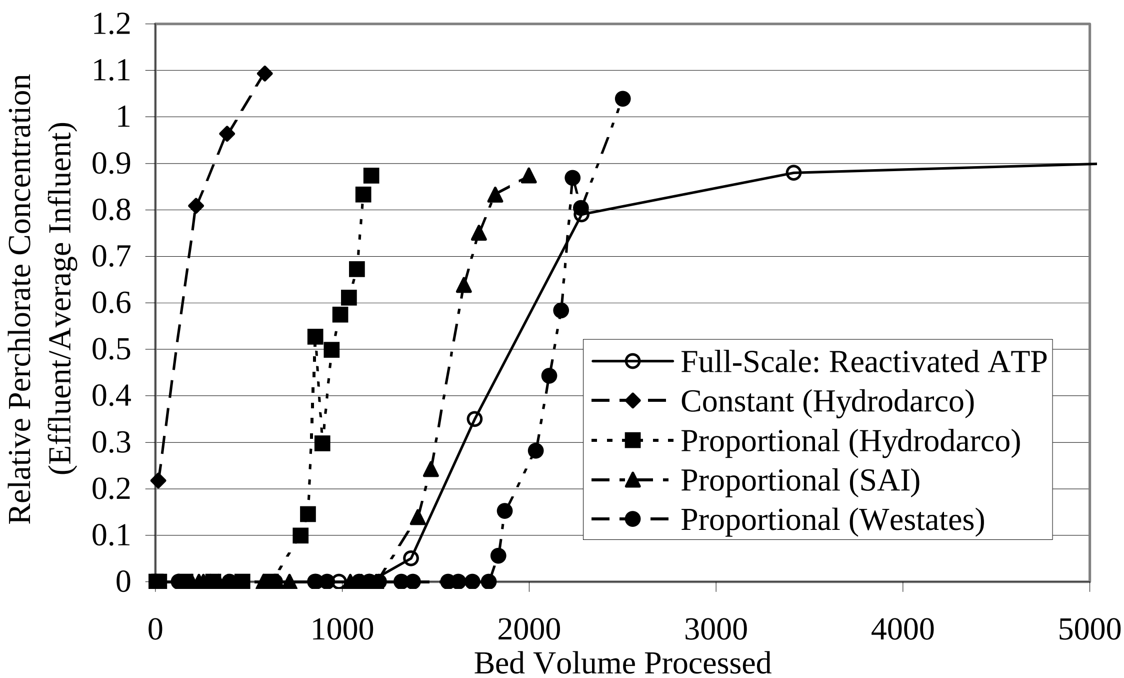

Figure 1 Comparison of RSSCT simulations and the full-scale breakthrough curve. All carbons are bituminous, except the lignite-based Hydrodarco. None of these carbons have been preloaded with iron. The proportional-RSSCT column length was 18 cm for SAI and Westates GACs, 13.1 for Hydrodarco GAC. The constant-RSSCT column length was 1 cm.

The 2,000-2,500 BV to full breakthrough represented roughly one-tenth of the bed volumes to break through that the City of Redlands has observed for the volatile TCE and pesticide DBCP.

The perchlorate data implies that after operating a bed at 40 minutes empty bed contact time (EBCT) for six weeks, the carbon would need to be replenished in its capacity to adsorb perchlorate. If this replenishment were to be achieved by merely replacing the GAC or thermally reactivating it, the costs and inconveniences would be too prohibitive for this to be a viable perchlorate treatment option. However, if the perchlorate capacity could be replenished by a less costly protocol of chemical regeneration, then GAC treatment could serve as a viable approach for removing perchlorate. Moreover, if the GAC could be tailored so that it had an enhanced capacity for removing perchlorate, this treatment approach could become yet more viable. It was these dual objectives that prompted this research herein. The first aim was to enhance the perchlorate adsorption capacity by preloading the GAC with iron and an organic complex solution.

Effects of Iron-Complex Preloading on Perchlorate Adsorption

In order to test whether preloading with an iron-organic complex solution could enhance the perchlorate adsorption capacity of GAC, the authors preloaded an iron-organic complexing solution onto the GAC. When the preloading was employed, the SAI carbons exhibited a significant enhancement in perchlorate adsorption as compared to their non-preloaded counterparts, as shown in Figure 2.

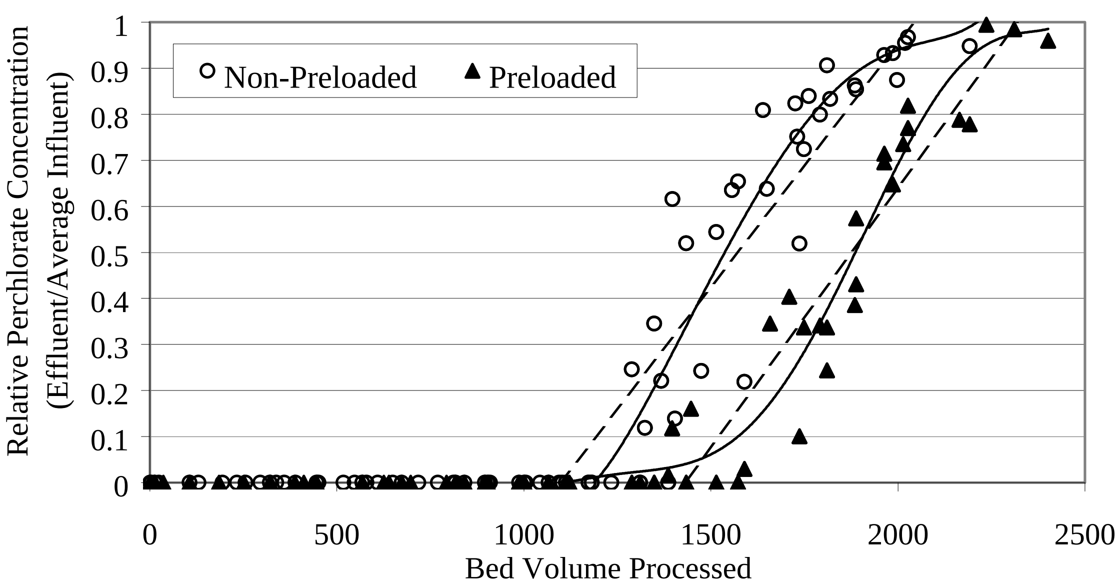

Figure 2 Enhancement of perchlorate removal introduced by preloading bituminous SAI GAC with iron-organic complexing solution.. The lines on the left are for non-preloaded SAI GAC and the lines on the right are for the preloaded SAI GACs.

Compared to an 80% breakthrough at 1780-1790 BV for the non-preloaded GAC, the preloaded GACs achieved 80% breakthrough at 2070-2220 BV, which represented

16-24% enhancement. The distinction between these two linear regressions was statistically significant, as determined by employing the F-test method.

Moreover, the non-preloaded GACs accumulated 0.24 mg perchlorate/g GAC by the time of full breakthrough, compared to 0.29 mg/g for the preloaded GAC and this represented a 22% improvement. The influent perchlorate concentration was 70 ppb.

Table 1 Comparison of Perchlorate Removal of Non-Preloaded SAI GAC and the SAI GAC Preloaded with iron-organic complexing solution

SAI GAC	Bed Volumes at 10% Break-through, BV_{10}	Bed Volumes at 80% Break-through, BV_{80}	Enhancement to 80% Breakthrough[2] (%)	ClO_4^- Adsorption Capacity[1], q (mg/g GAC)	Adsorption Capacity Enhancement[3] (%)
Non-Preloaded	1270	1780	---	0.236	---
Preloaded & Pre-dried	1570	2160	21	0.289	22
Preloaded & Maintained Wet	1920	2400[5]	35	0.336[4]	42

[1] The average influent perchlorate concentration of non-preloaded or preloaded carbon is calculated as the mathematical mean of all the RSSCT average influent concentrations. For the non-preloaded carbon, it was 75 ppb; for the preloaded carbon, it is 76 ppb. A carbon mass of 9.8 grams has been used in calculation;

[2] Calculated as $\frac{BV_{80,a2} - BV_{80,a1}}{BV_{80,a1}} \times 100$;

[3] Calculated as $\frac{q_{Preloaded} - q_{Non\text{-}Preloaded}}{q_{Non\text{-}Preloaded}} \times 100$;

[4] Breakthrough curves extrapolated to $C/C_0=1$ using a slope of 0.2 C/C_0 to 500 BV.

Chemical Regeneration

When GAC became exhausted in its capacity to adsorb perchlorate, a reducing solution was able to restore much of its adsorption capacity by washing out the adsorbed perchlorate. The wastewater from desorption contained perchlorate levels as high as 7,000-15,000 ppb, which was 100-215 times that in Redlands' groundwater. Experiments showed that after chemically regenerating the preloaded SAI carbon, the GAC restored 50-74% of its initial adsorption capacity.

Summary

In summary, the strategy of preloading with iron and and an organic complex solution and chemical regeneration offers a viable approach for removing perchlorate from groundwater, and this protocol could successfully achieve a proposed drinking water standard of 18 ppb perchlorate or lower. By preloading a GAC with an iron – organic complexing solution, one could improve perchlorate adsorption by 40-45%, and by chemically regenerating the GAC with a reducing solution, 50-74% of the GAC's perchlorate adsorption capacity could be restored. Researchers at Penn State could regain perchlorate adsorption capacity through 3 cycles. Thus this approach offers a technically viable method for removing perchlorate. Research continues by the Penn State team to improve this method and yet further enhance its viability and cost effectiveness. Full-scale demonstration testing is proceeding at Redlands, CA. The full scale data to date indicates that if the Redlands plant were to operate at 4.3 MGD, they could operate their tailored GAC beds for roughly 70-90 days for the first cycle of use, and then for 35-50 or more days following subsequent chemical regeneration cycles. This appears to represent a technically, economically, and practically viable approach to removing perchlorate from drinking water.