THERMAL REGENERATION OF AMMONIA-TAIORED GRANULAR ACTIVATED CARBON

Weifang Chen and Fred S. Cannon
The Pennsylvania State University, 212 Sackett Building, Univerisity Park, PA, 16802

Corresponding author email address: wzc102@psu.edu

Introduction

Recent years have seen increased application of activated carbon in both water and wastewater for removal of organic and inorganic compounds due to increasingly stringent water regulations. After its exhaustion, carbon can be replaced or regenerated. Regeneration is more cost-effective than replacement with virgin GAC because of carbon's high initial cost [1]. Much research has been conducted on regeneration since the rapid development in the use of activated carbon in both municipal and industrial sectors [2,3]. Thermal and chemical regeneration are two of the methods that have been under extensive investigation. Thermal regeneration usually is carried out in a multi-hearth furnace or a rotary kiln at elevated temperature. It's expected that adsorbed impurities would desorb by volatilization and oxidize at high temperature [4].

Thermal reactivation is divided into two stages: pyrolytic and oxidative. During the pyrolytic stage, spent carbon is exposed to temperatures up to 800°C under inert conditions. This stage eliminates volatile compounds, and moisture. Chars may be formed from decomposition of less volatile compounds during the process. Steam or carbon dioxide or a mixture of both is the most commonly used agent during the oxidative stage. Original carbon-type structure is restored after the oxidative stage [5].

In this research, thermal regeneration was aimed at regenerating perchlorate-exhausted carbon. Perchlorate has been found in the water source that 15 million American could otherwise drink [6]. Tailored activated carbon adsorption has been under studies as one of the more promising technologies in perchlorate removal. Currently available commercial activated carbons have very limited capacity for perchlorate when compared with its capacity for organics. Studies at the Texas Water Treatment Plant, City of Redlands, CA indicate that it takes about 1,100 bed volumes for perchlorate to occur while bed life for TCE was 18,000 [7]. Activated carbon tailoring to improve its capacity for perchlorate has been a research focus for the environmental group at Penn State University. Previous research revealed that carbon tailored by NH_3 obtained a 4-fold increase in perchlorate adsorption capacity. It was also believed that the improvement in perchlorate adsorption was mainly caused by the change in surface chemistry. The tailored carbon obtained a more basic surface than its non-tailored counterpart. The increased basicity was beneficial to perchlorate adsorption [8].

It's reported that perchlorate starts to decompose at temperature of 400-500°C [9]. Therefore, it's expected that adsorbed perchlorate would decompose at thermal regeneration temperatures (usually higher than 600°C), and thus restore the carbon capacity. Thermal reactivation has been in application in full-scale for quite a long time. Technology in the field is quite mature at the present stage. The objective of this study

on thermal reactivation therefore is mainly about its impact on surface chemistry of the tailored carbons and also on its perchlorate adsorption capacity. Three regeneration reactants were investigated, that is, steam, carbon dioxide and NH_3. The former two or their mixture was already widely employed in thermal regeneration of GAC. NH_3 was chosen because it was also the chemical that was used in carbon tailoring.

Experimental

Bituminous granular activated carbon (GAC) manufactured by Superior Adsorbents Inc. (Emlenton, PA) was used in this study, designated virgin SAI carbon hereafter. SAI GAC was ground and sieved to the U.S. mesh 60×80 (250-180 μm). Anhydrous NH_3 gas (min. purity 99.99%) was applied as a tailoring gas. Tailoring of SAI carbon was conducted in a TGA (Thermogravimetric Analyzer) under flowing nitrogen. The furnace was heated to 700°C in nitrogen gas flow and then it was switched to the ammonia. The sample was held for 60 min in NH_3 and then cooled to room temperature in nitrogen gas again. The tailored sample has been denoted as SAI-700-60 hereafter.

Before thermal regeneration, SAI-700-60 was preloaded with perchlorate via a batch method. Groundwater from City of Redlands, CA had perchlorate concentration around 50-80 ppb. This groundwater was spiked to a perchlorate concentration 5000 ppb and used as perchlorate-containing solution. 1 g of carbon was mixed with 200 mL of perchlorate-containing solution. The glass bottle that contained the mixture was put on a rotary shaker for 24 h. After 24 h, the carbon was separated from the aqueous solution, and the amount of perchlorate loading was calculated from the difference in perchlorate concentration of the aqueous solution before and after it was mixed with carbon. After 24 h of contact, about 0.80 mg perchlorate/g carbon was loaded onto SAI-700-60.

Thermal regeneration was performed in a TGA. There were two steps in thermal regeneration. The pyrolytic step was carried out under a constant flow (150 mL/min) of nitrogen for 10 min at temperatures between 600-800ºC. It was immediately followed by reactivation either with steam, or CO_2 or NH_3 at the same temperature. The gas flow rate was controlled so that 1 g reactivating agent/g carbon was applied every 10 min. For reactivation by steam, deionized-distilled water was injected into the furnace from the bottom at 0.0674 mL/min. Steam was created once the water entered the heated part of the TGA furnace. CO_2 or NH_3 were introduced through the furnace gas port into the TGA furnace. Regenerated samples were coded by T plus regeneration temperature and regeneration reagent. Therefore, T600S stands for thermal regeneration at 600ºC by steam. In addition, C stands for regeneration by CO_2 and N stands for NH_3. Samples with a 20 means those samples were regenerated for 20 min instead of 10 min for all the other samples.

Perchlorate adsorption was tested in rapid small-scale column test (RSSCT) to simulate full-scale carbon beds [9]. RSSCT columns were approximately 23 cm in length and have an inner diameter of 1.3 cm. Each test employed about 9.8 g of GAC held in place by glass wool. The actual empty bed contact time(EBCT, retention time of water in column when there is no carbon) is about 4.1 min to simulate a full-scale EBCT of 20 min. Groundwater from City of Redlands, CA (perchlorate 50-80 ppb) was applied as source water.

Results and Discussions

1. Mass loss

Mass loss was an indication of the amount of adsorbate that was removed from the GAC and the extent of base GAC oxidation [10]. Control of mass loss is important because it determines how much makeup carbon would be needed when the regenerated carbon is put back to operation in water treatment facilities. Mass loss is directly linked to regeneration time, temperature and the regeneration agent. Table 1 shows the mass loss during regeneration by steam, CO_2 and NH_3. Duplicate analyses showed that variation between two samples regenerated under the same conditions to be about 0.3 percent. As shown in Table 1, regeneration by steam caused the most mass loss after 10 min of regeneration. 10-12% of mass was lost for steam regeneration at 700-800°C. Mass loss for regeneration by NH_3 and CO_2 stayed at about 5-8%. In general, the mass loss increased with the increase of regeneration temperature and time.

Table 1
Mass loss during carbon regeneration for 10 min unless identified as 20 min

Sample	Mass loss (%)	Sample	Mass loss (%)
SAI70060	--	T800N	7.95
T600S	7.31	T600C	3.58
T700S	10.12	T700C	4.12
T800S	12.24	T700C20	6.35
T600N	4.88	T800C	6.54
T700N	5.23	T800C20	7.23

2. Apparent Density

The measurements of apparent density (AD) were conducted in accordance with ASTM procedure [11].

AD was determined for each GAC before and after regeneration. Duplicate analysis showed the variation between two samples regenerated under the same condition to be about 0.006 g/cm^3. Table 2 is the apparent density of regenerated carbons. SAI-700-60 had an AD about 0.457 g/cm^3.

Regeneration by steam and ammonia at 600 and 700°C achieved AD very close to that of SAI-700-60, while AD for T800S and T800N was much lower. The low AD for T800S and T800N indicated that regeneration at 800°C was possibly too harsh; and the carbon was slightly over-regenerated. Carbons regenerated by CO_2 at 600 and 700°C showed apparent density higher than that of SAI-700-60, which caused the concern that

T600C and T700C were not yet fully regenerated. Regeneration by longer time or higher temperature was tried next. As shown from Table 2, regeneration was extended to 20 min instead of 10 min for some samples and also regeneration at 800°C was tried. T700C20, T800C and T800C20 each had AD value lower than that of the SAI-700-60.

Table 2
Apparent density of regenerated carbons

Sample	Apparent density (g/cm^3)	Sample	Apparent density (g/cm^3)
SAI-700-60	0.450	T800N	0.442
T600S	0.449	T600C	0.452
T700S	0.449	T700C	0.452
T800S	0.440	T700C20	0.444
T600N	0.446	T800C	0.445
T700N	0.450	T800C20	0.445

3. Surface Charge distribution and pHpzc

Table 3 is the surface charge at pH 7.5 and pHpzc (pH of point of zero charge) of regenerated carbons. All the regenerated carbons had surface charge and pHpzc lower than SAI-700-60. Carbons regenerated by steam had less than half of the positive surface charge of that for SAI-700-60. And their pHpzc values were also more than 1 unit lower than SAI-700-60. The carbon regenerated by NH_3 obtained surface charge and pHpzc values closest to SAI-700-60. It has been found that perchlorate adsorption was closely related to surface chemistry. In general, the higher the positive surface charge and pHpzc, the higher the adsorption capacity for perchlorate [8]. If the relationship still stands here, it was expected that carbon regenerated by ammonia would have the best result on perchlorate regeneration.

Table 3
Surface charge and pHpzc of regenerated carbons

Sample	Surface charge at pH 7.5 (meq/g)	pHpzc	Sample	Surface charge at pH 7.5 (meq/g)	pHpzc
SAI-700-60	0.094	9.90	T800N	0.084	9.04
T600S	0.048	8.98	T600C	0.082	9.31
T700S	0.045	8.45	T700C	0.085	9.21
T800S	0.045	8.31	T700C20	0.084	9.24
T600N	0.089	8.57	T800C	0.081	9.24
T700N	0.091	9.45	T800C20	0.084	9.21

5. RSSCT for Perchlorate Removal

Perchlorate breakthrough profiles by RSSCT of regenerated carbons were shown in Figure 1, 2 and 3. Compared to SAI-700-60, carbons regenerated by steam (Figure 1) showed initial perchlorate breakthrough after around 2000 bed volumes as compared to 4400 by SAI-700-60. Carbons regenerated by NH_3 (Figure 2) had much better adsorption capacity than that from steam regeneration. T600N and T700N achieved bed volume to initial breakthrough similar to that of SAI-700-60. Regeneration by CO_2 at 600 and 700°C for 10 min only restored part of the perchlorate adsorption capacity. However, extending the regeneration time to 20 min or raising the temperature to 800°C was very effective in regenerating the carbon. T700C20, T800C and T800C20 all had much higher bed volume than T600C and T700C. In addition, T700C20 had a higher bed volume than T800C indicated that the changing regeneration time was more effective than changing the temperature. Patrick (1995) pointed out that CO_2 had a lower diffusion into carbon's porous network and lower reaction rate than steam due to its larger molecular dimension and higher activation energy barrier than H_2O [14]. In the cases where temperature was high enough to overcome the activation energy hurdle, extending the regeneration time guarantee that more CO_2 molecules could reach the carbon micropore surface where most of the adsorbate should be.

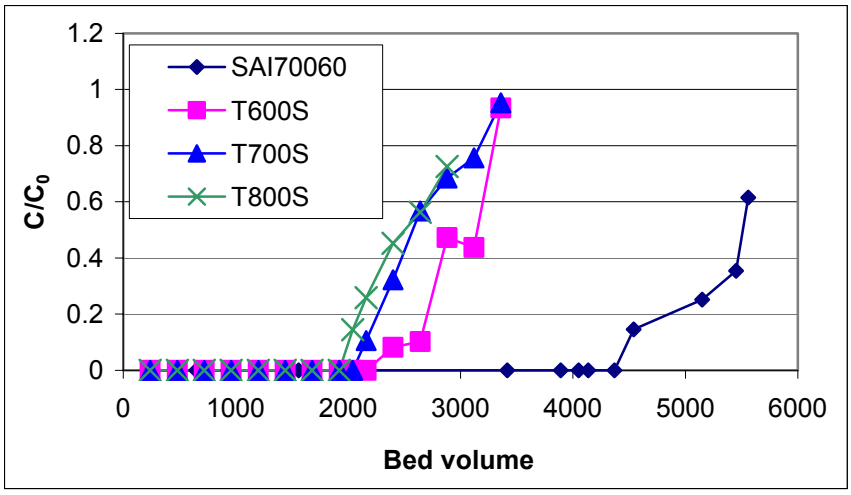

Figure 1: *Perchlorate breakthrough profile of Carbon regenerated by steam*

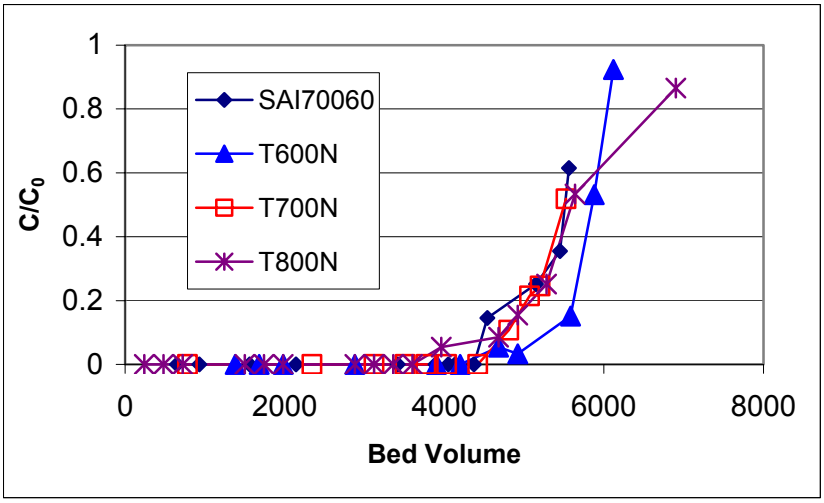

Figure 2: *Perchlorate breakthrough profile of Carbon regenerated by NH_3*

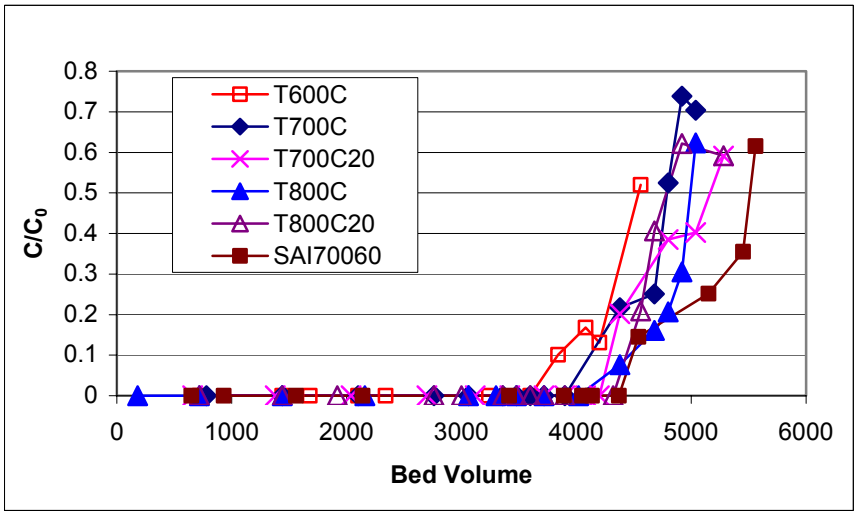

Figure 3: *Perchlorate breakthrough profile of Carbon regenerated by CO_2*

Conclusions

Regeneration by steam registered the most mass loss of 10-12% at temperatures between 700 and 800°C while mass loss from regeneration by NH_3 and CO_2 never exceeded 8% at all temperatures. Regenerations by NH_3 at 600 and 700°C for 10 min and by CO_2 at 800°C for 20 min were able to restore the adsorption capacity for NH_3 tailored carbon based on results from bench-scale column tests. Thus regeneration by NH_3 or CO_2 could be recommended for future practice.

References:

[1] Chiang PC, Chang, EE and Su, JS. Comparison of chemical and thermal regeneration of aromatic compounds on exhausted activated carbon. Water Science and Technology 1997; 35(7): 279-285.
[2] San Miguel G, Lambert SD and Graham NJD. The regeneration of field-spent granular activated carbon. Water Research 2001; 33(11): 2740-2748.
[3] Cannon FS, Snoeyink VL, Lee RG and Dagois G. Effect of iron and sulfur on thermal regeneration of GAC. Journal AWWA 1997; 89(11): 111-122
[4] Liu, PKT and Wagner, NJ, Thermal regeneration of granular activated carbon. Environmental Progress 1995; 4(2): 136-140.
[5] Cannon FS, Snoeyink VL, Lee RG and Dagois G. Reaction mechanism of calcium-catalyzed thermal regeneration of spent granular activated carbon. Carbon 1994; 32(7):1285-1301.
[6] Urbansky ET and Schock MR. Issues in managing the risks associated with perchlorate in drinking water. Journal of Environment Management 1999; 56: 79-95.
[7] Na C, Cannon FS and Hagerup B. Perchlorate removal via iron-preloaded GAC and borohydride regeneration. Journal AWWA 2002; 94(11): 90-102.
[8] Chen WF, Cannon FS and Rangel-Mendez JR. Perchlorate adsorption onto ammonia-tailored GAC. Submitted to Carbon.
[9] Nikitina ZK and Rosolovskii VY. Catalytic decomposition of sodium chlorate and perchlorate by oxygen compounds of sodium. Russian Journal of Inorganic Chemistry 1995; 40(3): 379-385.
[10] Crittenden JC, Berrigan JK and Hand DW. Design of rapid small-scale adsorption tests for a constant diffusitivity, Journal WPCF 1986; 58 (4): 313-319
[11] Sebastiani EG, Snoeyink VL and Angelotti RW. Thermal regeneration of spent and acid-washed GAC from the upper Occoquan sewage authority. Water Environment Research 1994; 66(3):199-205
[12] ASTM D2854-83. Annual Book of ASTM Standards, Vol. 15.01. Amer. Soc. For Testing and Materials, Philadelphia, PA 1983
[13] De Vooys F. The Pore size distribution of activated carbon: activated carbon…a fascinating material (Capelle A and de Vooys F, editors). Norit NV, Amersfoort, the Netherlands (1983)
[14] Patrick J W. Porosity in Carbons. New York, John Wiley & Sons, Inc. 1995