Granular Activated Carbon Filtration and Nitrification

By Shin-ichi Tokuno

Granular activated carbon (GAC) has been used in the water and wastewater industries to reduce taste, odors and dissolved organic compounds. GAC filter media in potable water treatment plants serve a dual purpose: filtration and adsorption. This article will focus on potential problems with bacteria in the application of GAC at a potable water treatment plant.

Case Study

The City of Corpus Christi, Texas, O.N. Stevens Plant has a capacity of 144 million gallons per day (MGD). By mid-February 1996, this plant was equipped with twenty-one filter beds; twelve sand filters (#1–#12) and nine sand anthracite filters (#13–#21).

Six filter's (#1–#6) media were replaced with Calgon GAC (Filtrasorb 820, 166,000 lbs. per filter bed) that is being developed for public water supply. The media in filters #7–#12 were replaced with the same type of GAC, four months later. Filters #13–#21 were not modified at this time.

There were no major changes to the plant's normal operations after GAC installation, except for post GAC rechlorination in which GAC filter effluent is treated with ammonia and chlorine gas. A new air scouring system to be used during backwash was also installed.

Attempts were made to study and compare the differences in the water quality between filter influent and effluent, and between GAC and sand filtration, while both filtration methods were operating simultaneously. Increasing numbers of water utilities have been applying GAC filter media to prepare to comply with more stringent standards for Disinfection By-Products (DBPs), and to reduce volatile and synthetic organics.

After installation, the filters with the new GAC media were studied to determine the removal rates for trihalomethanes (THM), monochloramine, and total organic carbon (TOC). The results were

- THM removal ranged from 72 to 89 percent after filtration
- TOC removal—13 to 42 percent
- Monochloramine removal was 97 to 100 percent complete

There were practically no changes in these parameters before and after filtration in filter #18. These results met the expectations that we had for GAC filter media prior to installation. However, there are common concerns with potential problems associated with use of GAC filter media. Most notably these concerns are desorption of contaminants, competitive effect, backwash effect on GAC performance and bacterial growth.

Nitrification in Plant

Extensive studies on nitrification have been well documented in the distribution system ("Nitrification Occurrence and Control in Chloraminated Water System," AWWA Research Foundation, 1995, *AWWA Journal*, July 1996, pp. 86–89), but little information exists on plant operations.

Several years ago, this laboratory reported (*Water Engineering & Management*, March 1994) that nitrification in the piping from basins to laboratory taps was responsible for changing the quality of basin water. This suggested that the laboratory tap water was not appropriate for checking certain parameters of basin waters. Nitrification in our plant occurred frequently with ammoniated waters in the piping from the primary basins having low levels of monochloramine (1.0–1.5 mg/L), but was rarely detected in the sand filters or in the piping from the secondary basins where ammoniated waters flow with high chloramine levels (3.5–4.5 mg/L).

It is possible that nitrification or some other bacterial metabolic activities were occurring in the GAC filters. This conclusion was based on the following facts: complete absence of disinfectant, constant presence of heterotrophic bacteria (104–105 cells/ml) in the filter effluent, and presence of the free and combined ammonia in the filter influent.

Nitrification in the GAC filters was detected within two months of installation. This was shown by an increase in nitrate and nitrite levels, and a simultaneous reduction of total ammonia in the filter effluent. The presence of these anions results not only in the reduction of chloramine in the distribution system, but it also has the potential to lead to adverse health effects such as methemoglobinemia. Therefore, strict monitoring for these anions or controlling their formation is necessary whenever nitrification is suspected

in GAC filters. Nitrite and nitrate are both regulated by primary maximum contaminant levels of 1 and 10 mg/L as N respectively, sampled at the source or entry to the distribution system.

During monitoring of the catalytic activity of GAC, it was found that ammonia determination plays an important role in understanding the nitrification process in the GAC filters. Thus, studies with ammonia specification (free, combined, and total ammonia) before and after filtration made it possible to investigate relationships between GAC aging (acclimatization), ammonia removal, and nitrite formation. The filter influent carries ammoniated water, both free and combined ammonia (monochloramine), that are potential substrates for nitrifying bacteria. This is true unless the concentration is very low. The raw water contains ammonia at a level that is less than 0.1 mg/L as an NH_3-N.

The monochloramine in plant is formed at two sites prior to filtration. The first chlorine injection is made just prior to the ammonia injection with a low dose of 1.5 mg/L at the receiving unit in front of the primary basin (PB). The second high dose chlorine injection (3.5–4.5 mg/L) is made at the site between the PB and SB (secondary basin). The settled waters from basin #1 and #2 (5.3 MG) are blended to feed the GAC filters (#1–#12), and basin #3 (7 MG) and #4 (7 MG) feed the sand anthracite filters #13–#21.

Ammonia in water exists, like chlorine, in three forms; Free Available Ammonia (FAA), Combined Available Ammonia (CAA), and Total Residual Ammonia (TRA). In previous papers, it was postulated that assaying for free and combined ammonia would make it possible to monitor ammonia dosages and the efficiency of chloramine formation. Thus, the information for maintaining the optimum ratio of chlorine to ammonia would be gathered. It was shown that an addition to chloramine containing water with thiosulfate (0.2 ml of 0.1 N to 100 ml of plant finished water) converts CAA to the free ammonia. This converted free ammonia from CAA plus endogenous free ammonia yields the total residual ammonia (TRA).

The Ion Selective Electrode (ISE) is capable of differentiating between FAA and CAA, while the Nessler methods can not. The ammonia assay method used in this report is an application of ISE with the Orion Ammonia Probe 95-12. The FAA is the result of a direct assay of sample water with ammonia probe, and TRA is the one after pretreatment of the sample water with thiosulfate. CAA is the difference between FAA and TRA.

Test Results

The three groups of ammonia (FAA, CAA, and TRA) have been followed with the GAC filter influent (IN) and effluent (EF) for several months. Figure 1 shows that small amounts of CAA are formed at the first chlorine gas injection in the receiving unit, and that most of CAA (monochloramine) is formed at the second chlorine gas injection between PB and SB, with a reduction of FAA in SB. TRA remains at the same concentration while the water flows from PB to SB.

The first backwash after GAC installation (Filter #1–#6) was conducted on 2/15/96, after about one month of GAC filtration (1.7 MGD per filter), with the filtered water being sampled for ammonia assays. The results of filter #1 and #2 (Figure 2) indicated that the total ammonia (TRA) concentration before and after filtration did not change at all, but all CAA dissipated in the filter effluent to convert to FAA (3/18/96).

Filter #18 (sand anthracite) did not show such a conversion, thus ammonia specification was the same before and after filtration. All sand anthracite filters tested (#13, #15, and #19) showed the same results as #18 in respect to ammonia specification.

This GAC is known to have catalytic activity on the monochloramine and convert it to free ammonia. Laboratory tests have demonstrated the same catalytic conversion in a beaker. The monochloramine in the filter influent or the lab tap finished water can be completely converted to FAA after 30 minutes contact time at room temperature even with just a small amount of GAC (five g GAC/100 ml). Test results from several different days confirmed this conversion in the filters (#1–#3), and it was reasoned that the same conversion must be occurring in the GAC filter (#4–#6).

However, about two months after the first backwash, TRA as well as FAA started to decrease by 70 percent (4/17/96) in the #1 and #2 GAC filter effluent. By 4/21/96 neither FAA nor TRA was detected in the filter EF of #1–#3 (Figure 3). As expected, there was also no change in ammonia specification as well as its concentration after filtration in #18.

At the same time, plant operators reported a low chlorine residual level (0.9 mg/L) in rechlorinated GAC filtered water, and were having difficulty in maintaining the desired chlorine residual (3.5–4.0 mg/L). The result of a chlorine demand test showed that #1 and #2 filter EF had values as high as 10–12 mg/L. This

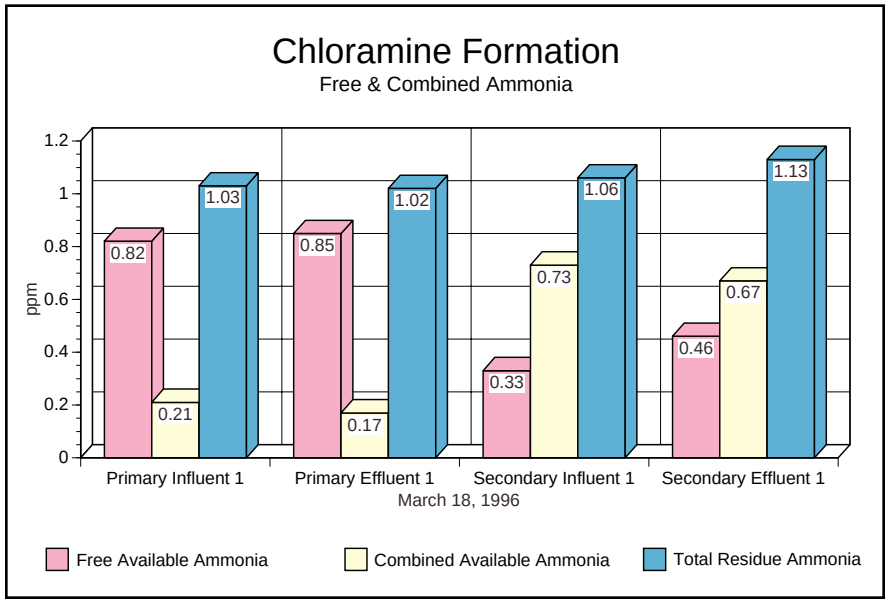

Figure 1. Change in Ammonia Specification in Basin #1 After Chlorine Injection.

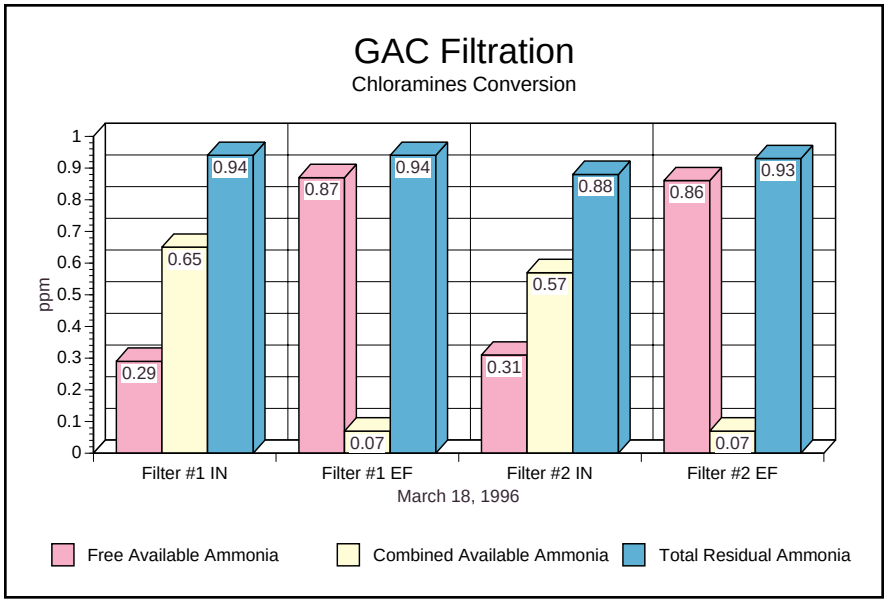

Figure 2. Change in Ammonia Specification by GAC Catalytic Conversion.

was completely in contradiction of the adsorption function of GAC filters. The GAC filters should have removed some compounds (e.g., TOC) responsible for chlorine demand.

Before trying to identify the compounds or ions with high chlorine demand, the nitrite was studied. This was done because the filter influent supplies TRA, a depletion of TRA was found in the effluent, there was a favorable bacterial growth condition due to the creation of disinfectant free environment in the lower part of beds, and there was a nitrite reaction with free and combined chlorine (monochloramine). There was a slight pH decrease (0.3-0.4) after filtration, but with a significant drop (50 to 85 percent removal) in the dissolved oxygen. These results also agree with changes that were observed during a nitrification occurrence.

The pipes connected between primary basins (influent and effluent) with low chloramine (1.0–1.5 mg/L) and laboratory taps in plant are very often subjected to the biofilm formation of nitrifying bacteria that alters water quality of the basin water. Thus, TRA reduction, and nitrate and nitrite formations were induced during the flow to the lab tap. This circumstantial evidence led us to search for nitrite and nitrate in the GAC effluent.

At that time, the laboratory was not equipped with Ion Chromatography (IC). Therefore, Aquacheck test strips (manufactured by Environmental Test System, Elkhart, IN) for nitrate and nitrite were applied to test these anions in the GAC filter EF (#1–#6). The results showed that the nitrate and nitrite of all six EF were detected with the same concentration (5 mg/L, NO_3 as nitrogen and 1.5 mg/L NO_2). None was detected in the filter influent (#1–#6), (4/25/96). The detection limit of Aquacheck NO_3/NO_2 is 1.0 mg/L as N for NO_3 and 0.15 mg/L for NO_2. The IC results (Figure 4) confirmed that a new nitrite peak developed in the effluent water of GAC filter #4 (2.8 mg/L as N), and filter #1 (3.0 mg/L, IC not shown). Several years of anions' analysis has shown that the plant waters (raw, basins and finished water) carry nitrite in the amount less than 0.03 mg/L, and nitrate in a range (0.05–0.18 mg/L as N) except several days after heavy rain fall. Thus, it is practically with no nitrite peak even in the IC (Figure 4, Influent).

The water quality test strip is very simple to use. It only requires one to dip the test strip into the sample. Aquacheck NO_3 and NO_2 can yield quick results (even in the field) and shorten the time needed to take further action, but the data needs to be confirmed by EPA or Standard Methods. Our laboratory is now applying this test strip to check nitrification in the sampled water in distribution as well as plant water.

Results

Action was taken to regulate the nitrite formation to the lowest possible amount by restricting the total ammonia to the GAC filters (4/23/96).

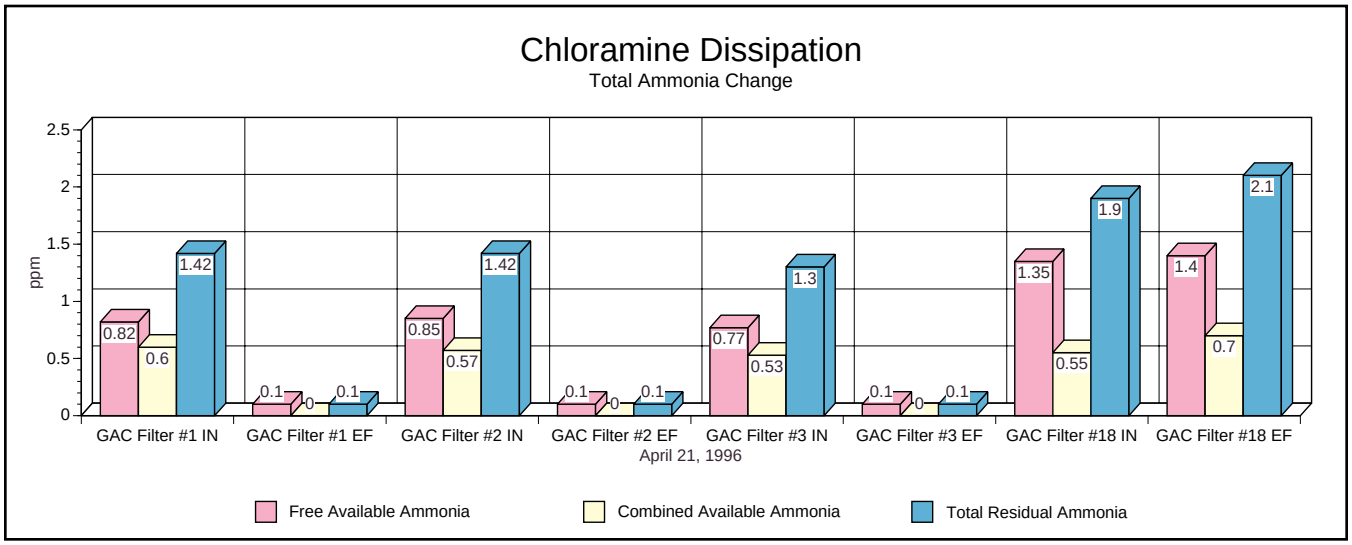

Figure 3. Ammonia Dissipation in GAC Filter Effluent. (Values of 0.1 should be read as <0.1.)

Total residual ammonia of #1 filter IN started to decline as follows; 4/24 (1.5 mg/L as N), 4/25 (1.5), 4/27(0.5), 4/28(<0.1). By 4/28/96, none of the GAC filters (#1–#6) were shedding nitrate and nitrite as checked by Aquacheck, and confirmed by IC, EPA 300 method.

The nitrite decline also was significant: 4/25, (NO_2, 3.0 mg/L as N), 4/26 (.46), 4/27 (<0.03), 4/28 (<0.03). All influent waters before filtration carried nitrite in an amount less than 0.03 mg/L. Filter #4 also showed the same trend of 100 x reductions. Filter #18 IN and EF were run concurrently for comparison with GAC filter. All data showed there was no nitrite formation after filtration. Increasing the TRA of filter IN (1.2–1.5 mg/L) on 5/1/96 to 5/7/96 resulted in the resumption of nitrite formation in the GAC filter. This action confirmed that controlling ammonia dosage is critical to avoiding production of this anion.

New GAC filters (#7–#9) became ready for filtration in late June. After the first backwash (6/24/96), the ammonia assay yielded unexpected results. The CAA of filters #7, #8, and #9 influent were all converted into the free ammonia after filtrations without any change in the TRA concentration. This was exactly the same catalytic conversion that was observed at an early phase of filtration of filter #1–#6 (Figure 2). This conversion had lasted for two months after the first backwash in February. However, as early as five days after backwash (6/29/96), dissipation of TRA began in the filter effluent with a significant amount of nitrite being generated. It was a surprise that the nitrite (0.12 mg/L) release occurred so quickly. The GAC filters (#7–#9) entered into the same pattern as filters (#1–#6) in ammonia specification and nitrite formation, except that they did so in a much shorter time frame. The swift appearance of nitrification may be related to the GAC temperature (daytime, 30 to 31°C) due to hot summers in South Texas (max. 92 to 98°F). This may have activated bacterial growth much faster than during the winter time and recirculation of back washed water. The GAC filters were all temporarily shut down and were reactivated with lower ammonia levels.

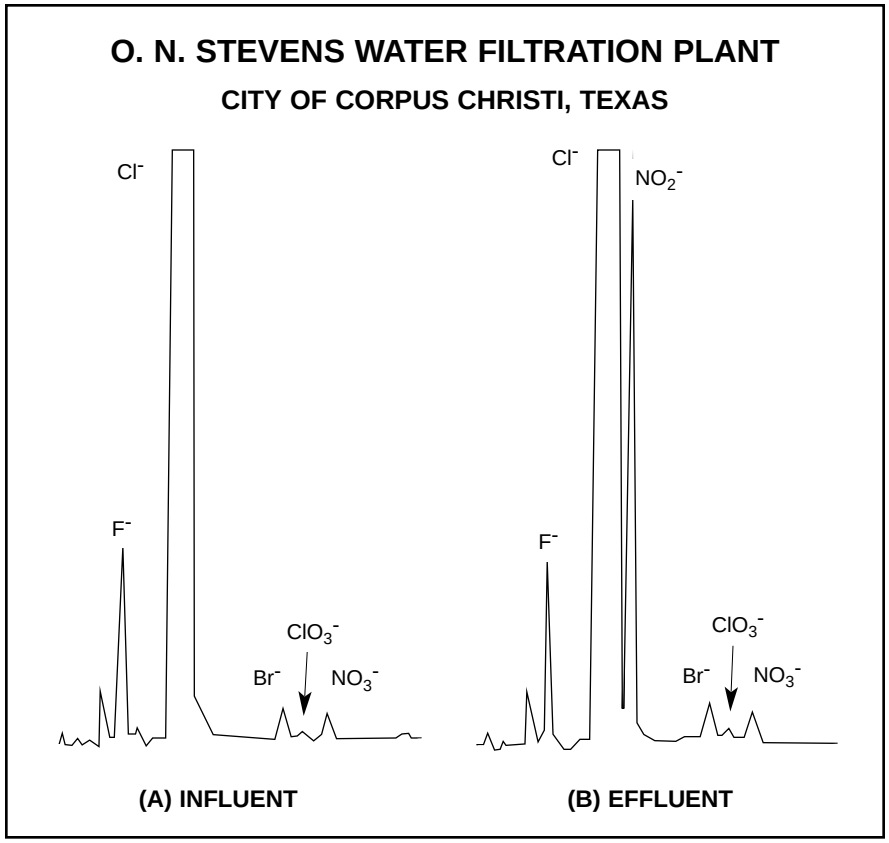

Figure 4. Ion Chromatogram of GAC Filter (#4) Influent and Effluent.

Nitrification problems such as this could be avoided by lowering the ammonia dosage (0.5–0.7 mg/l) and accurately monitoring the TRA of filter influent or by applying free chlorine treatment prior to GAC filtration. If the filter influent carries ammoniated water, it would be necessary to check the nitrate and nitrite at least once a day. Partial replacement with new GAC media (instead of all filters) would make it possible to blend and dilute with sand filtered water in case of GAC nitrification.

Conclusion

Occurrences of nitrification in GAC filters are mostly associated with high concentrations of the total ammonia in the filter influent (>1.5 mg/L). In some cases of feeding ammonia, free and combined forms dissipate and cannot be traced to either nitrate/nitrite or free ammonia after filtration. It would be interesting to pursue the fate of the lost ammonia in GAC filters. It may follow that at the inductive period, some activated carbon is converted to activated carbon oxides changing monochloramine to nitrogen gas. (This information was provided by a GAC supplier.) It is also well known that when nitrifying bacteria, ammonia is converted into N_2O under low dissolved oxygen. This type of metabolic pathway shift could be occurring in the GAC media. Therefore, ammonia dissipation could be continuing in effluent water without a nitrate and nitrite release.

The ammonia assay is simple to conduct with sample water, but can provide valuable information concerning the interaction between GAC and ammonia. It is interesting that if free chlorine or ammoniated water at a low concentration (<0.7 mg/L) had been fed to GAC filters, this report would not have been written. Much information about GAC is supplied by the manufacturer (e.g., Adsorption Isotherms, Iodine Number, Molecular interaction) but this information may not be practical in GAC filter operations such as this one.

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