



Project Summary

Chlorine Dioxide Disinfection and Granular Activated Carbon Adsorption

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A pilot plant study was designed to evaluate chlorine dioxide disinfection as an alternative to chlorine for drastically reducing or preventing the production of trihalomethanes. Also investigated was the effectiveness of post-treatment adsorption by virgin and reactivated granulated activated carbon (GAC) for removal of organic compounds that were either present in the source water or formed after disinfection.

The performance of a 0.38 m³/min (100 gpm) pilot plant using chlorine dioxide disinfection for both raw and treated water was compared with that of a full-scale plant applying chlorine disinfection at similar locations. Two parallel post-filtration adsorber contactors consisting of virgin in one contactor and reactivated GAC in the other were continuously operated and evaluated until exhaustion. After about 90 days of operation, the GAC was educted and reactivated offsite by an infrared furnace.

Composite samples of spent and reactivated GAC were collected during each run, and a representative virgin GAC sample was taken directly from the shipping bags for characterization. Various properties were determined on these samples to ensure that the spent GAC had been reactivated to essentially virgin conditions and to provide an opportunity to compare the performances of virgin and reactivated GAC.

Analyses performed during the project consisted of the quantification of 14 volatile and 8 extractable organic compounds along with qualitative (detected/nondetected) determinations by mass spectrometer scans of 32 additional volatiles and 54 extractable organics. Additional data were collected for 9 inorganic metals, total organic carbon (TOC), and other parameters such as turbidity, standard plate count (SPC), and total coliforms.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

An experimental study was initiated at the waterworks facility in Evansville, Indiana, to help satisfy a basic need within the water treatment and supply industry for producing drinking water relatively free of organics. This location provided insight into the feasibility of implementing an alternative method of disinfection in a typical surface water plant. The specific objectives established for this project included:

- to develop a water treatment process using chlorine dioxide as a disinfectant and to compare its

Table 1. *Experimental Modes of Operation for Pilot Plant*

Run	Chlorine	Chlorine Dioxide	Alum	Polymer	Mix	Settle	Lime	Filter	Carbon	Chlorine	Chlorine Dioxide
1	X		XX	X	X	X	X		X		
2	X		X	X	X	X	X	X	X	X	X
3			X	X	X	X	X	X	X		X
4		X	X	X	X	X	X	X	X		X

production of trihalomethanes with those produced during chlorine disinfection.

- to determine whether any organic byproducts are formed when using chlorine dioxide as opposed to chlorine as a disinfectant.
- to determine the disinfection efficiency of chlorine dioxide and its ability to provide residual necessary for full-scale distribution use.
- to determine the effectiveness of virgin and reactivated GAC for removing organic compounds that were either present in the filtered water or formed after chlorine dioxide disinfection.

Treatment Method Selection

The initial phase of the project consisted of a control study and three experimental modes of operation (Table 1). For the control study (Run 1), the pilot plant was operated for 2 weeks using pre- and post-treatment chlorine disinfection and bypassing the GAC contactors to allow a performance comparison with the full-scale plant. This study revealed that the average concentrations of the two plant effluents were comparable. In addition to average values, the data for total instantaneous trihalomethanes (THM's) and TOC were subjected to the t-test at a 95 percent confidence level. This test showed no significant difference for either parameter when data from the pilot plant were compared with those for the full-scale plant; the full-scale plant could thus be used as a control for subsequent experimentation.

The other three runs were 3 weeks long and were evaluated to determine which treatment method would be used during the long-term operating phase. The method of disinfection used for Run 2 consisted of chlorine addition to the raw water and to the GAC effluent just before it entered the clearwell. For this and subsequent runs, the GAC contactors were placed in operation.

The instantaneous average data for the second run showed an increase in the total trihalomethane (TTHM) concentration from 1.3 $\mu\text{g/L}$ in the raw water to 31.3 $\mu\text{g/L}$ in the GAC influent. After passing through the GAC contactors, the total instantaneous THM concentration decreased to 0.1 $\mu\text{g/L}$. The average TOC concentration decreased from 2.6 mg/L in the raw water to 2.1 mg/L after mixed media filtration, and it was further reduced to 0.3 mg/L by the GAC contactors.

Total coliform counts were reduced from an average of 4,800/100 mL in the second run raw water to <1/100 mL after pre-treatment disinfection. Very little regrowth occurred through the carbon, with the average GAC effluent containing 1/100 mL. Subsequent disinfection reduced the total coliforms to <1/100 mL.

Mass spectrometer scans of both the volatiles and extractables showed only those instantaneous compounds previously identified by gas chromatography (GC) evaluation and verified the removal of these compounds by GAC treatment.

The third run consisted of a treatment method using no pre-GAC disinfection. Chlorine dioxide disinfection was used only after the GAC contactors. This method of treatment permitted the study of organic removal with GAC and without interference from those organic compounds attributed to disinfection; it could also be used to determine whether any byproducts were formed when chlorine dioxide was used after GAC treatment.

The TOC concentrations were reduced by almost 40 percent (4.2 to 2.5 mg/L) after pilot plant treatment. Complete treatment, including GAC, reduced TOC concentrations by 80 percent (4.2 to 0.8 mg/L). Breakthrough occurred in TOC concentrations in about 1 week at GAC depths of 6 and 18 in. At 30 and 78 in. (with 7.7 min of empty bed contact time at 78 in.), no breakthrough was detected during the run.

Various samples were stored for 3 days with chlorine and chlorine dioxide. The average concentrations showed a large increase in the raw water THM level when stored with chlorine (1.2 to 247 $\mu\text{g/L}$) and a slight increase in those samples stored with chlorine dioxide (1.2 to 2.9 $\mu\text{g/L}$). The slight increase with chlorine dioxide is attributed to a small amount of unreacted chlorine present after generation. The final THM concentration after 78 in. of GAC was 38 $\mu\text{g/L}$ and 0.7 $\mu\text{g/L}$, respectively, for chlorine and chlorine dioxide storage. Although chlorine dioxide disinfection after the GAC contactors reduced the total coliform and SPC to acceptable values, slime growths were a problem in the treatment plant because no disinfectant was added to the raw water.

The objectives of the fourth run were to determine whether any byproducts were formed when chlorine dioxide was used as a pre-treatment disinfectant, and to evaluate GAC removal of any organic compounds present or formed.

Average concentrations for the instantaneous THM's showed the raw water value of 3.6 $\mu\text{g/L}$ being reduced to 0.2 $\mu\text{g/L}$ through the pilot plant clearwell. Very similar values were noted for the THM's produced when stored with a chlorine dioxide residual (3.7 $\mu\text{g/L}$ for the raw water and 1.1 $\mu\text{g/L}$ for the clearwell effluent).

As in previous runs, the qualitative mass spectrometer scans did not indicate the formation of any byproducts relative to this mode of treatment. Also, no increase in the concentration of metals occurred after passage through the activated carbon contactors.

Because a pre-disinfectant is required to control slime growth in the treatment plant, Run 3 was eliminated from consideration for further study. The second and fourth runs were evaluated based on an estimate of what the consumer might receive from each of the treatment modes. In both of these modes, adequate

disinfection was accomplished and mass spectrometer scans of the priority pollutants did not show the formation of any byproducts relative to the disinfectant used other than the THM's. Therefore, a desire to adhere to the original study objectives resulted in selecting chlorine dioxide as a pre- and post-treatment disinfectant for long-term evaluation.

Pilot Plant Operation

After the pre- and post-chlorine dioxide disinfection operational mode was selected for long-term studies, four additional runs were completed. Each run was approximately 3 months. For all runs, the performance of the pilot plant through GAC treatment was compared with the performance of the full-scale plant under normal operation (pre- and post-treatment chlorine disinfection). Also, two parallel contactors were used with one always containing virgin GAC, and the other one containing virgin GAC during the first run and once, twice, and thrice reactivated GAC for the remaining three runs.

The effect of using pre-treatment chlorine dioxide disinfection for maintenance of bacterial water quality and the reduction of THM's was evaluated by comparing the sand filter effluents of both plants. Terminal THM reduction through coagulation and settling was determined by storing all samples for 3 days (estimated residence time in the Evansville distribution system) at ambient temperature with a free chlorine residual.

The use of pre-treatment chlorine dioxide disinfection allowed substantially more of the THM precursors to be removed by coagulation and settling than with pre-treatment chlorination. This was caused by less precursors being converted to THM's in the presence of chlorine dioxide thereby allowing more to be available for removal by coagulation and settling. Therefore, the THM's formed during post-treatment chlorination and subsequently in the distribution system would be reduced. A comparison of the average terminal THM concentration for all runs of both disinfectants showed about 60 percent less concentration of THM's when chlorine dioxide was used for pre-treatment disinfection. Though THM precursors were reduced by using pre-treatment chlorine dioxide, no difference was noted in the average TOC concentration, regardless of the type of pre-treatment disinfectant used.

Because of the THM reductions noted by the use of pre-treatment chlorine dioxide disinfection, an additional study was completed to determine the feasibility and benefits of using chlorine dioxide in Evansville's full-scale plant. Although chlorine dioxide could be used as a pre-treatment disinfectant, chlorine was desired as the post-treatment disinfectant because of the size of Evansville's distribution system and the need to maintain a sufficient disinfectant level throughout this system. Data generated from previous runs indicated that maintenance of a chlorine dioxide residual over an extended period of time was difficult.

The pilot plant GAC contactors were bypassed to simulate the full-scale plant as closely as possible. Chlorine dioxide was introduced into the raw water in sufficient quantities to maintain a slight residual through mixed media filtration (an average addition was 1.1 mg/L, and the average residual after filtration was 0.1 mg/L). An attempt was made to keep the total oxidant level below 0.5 mg/L. During this run, the average concentration of chlorine dioxide plus chlorite was 0.7 mg/L. The instantaneous THM data after filtration again showed a reduction in THM's when pre-treatment chlorine dioxide disinfection was used. No difference in the bacteriological quality of the two plant effluents was noticed when chlorinated effluents were compared.

Each of the parallel contactors contained 545 to 590 kg (1,200 and 1,300 lb) of a lignite-based GAC. During each of the four runs, one contactor always contained virgin GAC and the other contained reactivated GAC. Analysis of the GAC showed that the spent carbon in each reactivation was restored at least to its virgin state.

Cumulative surface area distribution curves indicated that reactivated GAC for all runs had a total surface area greater than the virgin GAC. This additional surface area was developed primarily in the small pore region (less than 30 Angstroms). Also, the iodine number and cumulative surface area correlated almost exactly indicating that the pores were open and maintained. Thus it was unlikely that any gradual degradation of adsorptive capacity would occur after subsequent reactivations. Ratios for Brunauer-Emmett-Teller (BET) surface area/iodine number for an average of two virgin samples and each

of the three reactivation cycles were 1.08, 1.06, 1.08, and 1.03, respectively.

Organic loading on the GAC was evaluated for TOC by comparing the sum of TOC removed to the sum of TOC applied per unit weight of carbon. This loading indicated that the virgin and subsequently reactivated GAC performed essentially the same (see Figure 1). The average TOC carbon use rate for both the virgin and the reactivated GAC was about 0.05 kg/m³ at the steady-state conditions that occurred after about 60 days of operation.

Conclusions

Pilot-plant evaluation of chlorine dioxide disinfection and GAC treatment have provided some insight into this treatment scheme. The use of either chlorine dioxide or chlorine in raw water provides similar disinfection qualities through conventional treatment. Also, because chlorine dioxide has less demand and possibly strong oxidative properties, smaller concentrations were needed to produce effective disinfection. By using less applied chlorine dioxide, some of the difference between the cost of chlorine dioxide and chlorine can probably be recouped.

Application of chlorine dioxide to the raw water produced less concentration of THM's in the finished water than did chlorine addition (average of 51 µg/L as opposed to 130 µg/L for all runs). Furthermore, chlorine dioxide disinfection produced no organic byproducts other than those noted with chlorine disinfection (i.e., among priority pollutants).

GAC was spent and reactivated three successive times and essentially restored to virgin state as indicated by several GAC properties and performance comparisons with virgin GAC. Gross estimates of volumetric losses during GAC offsite reactivation were about 5 percent, and overall system losses (education, handling, transport, and reactivation) averaged about 8 percent.

Production of chlorine dioxide did not proceed stoichiometrically, and thus some chlorite and chlorine were produced. Out of the generator, on the average, the percentage of chlorine dioxide, free chlorine, and chlorite produced was 64, 6, and 30, respectively. Both chlorine and chlorine dioxide were effectively removed by the GAC and the chlorite concentration was lowered.

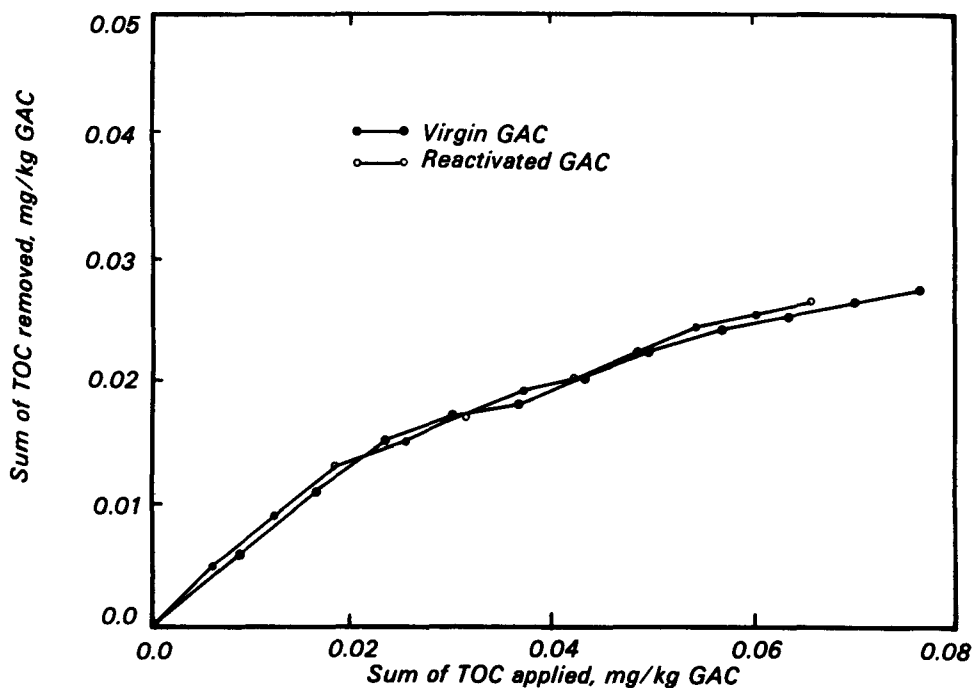


Figure 1. Comparison of virgin and once reactivated GAC for TOC removed vs TOC applied.

In some situations, the use of chlorine dioxide as the primary raw water disinfectant is a viable alternative to chlorine disinfection when the THM concentrations must be reduced to meet promulgated drinking water standards.

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The complete report, entitled "Chlorine Dioxide Disinfection and Granular Activated Carbon Adsorption," (Order No. PB 82-227 737; Cost: \$10.50, subject to change) will be available only from:

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