



Project Summary

Removing Trace Organics From Drinking Water Using Activated Carbon and Polymeric Adsorbents

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"Bench-Scale Evaluation of Resins and Activated Carbons for Water Purification," by V.L. Snoeyink, W.A. Chudyk, D.O. Beckmann, P.H. Boening, and T.J. Temperly. In the first of a three-volume study, adsorption isotherms and bench-scale column studies were used to compare the performance of five types of commercially available activated carbons and four types of resins for removing humic acids, fulvic acids, 2-methylisoborneol (MIB), and chloroform from water. For adsorbing humic materials, some of the activated carbons and the weak base phenol-formaldehyde resins performed satisfactorily. The same activated carbons provided satisfactory removal of MIB, although the capacity was reduced somewhat in the presence of humic acid. The carbonaceous resin and one of the activated carbons has about the same capacity for chloroform removal at concentrations under 0.5 mg/L. The presence of 10 mg/L of humic acid had little effect on their capacity for adsorbing chloroform.

"The Removal of Trace Organics from Drinking Water Using Activated Carbon and Polymeric Adsorbents," by J.T. O'Connor, D. Badorek, and L. Thiem. In the second volume, a pilot plant was operated at the Kansas City, Missouri, Water Treatment Plant to study adsorption as a means of removing trihalomethanes (TTHM) and total

organic carbon (TOC) from drinking water. The pilot plant consisted of 15 columns, 15 cm (6 in.) in diameter, and each containing about a 0.9-m (3-ft) depth of a granular adsorbent. Granular activated carbons and polymeric adsorbents were compared in four extended tests conducted over periods of 183, 111, 65, and 129 days. The pilot-plant studies demonstrated the effects of regeneration, variations in trace organic concentration, and depth of adsorbent on trace organic removal including effluent concentration and adsorption capacity.

"Trace Organics Removal Using Activated Carbon and Polymeric Adsorbents," by C.S. Oulman. In the third volume, a survey was made to determine the trace organic matter in raw and treated water from 14 water utilities across the United States. Monthly analyses were made for TTHM and TOC. Analyses were made on carbon/resin adsorbable ether extracts from each utility for a number of indicator compounds and for bacterial mutagenicity as measured by the Ames test. The results of the water quality survey indicated that most of the water utilities are able to produce an acceptable finished water with conventional treatment methods. In those places where additional treatment is needed for trace organics removal, activated carbon will probably

be the more versatile adsorbent to use. The results from this effort have been published by Glatz, et al. in the *Journal American Water Works Association*, 70(8):465-468, 1978.

EPA did not participate in this portion of the overall project, but some of the results have been included in the full report. This third volume also contains an executive summary of results obtained from the first and second volumes. Only the bench-scale activities (first volume) and the pilot-scale adsorption studies (second volume) are discussed in this Project Summary.

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 three separate reports (see Project Report ordering information at back).

Introduction

In 1975, the American Water Works Association (AWWA) listed 15 high-priority problems needing study. One problem was called "Reliable Screening Tests and Techniques for Determining an Evaluation of Organics in Drinking Water," and another was "Method for Removal of Organics in Drinking Water." Likewise, the U.S. Environmental Protection Agency (EPA) was concerned that many organic compounds were not being removed by conventional water treatment practice; and further, that chlorine used for disinfection was shown to produce halogenated by-products. A cooperative research effort was initiated to (1) examine the occurrence of trace organics in drinking water; and (2) evaluate the efficiency of their removal by a "broad spectrum" adsorbent, granular activated carbon, and more selective adsorbents—polymeric resins.

The project was divided into three parts and reported separately. Bench-scale studies (first volume) were conducted at the University of Illinois to select the adsorbents for pilot-scale column use. In the second volume, adsorption columns were designed, fabricated, and operated by personnel from the University of Missouri—Columbia and located at the Kansas City, Missouri, water treatment plant. The third volume of the project was a survey of trace organics in 14 different water utilities across the United States. That

work was supported by the AWWA Research Foundation and its participating members and conducted by the Ames Laboratory at Iowa State University. The results and conclusions from the first and second volumes will be discussed individually in this Project Summary.

A major objective of the overall study was an evaluation of the removal of taste-and-odor-producing compounds as measured by threshold odor number (TON). The influent TON values were, however, consistently low, which made clear-cut evaluations of the removal of odor-producing compounds inconclusive.

Bench-Scale Studies (first volume)

Bench-scale studies were made to determine which of the various commercially available adsorbents should be used in the side-by-side comparison pilot-scale study of activated carbon and polymeric adsorbents. Adsorption isotherms, using water-containing chloroform, humic and fulvic acids, and MIB as solutes, were determined on five types of activated carbons and four different resins.

The macroporous, phenol-formaldehyde, weak-base resin had a high capacity for humic substances and could be regenerated with sodium hydroxide but was not able to remove the earthy-musty odor compound, MIB. The styrene-divinyl benzene resin did not adsorb humic substances, but it did have some capacity for MIB. The acrylic and carbonaceous resins did not adsorb humic materials or MIB, but the carbonaceous resin had an excellent capacity for chloroform. The activated carbons could remove the humic substances and the MIB but had a relatively small capacity for chloroform.

A number of adsorbents were recommended for use in the pilot-plant tests, based on the adsorption isotherms and the mini-column studies. Initially, one carbon, Westvaco Nuchar® WVG,* was recommended for a side-by-side comparison with polymeric adsorbents because of its good capacity for both humic substances (27.6 mg/g**) and MIB (112.6 mg/g). Later, other carbons were selected for inclusion in the pilot plant tests.

*Mention of commercial products does not constitute approval or endorsement by EPA.

**Isotherm capacities reported for an equilibrium concentration of 1,000 µg/L.

No one polymeric adsorbent could be recommended as having the capacity to remove organic matter in such a wide range of molecular weights as did any of the activated carbons. Therefore, two materials were selected to be used in tandem—an adsorbent for high molecular weight compounds such as humic acids and an adsorbent for low molecular weight compounds such as MIB and chloroform. Diamond Shamrock ES-561 was recommended for the humic acid removal application because of its reasonably low swelling properties and fairly high capacity for humic acids in the neutral pH range. This was not one of the polymeric adsorbents evaluated in the bench-scale tests, but its properties are similar to one of the phenol-formaldehyde resins tested. Rohm and Haas Ambersorb® XE340 was the other polymeric adsorbent tested; it has a high capacity (18.2 mg/g) for chloroform removal. In the later phases of the pilot-plant experimentation, however, additional resins were selected for study.

Pilot-Scale Adsorption Studies (second volume)

Results

Fifteen glass columns, each 15 cm in diameter and containing approximately 0.9 m of adsorbent, were located at the Kansas City, Missouri, water treatment plant and operated in a post-filtration mode. Table 1 indicates the way the various columns were loaded during each phase of the study. The average concentrations of TTHM and TOC were 42 µg/L and 2.5 mg/L, respectively.

Phase I

Over an initial period (Phase I) of 133 days, a 0.9-m bed of bituminous-base granular activated carbon (Nuchar® WVG) removed 70%* of the influent TTHM. Approximately 2.7 m of Nuchar® WVG were required to remove 99% of the influent TTHM. A 0.9-m-deep bed of a carbonaceous resin Ambersorb® XE-340 provided 98% TTHM removal during the same period. Steaming the Nuchar® WVG increased TTHM removal to 87%, whereas steaming the weak-base anion exchange resin (Diamond Shamrock ES-561) had no significant measurable effect on an initially low removal efficiency. The periodic steaming of the

*All removal efficiencies are based on influent and effluent concentrations averaged over the project phase period

Table 1. Identification of Adsorbents Utilized in Kansas City, Missouri Pilot Plant Evaluation of Removal of Organic Substances from Drinking Water

Column	Phase I I (133 days) Feb.-Aug. '77	Phase II II (111 days) Aug.-Dec. '77	Phase III III (65 days) Mar-June '78	Phase IV IV (129 days) July-Nov. '78
1	WVG _(v)	WVG _(v)	WVG _(1R)	WVG _(2R)
2	WVG _(v)	WVG _(v)	WVG _(1R)	WVG _(2R)
3	WVG _(v)	WVG _(v)	WVG _(1R)	WVG _(2R)
4	ES-561 _(v)	ES-561 _(1R)	XE-340 _(2R) **	XE-340 _(3R) *
5	ES-561 _(v)	ES-561 _(1R)	IRA-904 _(v)	IRA-904 _(1R) *
6	XE-340 _(v) **	XE-340 _(1R) **	WVG _(v)	WVG _(v) *
7	—	HD-1030 _(v)	HD-1030 _(1R)	HD-1030 _(2R)
8	—	HD-1030 _(v)	HD-1030 _(1R)	HD-1030 _(2R)
9	—	HD-1030 _(v)	HD-1030 _(1R)	HD-1030 _(2R)
10	—	LCK _(v)	A-162 _(v)	WVG _(1R)
11	—	C-THM _(v)	WVG _(v)	WVG _(v)
12	—	ROW 0.8 _(v)	HD-1030 _(v)	HD-1030 _(v)
13	—	Sand	Sand	HD-1030 _(v)
14	XE-340 _(v)	WVG _(v) **	LCK _(v)	WVG _(v)
15	EX-561 _(v) **	ES-561 _(1R) **	WVG _(v)	WVG _(v) **

Empty Bed Contact Time:

- [11.2 min @ 2 gpm/sf
- *2.2 min @ 10 gpm/sf

WVG Bituminous Base Carbon - Westvaco

HD-1030 Lignite Base Carbon - ICI

LCK Petroleum Base Carbon - Union Carbide

C-THM Bituminous Base Carbon developed by Calgon for enhanced removal of trihalomethanes.

ROW 0.8 Extruded Peat Base Carbon - American Norit

ES-561 Weak Base Anion Exchange Resin - Diamond Shamrock

XE-340 Carbonaceous Resin - Rohm and Haas

IRA-904 Strong Base Anion Exchange Resin - Rohm and Haas

A-162 Strong Base Anion Exchange Resin - Diamond Shamrock

[**Adsorbents subjected to steaming

(v) Virgin adsorbent

(1R) Once regenerated

(2R) Twice regenerated

(3R) Thrice regenerated

Nuchar® WVG reduced the number of microorganisms recovered from the adsorbent from 89,000 to 5,800 colonies/gram.

Throughout Phase I, the influent concentration of TTHM steadily increased from less than 10 µg/L (February) to over 80 µg/L TTHM (June) as influent water temperature increased. An important outgrowth of the present study was the establishment of the seasonal pattern of TTHM formation in the finished

water at Kansas City. This facilitated subsequent decisions as to when virgin and regenerated adsorbents should be placed in service. TOC measurements were included in the sampling protocol near the end of Phase I.

Phase II

During Phase II, all 15 columns were in operation; this permitted the performance of the carbons made from bituminous coal, lignite, peat, and petroleum

to be compared. TTHM levels had increased to a peak of approximately 200 µg/L in the late summer, establishing a pattern that was to be repeated in the following year. This maximum TTHM level provided a more significant challenge for the adsorbent than was present in Phase I. Over the 111 days of Phase II operation, the TTHM removals were comparable to those observed during the first 111 days of Phase I with the following removals: bituminous, 80%; lignite, 83%; petroleum, 82%; bituminous base carbon enhanced for TTHM removal, 85%; and extruded peat base carbon, 68%. Steaming of the Nuchar® WVG column again increased TTHM removal. The steamed column removed 92% of the TTHM over a period of 111 days, exactly equaling the percent removal observed over the first 111-day period of Phase I.

Once again, the Amborsorb® XE-340 was effective in removing 90% of the influent TTHM. Because the Diamond Shamrock ES-561 continued to be erratic and generally ineffective, it was eliminated from further pilot-plant testing. The 0.9-m-deep beds of granular activated carbon removals of TOC were bituminous, 51%; lignite, 37%; petroleum, 30%; bituminous carbon enhanced for TTHM removal, 19%; and extruded peat base carbon, 45%. It became evident that there were far greater differences in carbon performances with TOC than with the removal of the small amounts of TTHM in the influent. Moreover, the Calgon carbon (Filtrisorb® C) developed to enhance TTHM removal did achieve superior removal of TTHM but at the expense of reduced TOC removal capability. Apparently, the pore size distribution that results in more effective TTHM removal retards the removal of a range of other, larger adsorbates. Steaming of the Nuchar® WVG column appeared to increase TOC removal modestly to 56%. Perhaps most significant was that the 2.7-m depth of Nuchar® WVG was incapable of removing more than 75% of the influent TOC at the 5 m/hr (2 gpm/ft²) application rate.

Neither Diamond Shamrock ES-561 nor Amborsorb® XE-340 showed any significant TOC removal. At the end of Phase II, the Nuchar® WVG and Hydrodarco® 1030 were returned to the respective manufacturers for thermal reactivation to prepare for a study of the effect of reactivation on adsorbent performance (Phase III).

Phase III

Reactivating the carbons restored their virgin adsorption capacity, as measured by Iodine Number and Decolorizing Index. During Phase II of the study, comparison of TOC removal indicated similar performance between 0.9-m-deep beds of Nuchar® WVG, whether it was a once-reactivated (60%), virgin (62%), or regularly backwashed virgin (61%) product. Once-reactivated and virgin lignite base carbon (Hydrosorb® 1030) removed 43% and 51% of the TOC, respectively, over the period of Phase III.

No steaming was done during Phase III. Since the influent concentrations of TTHM were generally less than 5 µg/L, little information on TTHM removal was obtained. Thus, Phase III was terminated after only 65 days so that Phase IV could be initiated immediately before the time when the maximum TTHM influent concentration was expected, based on the previous year's seasonal pattern.

The Ambersorb® XE-340 was again ineffective in TOC removal during Phase III, whereas a 0.9-m-deep bed of a strong-base anion exchange resin (Rohm and Haas Amberlite® IRA-904) appeared to remove roughly one-third of the influent TOC. Another bed of a different strong-base anion exchange resin (Diamond Shamrock A-162) removed 47% of the influent TOC. On a weight basis, Diamond Shamrock A-162 was only one-half as effective as Nuchar® WVG activated carbon.

The Ambersorb® XE-340 was placed first in the series of three columns to observe the effect of high molecular weight components of TOC on the adsorption of TTHM by the resin. Laboratory studies had indicated that high molecular weight organic substances might be irreversibly adsorbed to the carbonaceous resin leading to "fouling" and loss of TTHM removal capability. Since this resin is still under development and evaluation, the manufacturer was uncertain of the appropriate regeneration procedure. After subsequent EPA studies, a far more vigorous steaming procedure is now being recommended for the Ambersorb® XE-340 than was recommended at the time of the present study.

Large numbers of microorganisms were dislodged from the adsorbents at the end of Phase III in June 1978. The inert sand media and the resins harbored few microorganisms whereas the activated carbon supported significant growth, particularly in those columns

that had the most TOC removed. Backwashing of a column containing virgin Nuchar® WVG resulted in more than an order of magnitude reduction in bacterial count. For example, 850,000 colonies/gram were found on the activated carbon in the undisturbed column, compared with 52,000 colonies/gram on the backwashed activated carbon, indicating the effectiveness of backwash in controlling accumulations of organisms.

Phase IV

Nuchar® WVG and Hydrosorb® 1030 were both reactivated to levels beyond their virgin capacities by the manufacturers in preparation for Phase IV. This resulted in the following TTHM removals by 0.9-m-deep beds of Nuchar® WVG: twice-reactivated, 75%; once-reactivated, 67%; virgin, 66%; and virgin (replicated), 67%. The regularly steamed column of virgin Nuchar® WVG removed 96% of the influent TTHM over the 129-day period. The twice-reactivated, once-reactivated, and virgin Hydrosorb® removed 77%, 72%, and 62% of the influent TTHM. Again, the reactivation of this activated carbon beyond its virgin capacity resulted in slightly enhanced TTHM removal.

TOC removals were marginal, as before. The 0.9-m-deep beds of Nuchar® WVG removals were twice-reactivated, 55%; once-reactivated, 50%; virgin, 56%; and virgin (replicated), 53%. Steaming increased the TOC removal of the virgin Nuchar® WVG to 63%. Approximately 2.7 m of the twice-reactivated Nuchar® WVG removed a total of 78% of the TOC from fairly constant influent levels of 2 mg/L. The 0.9-m-deep beds of Hydrosorb® 1030, twice-reactivated, once-reactivated, and virgin removed 39%, 38%, and 36% of the influent TOC. Approximately 2.7 m of the Hydrosorb® 1030 removed just under 58% of the TOC.

The Ambersorb® XE-340 was regenerated after each of the first three phases with 1-1/2-bed volumes of low pressure (12 psig) steam. Despite this procedure, the performance of the Ambersorb® XE-340 declined. In Phase IV, at the higher (20 m/hr) application rate, Ambersorb® XE-340 removed only 54% of the influent TTHM and 5% of the influent TOC. As observed a year earlier, the cool (November) water temperatures suppressed organism growth on all of the adsorbents.

Overall, the influent adsorbate concentrations and column removals were consistent between replicates, in successive phases of operation, and with successive regenerations. Granular activated carbon exhibited the potential for prolonged removal of both TTHM and TOC.

Conclusions

1. In studies using pilot plant adsorption columns to adsorb halogenated organic substances from softened, filtered Kansas City water, activated carbon and carbonaceous resin were able to remove TTHM for extended periods. Conversely, strong and weak-base anion exchange resins were not able to remove the TTHM. Only the granular activated carbons were effective in removing significant amounts of the TOC present. Periodic steaming of the activated carbon columns reduced bacterial growth and enhanced TTHM and TOC removal. Regular backwashing of the activated carbon columns was also effective in reducing the accumulation of bacterial growth.
2. Little or no difference was observed in removals obtained by twice-reactivated, once-reactivated, and virgin activated carbons, indicating that calcium carbonate deposits from lime-softened water did not coat the adsorbent and impair its adsorption capacity.

The full three-volume report was submitted in fulfillment of Grant No. R-804433 by the University of Illinois, University of Missouri—Columbia, and Iowa State University, under the sponsorship of the U.S. Environmental Protection Agency.

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Thomas Love, Jr. is the EPA Project Officer (see below).

The complete reports, entitled:

"The Removal of Trace Organics from Drinking Water Using Activated Carbon and Polymeric Adsorbents," (Order No. PB 81-196 768; Cost: \$11.00)

"Bench-Scale Evaluation of Resins and Activated Carbons for Water Purification," (Order No. PB 81-196 776; Cost: \$8.00)

"Trace Organics Removal Using Activated Carbon and Polymeric Adsorbents," (Order No. PB 81-196 784; Cost: \$8.00)

The above reports will be available only from: (prices are subject to change)

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